

## Modern Main Group Chemistry: From Renaissance to Revolution

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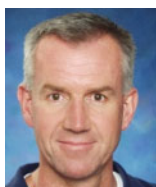
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The study of the main group (s- and p-block) elements and their compounds has been an ongoing theme in inorganic and organometallic chemistry for centuries. Indeed, many consider the birth of organometallic chemistry to be marked by Cadet's preparation of the foul smelling organo-arsenic compound,  $[(\text{Me}_2\text{As})_2\text{O}]$ , as long ago as 1760.<sup>[1]</sup> However, it was not for another century or so that main group organometallic chemistry began to flourish, and it continued to do so until the mid-20th century. By that time, it had been well explored and it was widely believed that all of the major discoveries had been made, and there were no great surprises left in store for synthetic chemists. Somewhat of a stagnation in the field followed, which was exacerbated by the rapid emergence of the fundamental and applied chemistry of the transition metal elements from the 1950s onwards. Despite this, main group chemistry stumbled on for several decades, until several enlightened chemists began to question the validity of rules and concepts (e.g. 'the double bond rule'<sup>[2]</sup>) that had been established to predict what coordination numbers and oxidation states main group elements could exhibit in their molecular compounds. In 1981, three landmark compounds were reported that disrupted this dogma forever. They were West's disilene,  $\text{Me}_2\text{Si}=\text{SiMe}_2$  (Mes = mesityl),<sup>[3]</sup> Yoshifuji's diphosphene,  $\text{Mes}^*\text{P}=\text{PMes}^*$

( $\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}_3^{1-2,4,6}$ ),<sup>[4]</sup> and Becker's phosphalkyne,  $\text{P}\equiv\text{CBu}^t$ .<sup>[5]</sup> The isolation of these remarkable compounds led to the realisation that 'all bets were off' when it came to what could or could not be achieved in main group chemistry, and three decades of renaissance in the field have followed.

The 're-birth' of main group chemistry has led to numerous fundamental advances, and the synthesis of ever more exotic compound types, many of which will populate the next generation of inorganic texts. While a full summary of these cannot be given here, they include compounds with main group elements in very low oxidation states, with very low coordination numbers, as part of metal–metal multiply bonded systems, and/or being incorporated into large multimetallic clusters.<sup>[6]</sup> Central to this field has been the need to develop increasingly bulky ligand systems to kinetically stabilise this new breed of compound from disproportionation, and other decomposition pathways. Similarly, new, and sometimes controversial, theories have been required to be developed to help us understand and explain the nature of the often unprecedented main group element–element bonding exhibited by these species. The importance of this aspect of modern main group chemistry is borne out by the increasing number of computational chemists who are attracted to it.



Professor Cameron Jones completed his B.Sc. (Hons) degree at the University of Western Australia in 1984. From 1985–1987, he worked as a Research Officer at the University Department of Surgery, Royal Perth Hospital. His Ph.D. degree was gained from Griffith University, Brisbane, under the supervision of Professor Colin L. Raston in 1992. He then moved to a post-doctoral fellowship (1992–1994) at Sussex University under the supervision of Professor John F. Nixon FRS. From 1994, he held a lectureship at the University of Wales, Swansea, before moving to a Readership in Inorganic Chemistry at Cardiff University (1998). There, he was promoted to a Personal Chair in Inorganic Chemistry in 2002. At Cardiff, he founded (in 2004) and co-directed The Centre for Fundamental and Applied Main Group Chemistry. In 2007, he moved to Monash University, Melbourne, as an ARC Australian Professorial Fellow and Professor of Chemistry. He is currently Professor of Chemistry at that institution. His current research interests are wide ranging, with particular emphasis being placed on the fundamental and applied chemistry of low oxidation state/low coordination number s-, p- and d-block metal complexes, unusual metal–metal bonded systems, main group hydrides, and the replacement of transition metal complexes in stoichiometric and catalytic synthetic procedures.



Professor George Koutsantonis is a synthetic chemist with an interest in functional materials that contain metals. He is a graduate of the University of Adelaide where he obtained his B.Sc. (Hons) and Ph.D. degrees, the latter under the supervision of Michael Bruce. He then undertook a post-doctoral position at the University of Kentucky, working with Jack Selegue. After a fruitful period in the USA, he returned to Australia on an inaugural ARC Postdoctoral Fellowship at Griffith University in 1991, working with Colin Raston. He was appointed to the staff at the University of Western Australia in 1995 where he remains. In Perth, he established an independent research program in organometallic and inorganic chemistry.

While the interest in the fundamental aspects of main group chemistry continues to grow unabated, a more recent revolution has begun to transform this discipline. In the early years of the new millennium, it began to be realised that low oxidation state main group compounds possess similar electronic properties and frontier orbital arrangements to those of many late transition metal complexes. Accordingly, it was proposed that these complexes may participate in reactions (e.g. oxidative additions and reductive eliminations) that have implicated transition metal complexes in countless catalytic and synthetic processes. In 2005, Power gave the first hint that this might indeed be the case when he reported an unprecedented activation of H<sub>2</sub> under ambient conditions with a main group compound.<sup>[7]</sup> Since then, there has been a competitive drive to develop main group systems that display 'transition metal-like' reactivity with respect to synthesis, catalysis, materials chemistry, and hydrogen storage system development, to name but a few.<sup>[8]</sup> These efforts are largely driven by the economic and environmental advantages that cheap, non-toxic, earth abundant main group elements possess over their often expensive and toxic heavier transition metal counterparts. While this aspect of modern main group chemistry is in its infancy, it is clear that the next decade will see major breakthroughs in the area, with main group systems becoming commercially applied to processes which were once the sole realm of transition metal complexes.

In this special issue of the Journal, we sought to attract contributions from leading national and international researchers in the field of main group chemistry, in order to provide a snapshot of the cutting-edge work that is being carried out around the globe at this time. We believe we have succeeded in attaining this goal, as the issue incorporates a total of 25 high quality papers from groups in Australia, New Zealand, Germany, United Kingdom, USA, and Canada. More importantly, we obtained a very high acceptance rate for the invitations that were sent out to potential contributors to this issue. It is our view that a good part of the reason for this is that Australia is fast gaining international recognition as a world leader in the field of modern main group chemistry. This situation will only be cemented with the growing number of young researchers who are being attracted from abroad, and from within our own shores, to start their academic careers carrying out research into topical aspects of main group chemistry. The future is surely bright for this fascinating field of study in Australia.

Considering the large number of papers we received for this issue, space constraints do not allow a summary of each here. However, it is worthwhile to give an indication of the broad areas of the field that are covered by the authors. Aspects of low oxidation state main group chemistry and ligand design are covered by Driess,<sup>[9]</sup> Goicoechea,<sup>[10]</sup> Jones,<sup>[11]</sup> Rivard,<sup>[12]</sup> Stasch,<sup>[13]</sup> and Weigand.<sup>[14]</sup> The application of main group compounds to synthetic methods is addressed in papers by Coles,<sup>[15]</sup> Driess,<sup>[9]</sup> Dutton,<sup>[16]</sup> Mulvey,<sup>[17]</sup> Scheschkewitz,<sup>[18]</sup> and Westerhausen.<sup>[19]</sup> The use of main group compounds as novel ligands in coordination chemistry is discussed in accounts by Aldridge,<sup>[20]</sup> Driess,<sup>[9]</sup> Gabbai,<sup>[21]</sup> and Hey-Hawkins.<sup>[22]</sup> Reports of structural studies of unusual main group compounds are provided by Coles,<sup>[15]</sup> Deacon,<sup>[23]</sup> Junk,<sup>[24]</sup> Koutsantonis,<sup>[25]</sup> Parkin,<sup>[26]</sup> and Turner.<sup>[27]</sup> The application of main group compounds to materials chemistry is investigated by Carmalt<sup>[28]</sup> and Baumgartner.<sup>[29]</sup> Spectroscopic and electrochemical analyses of low valent p-block compounds are presented by Baines<sup>[30]</sup> and Boere.<sup>[31]</sup> Finally, the application of main group compounds to

medicinal chemistry is discussed in a paper by Andrews<sup>[32]</sup> and a highlight article by Rendina.<sup>[33]</sup>

We would like to sincerely thank all of the authors who have contributed to this issue for the time they have taken out of their busy schedules to make this special issue a success. Of course, we would also like to pay tribute to their co-workers who contributed greatly to the work presented in the papers in this issue. Our jobs as guest editors were made all the more easy by the close attention of all authors to the submission deadline that we had to impose for the issue. We are also greatly indebted to the editorial and production teams of the Journal for their professionalism, and their hard work in getting this issue to press in a timely fashion.

## References

- [1] D. Seyferth, *Organometallics* **2001**, *20*, 1488. doi:10.1021/OM0101947
- [2] K. S. Pitzer, *J. Am. Chem. Soc.* **1948**, *70*, 2140. doi:10.1021/JA01186A043
- [3] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343. doi:10.1126/SCIENCE.214.4527.1343
- [4] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587. doi:10.1021/JA00405A054
- [5] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1981**, *36*, 16.
- [6] Selected recent reviews: (a) C. Jones, A. Stasch, *Top. Organomet. Chem.* **2013**, *45*, 73. doi:10.1007/978-3-642-36270-5\_3  
(b) C. Jones, A. Stasch in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities* (Eds A. J. Downs, S. Aldridge) **2011**, Ch. 5, pp. 285–341 (Wiley-Blackwell: Chichester).  
(c) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877. doi:10.1021/CR100133Q  
(d) H. Schnöckel, *Chem. Rev.* **2010**, *110*, 4125. doi:10.1021/CR900375G
- [7] G. H. Spikes, J. C. Fetting, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232. doi:10.1021/JA053247A
- [8] Selected recent reviews: (a) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354. doi:10.1021/CR100216Y  
(b) P. P. Power, *Acc. Chem. Res.* **2011**, *44*, 627. doi:10.1021/AR2000875  
(c) P. P. Power, *Nature* **2010**, *463*, 171. doi:10.1038/NATURE08634  
(d) S. Harder, *Chem. Rev.* **2010**, *110*, 3852. doi:10.1021/CR9003659  
(e) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46. doi:10.1002/ANIE.200903708
- [9] M. Stoezel, C. Präsang, B. Blom, M. Driess, *Aust. J. Chem.* **2013**, *66*, 1163. doi:10.1071/CH13196
- [10] R. S. P. Turbervill, J. M. Goicoechea, *Aust. J. Chem.* **2013**, *66*, 1131. doi:10.1071/CH13115
- [11] E. W. Y. Wong, D. Dange, L. Fohlmeister, T. J. Hadlington, C. Jones, *Aust. J. Chem.* **2013**, *66*, 1144. doi:10.1071/CH13175
- [12] S. M. I. Al-Rafia, P. A. Lummis, A. K. Swarnakar, K. C. Deutsch, M. J. Ferguson, R. McDonald, E. Rivard, *Aust. J. Chem.* **2013**, *66*, 1235. doi:10.1071/CH13209
- [13] C. P. Sindlinger, A. Stasch, *Aust. J. Chem.* **2013**, *66*, 1219. doi:10.1071/CH13229
- [14] M. H. Holthausen, D. Knackstedt, N. Burford, J. J. Weigand, *Aust. J. Chem.* **2013**, *66*, 1155. doi:10.1071/CH13141
- [15] M. P. Coles, P. B. Hitchcock, *Aust. J. Chem.* **2013**, *66*, 1124. doi:10.1071/CH12560
- [16] D. C. Georgiou, P. Butler, E. C. Browne, D. J. D. Wilson, J. L. Dutton, *Aust. J. Chem.* **2013**, *66*, 1179. doi:10.1071/CH13202
- [17] R. Campbell, E. Crosbie, A. R. Kennedy, R. E. Mulvey, R. A. Naismith, S. D. Robertson, *Aust. J. Chem.* **2013**, *66*, 1189. doi:10.1071/CH13157
- [18] A. Rammo, I. Bejan, A. Meltzer, K. Radacki, H. Braunschweig, D. Scheschkewitz, *Aust. J. Chem.* **2013**, *66*, 1311. doi:10.1071/CH13265

- [19] S. Härling, J. Greiser, T. M. A. Al-Shboul, H. Görls, S. Krieck, M. Westerhausen, *Aust. J. Chem.* **2013**, *66*, 1264. doi:[10.1071/CH13259](https://doi.org/10.1071/CH13259)
- [20] D. A. Addy, J. I. Bates, M. J. Kelly, J. Abdalla, N. Phillips, I. M. Riddlestone, S. Aldridge, *Aust. J. Chem.* **2013**, *66*, 1211. doi:[10.1071/CH13106](https://doi.org/10.1071/CH13106)
- [21] I.-S. Ke, F. P. Gabbaï, *Aust. J. Chem.* **2013**, *66*, 1281. doi:[10.1071/CH13260](https://doi.org/10.1071/CH13260)
- [22] I. Sárosi, M. B. Sárosi, P. Lönnecke, L. Silaghi-Dumitrescu, E. Hey-Hawkins, *Aust. J. Chem.* **2013**, *66*, 1246. doi:[10.1071/CH13262](https://doi.org/10.1071/CH13262)
- [23] G. B. Deacon, P. C. Junk, J. Luu, *Aust. J. Chem.* **2013**, *66*, 1253. doi:[10.1071/CH13227](https://doi.org/10.1071/CH13227)
- [24] G. B. Deacon, P. C. Junk, R. P. Kelly, *Aust. J. Chem.* **2013**, *66*, 1288. doi:[10.1071/CH13228](https://doi.org/10.1071/CH13228)
- [25] M. C. Adams, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Aust. J. Chem.* **2013**, *66*, 1260. doi:[10.1071/CH13314](https://doi.org/10.1071/CH13314)
- [26] Y. Rong, G. Parkin, *Aust. J. Chem.* **2013**, *66*, 1306. doi:[10.1071/CH13263](https://doi.org/10.1071/CH13263)
- [27] G. B. Deacon, P. C. Junk, D. R. Turner, J. A. Walker, *Aust. J. Chem.* **2013**, *66*, 1138. doi:[10.1071/CH13185](https://doi.org/10.1071/CH13185)
- [28] I. A. Hassan, A. Ratnasothy, D. S. Bhachu, S. Sathasivam, C. J. Carmalt, *Aust. J. Chem.* **2013**, *66*, 1274. doi:[10.1071/CH13226](https://doi.org/10.1071/CH13226)
- [29] Z. Wang, A. Y. Y. Woo, T. Baumgartner, *Aust. J. Chem.* **2013**, *66*, 1171. doi:[10.1071/CH13220](https://doi.org/10.1071/CH13220)
- [30] M. A. Hanson, A. Schnepf, V. V. Terskikh, Y. Huang, K. M. Baines, *Aust. J. Chem.* **2013**, *66*, 1202. doi:[10.1071/CH13122](https://doi.org/10.1071/CH13122)
- [31] M. Taghavikish, B. L. Price, T. L. Roemmele, R. T. Boéré, *Aust. J. Chem.* **2013**, *66*, 1226. doi:[10.1071/CH13244](https://doi.org/10.1071/CH13244)
- [32] P. C. Andrews, P. C. Junk, L. Kedzierski, R. M. Peiris, *Aust. J. Chem.* **2013**, *66*, 1297. doi:[10.1071/CH13374](https://doi.org/10.1071/CH13374)
- [33] J. Kahlert, C. J. D. Austin, M. Kassiou, L. M. Rendina, *Aust. J. Chem.* **2013**, *66*, 1118. doi:[10.1071/CH13256](https://doi.org/10.1071/CH13256)