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Polymers Incorporating Low-Valent/Low-Coordination Number Main  
Group Centres: Novel, Multi-Functional Materials

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14. ABSTRACT The PI has successfully accomplished the research goals as proposed. The initial aim of this program to develop highly novel examples of 'inorganic polymers' where the backbone elements would be expanded to other elements to include metals. The PI proposed that these topical and highly reactive materials will most likely exhibit unusual, and potentially applicable, electronic, optical, catalytic, charge storage and/or synthetic properties. The PI targeted polymers incorporating low oxidation state group 2 (e.g. MgI) or group 14 (e.g. SiI, GeI or SnI) metal-metal single/multiple bonds within the backbone chain, in addition to two-coordinate heavier group 14 elements, i.e. heavier carbene analogues (:EIR <sub>2</sub> ), within the chain. These were to be accessed utilizing unique reduction methodologies developed at Monash, previously utilized in the preparation of the monomeric counterparts of the targeted polymers. Furthermore, the researchers aimed to prepare and stabilize the phosphorus analogues of linear unhindered polyacetylenes, i.e. {-P=C(R)-}n (R = H, Me etc.), by initial entrapment of phosphalkynes (P-triple bond-CR) within suitable 1-dimensional channels of zeolites and metal organic frameworks. This was to be followed by thermal, photolytic or metal-induced polymerization of the phosphalkyne, yielding polymers, which should be protected from undergoing cyclization reactions by the constraints of the solid state host. This 3 year grant yielded 13 peer reviewed scientific papers, 8 conference presentations and multiple collaborations with other academic and DoD agencies.					
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**Final Report for AOARD FA9550-2386-18-1-0125 "Polymers Incorporating  
Low-Valent/Low-Coordination Number Main Group Centres: Novel, Multi-Functional  
Materials"**

**Date 19th August 2019**

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**Summary:** The development of polymer chemistry represents one of the most important advances to the chemical sciences over the last century. However, with a few exceptions, industrially important polymers are restricted to those with an organic backbone, containing only the elements, C, N and O. This, of course, neglects the vast possibilities offered by incorporation of other elements, including metals, within polymer backbones, yielding so-called "inorganic polymers". It was the initial aim of this program to develop highly novel examples of such systems, which incorporate low oxidation state and/or low-coordinate main group elements within their backbones. These topical and highly reactive materials will likely exhibit unusual, and potentially applicable, electronic, optical, catalytic, charge storage and/or synthetic properties.

Systems that were to be targeted in this programme include polymers incorporating low oxidation state group 2 (e.g.  $\text{Mg}^{\text{I}}$ ) or group 14 (e.g.  $\text{Si}^{\text{I}}$ ,  $\text{Ge}^{\text{I}}$  or  $\text{Sn}^{\text{I}}$ ) metal-metal single/multiple bonds within the backbone chain, in addition to two-coordinate heavier group 14 elements, i.e. heavier carbene analogues ( $:\text{E}^{\text{II}}\text{R}_2$ ), within the chain. These were to be accessed utilizing unique reduction methodologies developed at Monash, previously utilized in the preparation of the monomeric counterparts of the targeted polymers. Furthermore, we aimed to prepare and stabilize the phosphorus analogues of linear unhindered polyacetylenes, i.e.  $\{-\text{P}=\text{C}(\text{R})-\}_n$  ( $\text{R} = \text{H}$ , Me etc.), by initial entrapment of phosphalkynes ( $\text{P}\equiv\text{CR}$ ) within suitable 1-dimensional channels of zeolites and metal organic frameworks. This was to be followed by thermal, photolytic or metal-induced polymerization of the phosphalkyne, yielding polymers, which should be protected from undergoing cyclization reactions by the constraints of the solid state host.

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 13 papers, with another several to be submitted in the near future. PI Jones has delivered 8 invited or plenary lectures on project results at conferences and institutions in the period.

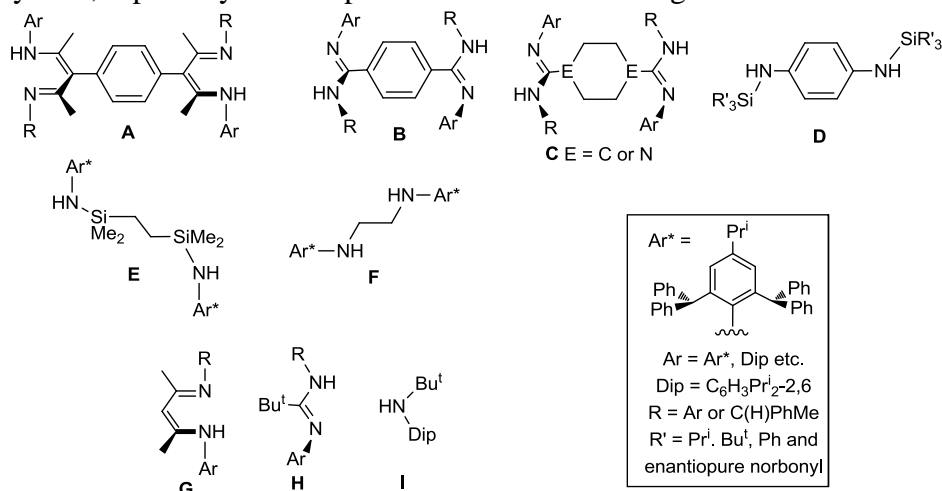
**Introduction:** Polymer chemistry represents one of the most important branches of chemistry developed over the last century. It is now difficult to imagine our daily lives devoid of polymers. These materials are ubiquitous, and are present to some extent in almost every manufactured item around us (e.g. packaging, textiles, paints, molded plastics, electronic materials etc.). However, with a few notable exceptions (e.g. polysilanes and polyphosphazenes), industrially important polymers are restricted to those with an organic backbone, containing only the elements, C, N and O. This, of course, neglects the vast possibilities offered by incorporation of all other elements of the periodic table within polymers. With that said, the field of "inorganic polymers" has rapidly developed over the last decade, largely due to improved technologies

surrounding the linking of inorganic moieties into long chains.<sup>1,2</sup> For economic reasons, these polymers are typically not suited to bulk, low value industrial manufacture. However, they are finding many "high value" applications in areas such as materials science, electronic device manufacture, implantable medical device development and catalysis.<sup>1,2</sup>

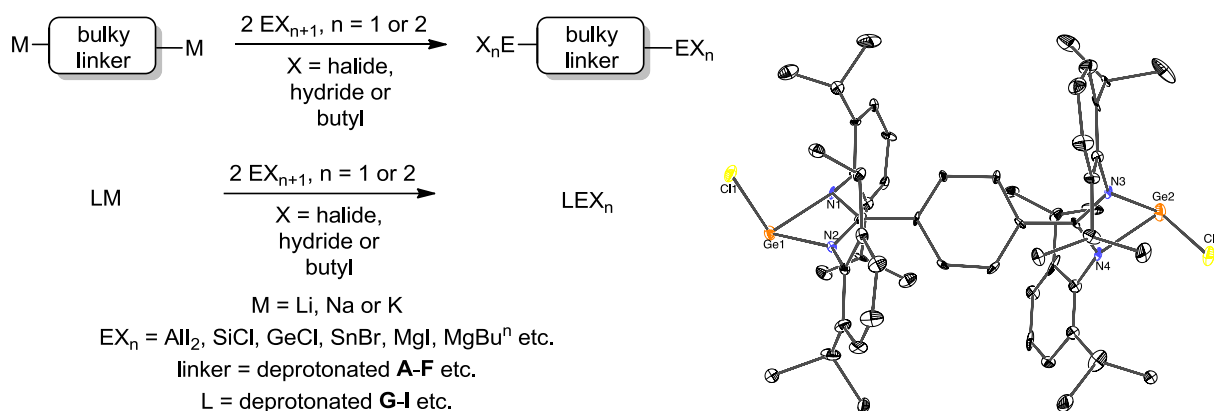
The majority of known inorganic polymers incorporate the elements of the p-block in their backbones (e.g. P, Si and S). It is very surprising, given the recent explosion of interest in low-oxidation state p-block chemistry, that almost no polymeric materials containing main group elements in unusually low oxidation states are known. We are international leaders in the field of molecular low oxidation state s- and p-block chemistry, and as such we have identified the opportunity to initiate and exploit the field of functional low oxidation state main group polymers. In this one year program we are tackling several approaches to developing such systems, thereby maximizing the possibility of preliminary success in such a high risk, yet high return, project. All prepared polymers are to be thoroughly characterized, with the expectation that they will exhibit unusual, and potentially applicable, electronic, optical, catalytic, charge storage and/or synthetic properties. This program of research is intentionally very broad in scope. An advantage of this is that if one area of the proposed research is not as successful as hoped, greater attention can be given to its other goals, thereby assuring that it will not stagnate and will generate quality results.

**Results and Discussion:** Of the two initially proposed main areas of investigation, most progress has been made toward the development of 1-dimensional low oxidation state main group polymers and related oligomers, with a number of high profile spin-off areas also being generated. Less success was had with the development of zeolite and metal organic framework encapsulated poly(phosphaalkynes), and so resources were redirected from that area to the first. A summary of some of the results of the completed project is given below.

*(i) 1-Dimensional low oxidation state main group polymers.* The first stage of this target was the development of a library of "bridging" ligands to be used in the synthesis of target polymers. This has been very fruitful, and just some of the novel developed pro-ligands are depicted in Scheme 1. These include extremely bulky bifunctional pro-ligands (novel and known), and chiral and achiral, monodentate and bidentate examples (A-F). It was decided to include "monofunctional" (i.e. unbridged) ligands (e.g. G-I), to be further used in the synthesis of well defined, molecular models of the target polymers, to aid the understanding of the nature of the prepared polymers, especially with respect to their M-M bonding and solid state structures.

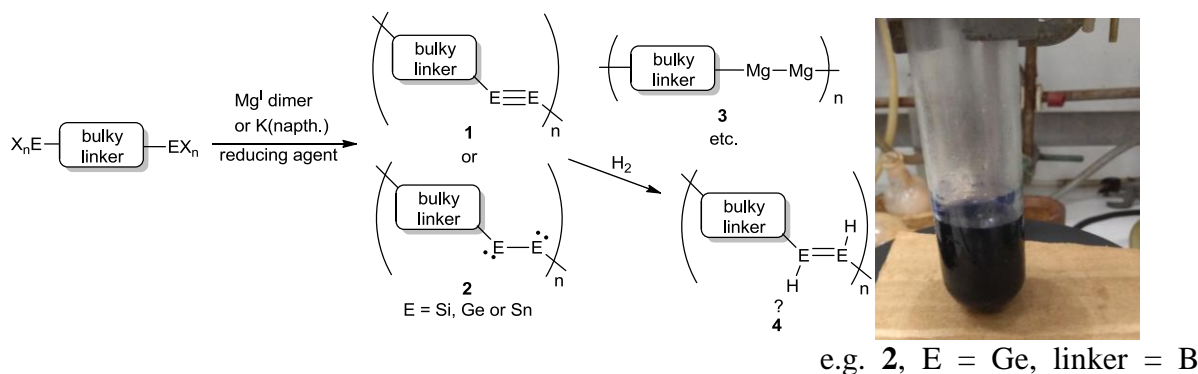


All ligands are readily deprotonated and have been used in the synthesis of numerous chiral and achiral ligand bridged precursor complexes, and non-bridged model complexes. All have been fully characterized and their preparations are simple and high yielding (Scheme 2).



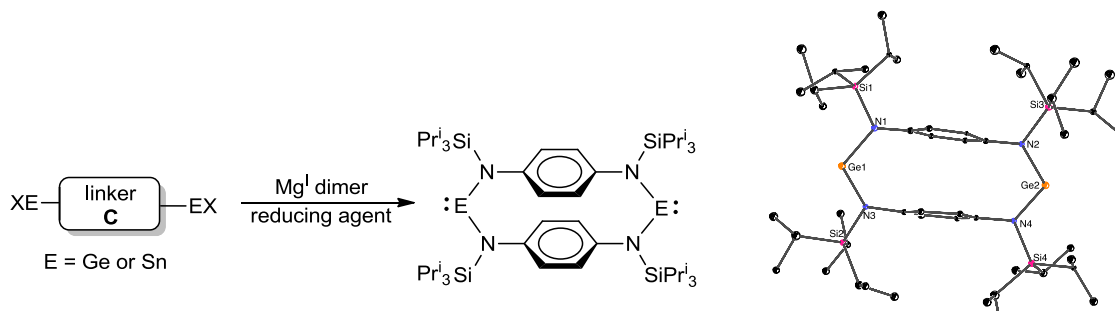
**Scheme 2.** Synthesis of polymer precursor complexes and related model systems.

Reductions of precursor complexes need to be carried out with selective and soluble reducing agents. We have found that Monash developed (and previously AFOSR funded) magnesium(I) dimers are best suited to this task. For a recent review of the reducing abilities of MgI dimers, see *Nature Rev. Chem.*, 2017, **1**, 0059 (Scheme 3). At this stage, polymers are not fully characterized, and more information is required on their chain length, optical and electronic properties, and nature of M-M bonds. However, they are typically highly colored and very reactive species that have moderate solubility in aromatic solvents, and are amorphous solids. The heavier group 14 polymers, e.g. **1** and **2**, rapidly react with small molecules such as H<sub>2</sub> and ethylene, to give as yet unknown typically colorless products. Work continues on the characterization of all polymers, post project.



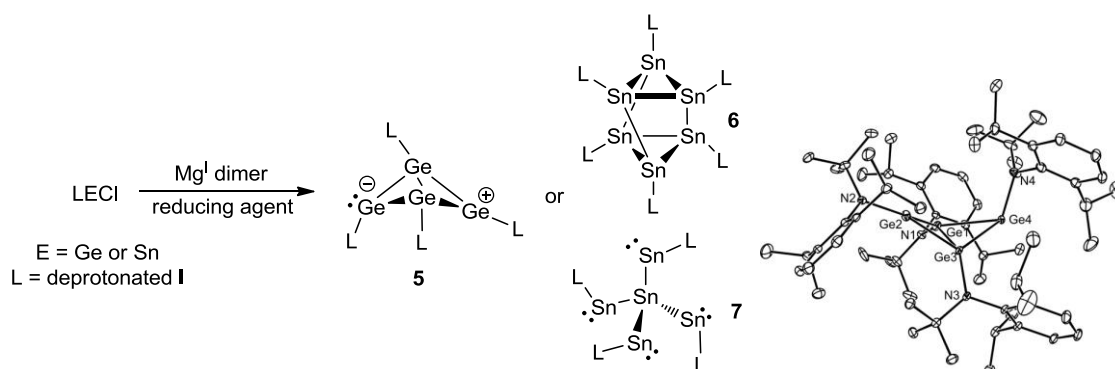
**Scheme 3.** Synthesis of low oxidation state main group polymers.

During the course of the study it was found that when smaller bifunctional monodentate ligands (e.g. deprotonated C) are employed, reduction additionally leads to novel oligomeric species, sometimes *via* disproportionation processes. Examples are the unusual heavier carbene analogue bridged cyclophane like systems shown in Scheme 4. The use of these as Lewis donor ligands in the formation of linear bimetallic polymer systems is currently being explored.



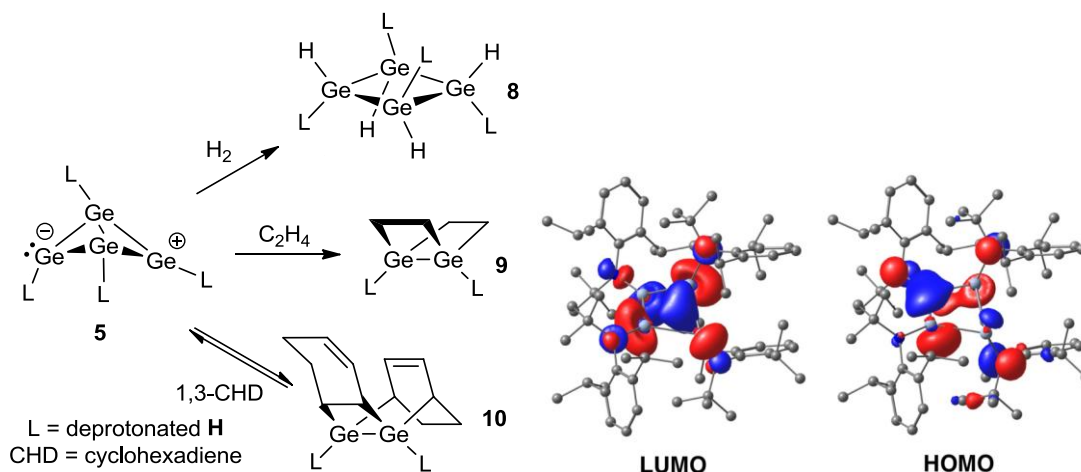
**Scheme 4.** Synthesis and crystal structure of Ge<sup>II</sup> "cyclophane" oligomer.

In order to shed light on the nature of the metal(I) polymers in Scheme 3, a variety of non-bridging ligand systems were developed (Scheme 1) with a view to prepare oligomeric/cluster metal(I) model, or similar, compounds. Using the less bulky amide I (Scheme 1) led to a variety of group 14 element(I) and mixed valence clusters, bearing M-M bonds. Several examples are shown in Scheme 5 which are particularly novel and have no precedence.<sup>3</sup>



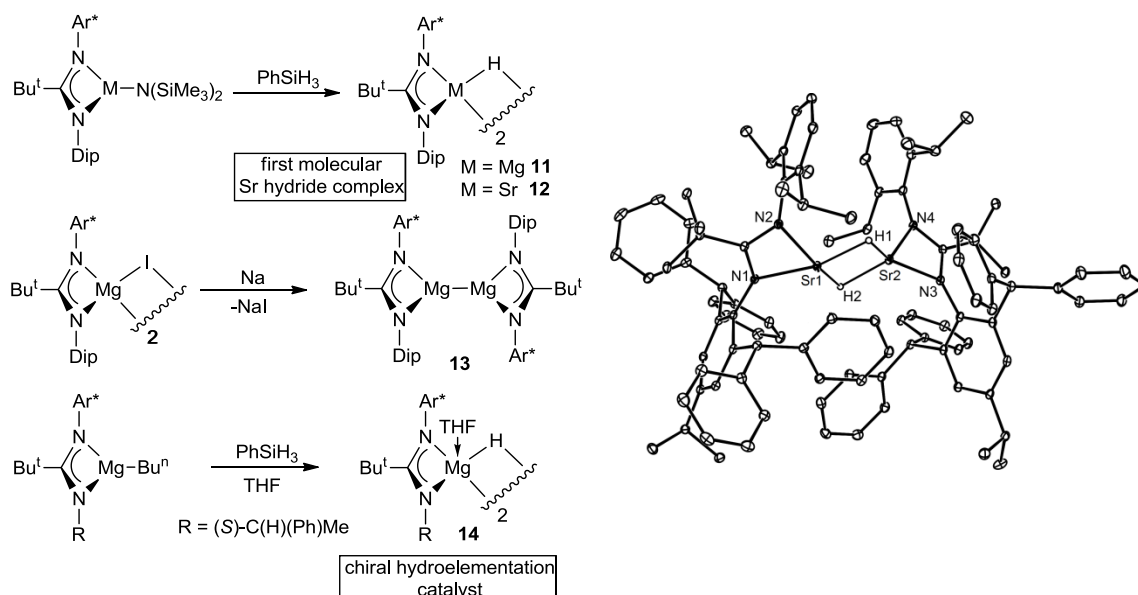
**Scheme 5.** Synthesis of Ge<sup>I</sup> and Sn<sup>I</sup> oligomers (right: crystal structure of **5**)

The folded butterfly germanium(I) complex, **5**, is particularly novel as it would be expected to take on a tetrahedrane like structure. Instead **5** possesses two 4-coordinate and two 3-coordinate Ge centers. This could lead to it being a triplet or a singlet biradical (at the 3-coordinate centers). Instead DFT studies show it to have a closed shell zwitterionic structure, in line with the pyramidal and trigonal planar geometries of the two 3-coordinate Ge centers. It reacts rapidly with a variety of small molecules, e.g. facilely activates H<sub>2</sub> to give **8** (Scheme 6). Remarkably, reactions with alkenes show **5** to act as a masked source of the digermynes, LGeGeL, giving **9** via two [2+2] cycloaddition reactions with ethylene. Reaction with 1,3-cyclohexadiene proceeds via [4+2] and [2+2] cycloadditions to give **10**. This reaction is in rapid equilibrium at room temperature, and **5** is regenerated when solutions of **10** are pumped dry (due to the volatility of 1,3-CHD).



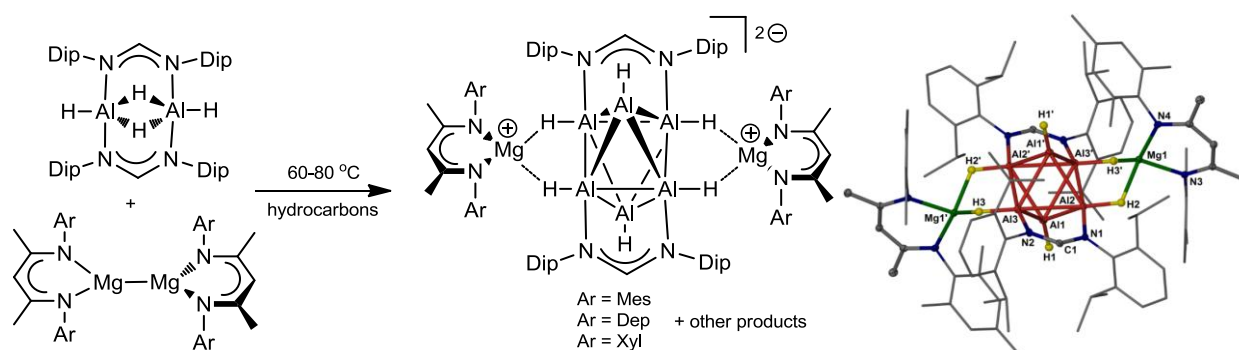
**Scheme 6.** "Transition metal-like" reactivity of **5** towards small molecules (left); frontier orbitals of **5** (right).

Both chiral and achiral asymmetric amidinate ligands have been developed as models for the asymmetric bridged bifunctional ligands shown in Scheme 1. Considerable success has been had with these in the formation of group 2 complexes. For example the first molecular Sr hydride and chiral Mg hydride/MgI dimer complexes have been prepared (Scheme 7).<sup>4</sup> Given that molecular magnesium hydride systems have proved to be highly efficient and applicable catalysts for numerous unsaturated substrate hydroelementation reactions in recent years, it is very surprising that enantioselectivity has not been explored in such work. In initial studies we have shown that systems such as **14** have shown significant, if not ideal, enantio-selectivity as efficient catalysts for hydroborations and hydroaminations of unsaturates. We are currently working on preparing systems with more advantageous "chiral pockets" to enhance this enantioselectivity, and to extend it to a wider range of reaction types. The hope is to also extend this to polymeric metal hydrides incorporating ligands such as I (Scheme 1).



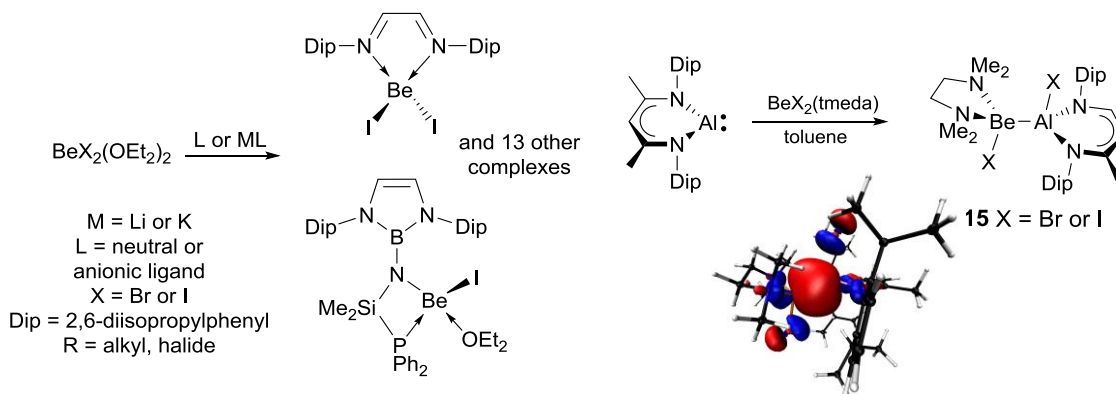
**Scheme 7.** Synthesis of asymmetric and chiral group 2 hydride and magnesium(I) complexes (right: crystal structure of **12**).

In an attempt to prepare well defined molecular models of low-valent Al hydride polymers incorporating bis(amidinate) **B**, Mg<sup>I</sup> reduction of an amidinato Al<sup>III</sup> hydride complex has given the first Al<sup>I</sup> hydride complexes (Scheme 8). These possess an anion stabilized *hypercloso*-Al<sub>6</sub>H<sub>6</sub> cluster core which represents the first extension of the important field of polyhedral borane chemistry to Al hydrides, i.e. a new field of chemistry. The electronic structure of the 12 valence electron cluster core is closely related to that of the 14 valence electron core of classical B<sub>6</sub>H<sub>6</sub><sup>2-</sup>, but with the highest energy cluster MO unoccupied. Like B<sub>6</sub>H<sub>6</sub><sup>2-</sup> the cluster is aromatic.<sup>5</sup>



**Scheme 8.** Synthesis of the first Al<sup>I</sup> hydride systems, which are electronically similar to classical polyhedral boranes, e.g. B<sub>6</sub>H<sub>6</sub><sup>2-</sup>.

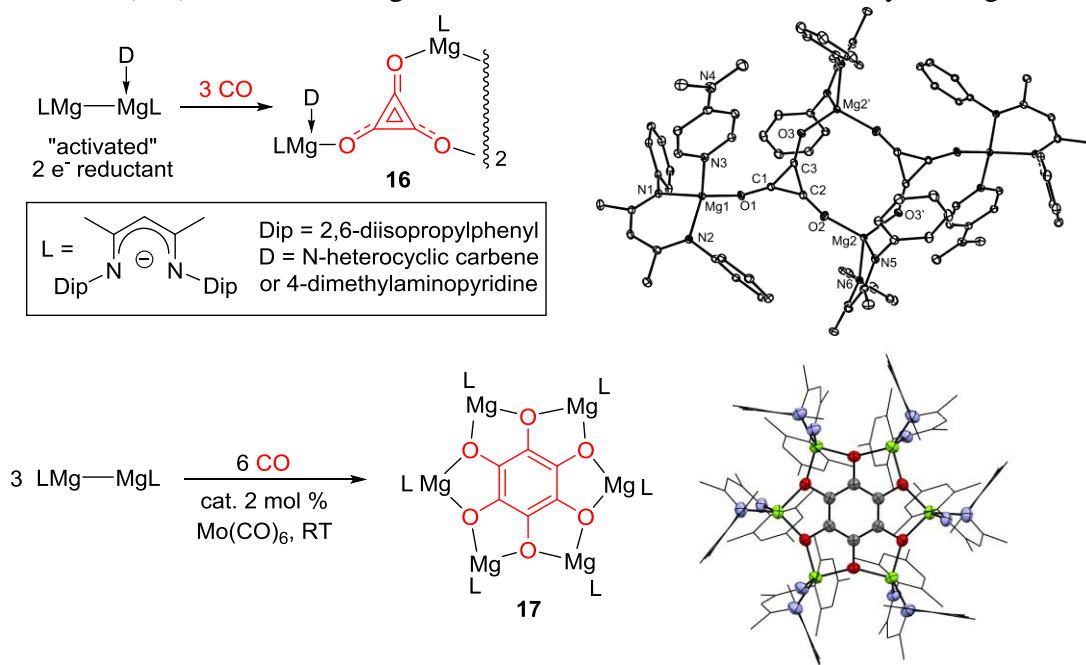
A number of other high profile results have been derived from this arm of the study. For example, as potential precursors to beryllium containing polymers, a library of beryllium halide complexes have been prepared and the work published (Scheme 9).<sup>6</sup> These have been utilised to prepare the first examples of Be-Al bonded compounds **15**, *via* reduction with a known aluminum(I) heterocycle.<sup>7</sup> These compounds contain the first examples of unsupported covalent bonds between beryllium and any metal, and could have potential as single source precursors for Al/Be alloys, which are widely used in aerospace and satellite technologies.



**Scheme 9.** Synthesis of Be halide complexes, and the first Be-Al bonded compounds.

In a related study, another very high profile result has been the reductive oligomerisation of CO with Mg<sup>I</sup> complexes to give the first main group delate [C<sub>3</sub>O<sub>3</sub>]<sup>2-</sup> complexes **16** (Scheme 10).<sup>8</sup> Such reductive oligomerisations are thought to be involved in the early stages of the Fischer Tropsch process for the conversion of syn-gas (H<sub>2</sub>/CO) to alkanes and higher alcohols. To achieve this result here, in solution, and at room temperature gives hope for making the process catalytic in the future. It is of note that the reductive trimerization of CO to the delate anion has

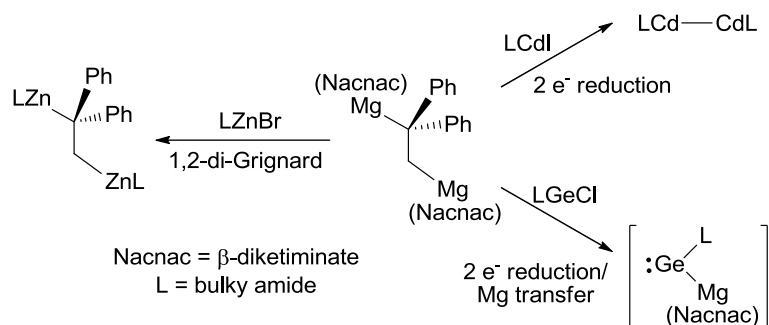
only been achieved once before, using a uranium(III) complex as the reducing agent.<sup>9</sup> In closely related, and as yet unpublished work, we have sought to extend this result to form larger reduced CO oligomers/polymers. Success has been had here with the  $\text{Mg}^{\text{I}}$  reductive hexamerization of CO to the remarkable benzenehexolate complex, **17**.<sup>10</sup> This reaction is catalysed with small amounts of  $\text{Mo}(\text{CO})_6$ , which is thought to activate CO towards reduction by the  $\text{Mg}^{\text{I}}$  dimer.



**Scheme 10.** Fischer-Tropsch like reductive trimerization and hexamerization of CO by  $\text{Mg}^{\text{I}}$  compounds.

In other work, reactions of three magnesium(I) dimers with several alkenes have led to the 1,2-addition of Mg–Mg bonds across the double bond of the substrate.<sup>11</sup> In the cases of 1,1-substituted alkenes, the reaction products were shown to be in equilibrium with a significant proportion of the starting materials at room temperature. Variable temperature NMR spectroscopy showed these equilibria to be rapidly reached, which indicates low kinetic barriers to these rare examples of redox reversible, and weakly exergonic, processes involving group 2 metals.

The use of 1,2-dimagnesioethane and 1,2-dimagnesioethene complexes as reagents in organometallic chemistry was explored. This study showed the complexes to have multifunctional, and potentially very useful, capabilities in this realm. For example, both magnesium reagents behave as 1,2-di-Grignard transfer reagents in their reactions with amido-metal halides. The importance of this result is compounded by the fact that acyclic 1,2-di-Grignard reagents are unknown, despite attempts to prepare them going back more than 100 years. Divergent reactivity has been shown by the 1,2-dimagnesioethane, which behaved as a two-electron reducing agent when treated with other amido-metal halides. A further class of reactivity for the 1,2-dimagnesioethane was uncovered when it was treated with an amido-germanium chloride. Here it behaved as a two-electron reducing, magnesium transfer reagent in the synthesis of a highly reactive, and unprecedented magnesium-germylene.



**Scheme 11.** Multifunctional reactivity of the first 1,2-dimagnesiumethane complex.

Several other areas of chemistry have been investigated in this study, and these have led to 3 further publications. Firstly, we have explored the reactivity of magnesium(I) dimers towards pinacolborane, HBpin, as this reactant is widely utilized in catalytic hydroborations of unsaturated substrates, as we have achieved with magnesium(II) hydrides (see above). However, here we found these reactions are extremely complicated and lead to many products, which rules out the likelihood of  $\text{Mg}^{\text{I}}$  systems being useful in catalytic hydroborations. Our study refuted the results of a series of papers and patents from a Chinese group, that claimed exactly the opposite.<sup>12</sup>

Project work which has led to other publications include our development of new synthetic routes to group 2 metal halide complexes, LMI (e.g. L = amidinate), which have served as precursors to some of the amidinato group 2 chemistry described above. The complexes were prepared by the novel technique of reaction of proligand LH with *in situ* generated heavier Grignard reagents, “PhMI” (M = Mg, Ca, Sr or Ba).<sup>13</sup> Finally we have been successful in preparing the first examples of silaimine systems which have Si=N double bonds, the N-center of which is substituted with a very bulky boryl group,  $\text{LSi}=\text{N}(\text{BR}_2)$ . These have been shown to activate a range of small molecule substrates, including undergoing [2+2] cycloaddition reactions with  $\text{CO}_2$ .<sup>14</sup>

**(ii) Zeolite and metal organic framework encapsulated poly(phosphaalkynes)**

As mentioned above, less progress has been made to this arm of the study than has been with the development of low oxidation state M-M bonded polymers and oligomers. As a result, project resources have been redirected to that more successful project goal. That said, we have commenced a collaboration with an international expert in the inclusion of small molecules in MOFs, Prof. Len Barbour, Stellenbosch University. This collaboration will involve a personnel exchange, and will exploit Barbour’s state of the art technology in this area. For example, single desolvated MOF crystals can be mounted on an X-ray diffractometer and exposed to vapours of volatile phosphalkyne PCMe (boils at ca. 40 °C) under a variety of pressures and temperatures. The change in the crystal structure can be monitored with time. The crystal can then be irradiated with UV light, or heated, to hopefully effect phosphalkyne polymerization. Unfortunately, this collaboration, which is critical to this arm of the project, has been temporarily postponed due to personnel issues. Once it re-commences resources will be directed back to this project goal.

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## List of Publications and Significant Collaborations that resulted from your AOARD supported project:

a) papers published in peer-reviewed journals (AOARD acknowledged in all)

1. Low-Valent Group 14 Element Hydride Chemistry: Towards Catalysis, T.J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.*, 2018, **47**, 4176-4197. DOI: 10.1039/C7CS00649G
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3. Redox Transmetalation Approaches to the Synthesis of Extremely Bulky Amido-Lanthanoid(II) and Calcium(II) Complexes, C.N. de Bruin-Dickason, A.J. Boutland, D. Dange, G.B. Deacon, C. Jones, *Dalton Trans.*, 2018, **47**, 9512-9520. DOI: 10.1039/C8DT02138D
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5. Multi-Gram Syntheses of Magnesium(I) Compounds using Alkali Metal Halide Supported Alkali Metals as Dispersible Reducing Agents, J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics*, 2018, **37**, 4810-4813. DOI:10.1021/acs.organomet.8b00803

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10. The complex reactivity of  $\beta$ -diketiminato magnesium(I) dimers towards pinacolborane: implications for catalysis, D.D.L. Jones, A.J.R. Mathews, C. Jones, *Dalton Trans.*, 2019, **48**, 5785-5792. DOI:10.1039/C9DT01085H
11. Reductive Trimerization of CO to the Deltate Dianion Using Activated Magnesium(I) Compounds, K. Yuvaraj, I. Douair, A. Paparo, L. Maron, C. Jones, *J. Am. Chem. Soc.*, 2019, **141**, 8764-8768. DOI: 10.1021/jacs.9b04085
12. Diagonally Related s- and p-Block Metals Join Forces: Synthesis and Characterization of Complexes with Covalent Beryllium–Aluminum Bonds, A. Paparo, C.D. Smith, C. Jones, *Angew. Chem. Int. Ed.*, 2019, **58**, 11459-11463. DOI: 10.1002/anie.201906609
13. Synthesis and reactivity of boryl substituted silaimines, K. Yuvaraj, C. Jones, *Dalton Trans.*, 2019, **48**, 11961-11965. DOI: 10.1039/C9DT02657F

b) conference and institution presentations

1. "Super Bulky Amides: New Ligands for the Stabilisation of Synthetically Applicable Low-Valent Main Group Complexes", School of Chemistry, Stellenbosch University, South Africa, March, 2018.
2. "Magnesium(I) Dimers 10 Years on: Universal Reductants for the Synthetic Chemist?" Plenary Lecture, IRIS-15 conference, Kyoto, Japan, June, 2018.
3. "Magnesium(I) Dimers 10 Years on: Universal Reductants for the Synthetic Chemist?" Invited Lecture, 2nd International Symposium of New Molecules and Clusters, Shanghai, China, August, 2018.

4. "Magnesium(I) Dimers 10 Years on: Universal Reductants for the Synthetic Chemist?" Plenary Lecture, Wöhler GDCh conference, Regensburg, Germany, September, 2018.
5. "Super Bulky Amides: New Ligands for the Stabilisation of Synthetically Applicable Low-Valent Main Group Complexes", School of Chemistry, Regensburg University, Germany, October, 2018.
6. "Magnesium(I) Dimers 10 Years on: Universal Reductants for the Synthetic Chemist?" Aachen University, Germany, October, 2018.
7. "Magnesium(I) Dimers 10 Years on: Universal Reductants for the Synthetic Chemist?" Technische University, Berlin, Germany, October, 2018.
8. "Polymers Incorporating Low-Valent/Low-Coordination Number Main Group Centres: Novel, Multi-Functional Materials", USAF/AFOSR Organic Materials Chemistry Program Review, Wright-Patterson Air Force Base, Dayton, Ohio, June, 2019.

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

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). A new collaboration was commenced with Prof. Len Barbour (Stellenbosch University). During the Organic Materials Chemistry Program Review in June, 2019, discussions with respect to collaboration with Dr. Rusty Blanski, AFRL, Edwards Air Force Base took place. Jones will travel to Edwards in September 2019 to explore forwarding this, and other, collaborations. All collaborations are greatly beneficial to the project, and have been central to the majority of publications arising from the project.