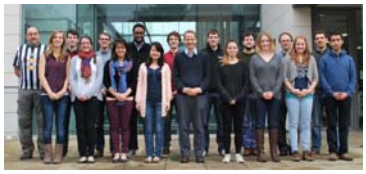
DEPARTMENT OF CHEMISTRY

UNIVERSITY OF OXFORD

Professor P. Mountford

Head of Inorganic Chemistry and Professor of Organometallic Chemistry & Catalysis

Email and other contact details
For a biography and CV click here



Research Group

St Edmund Hall

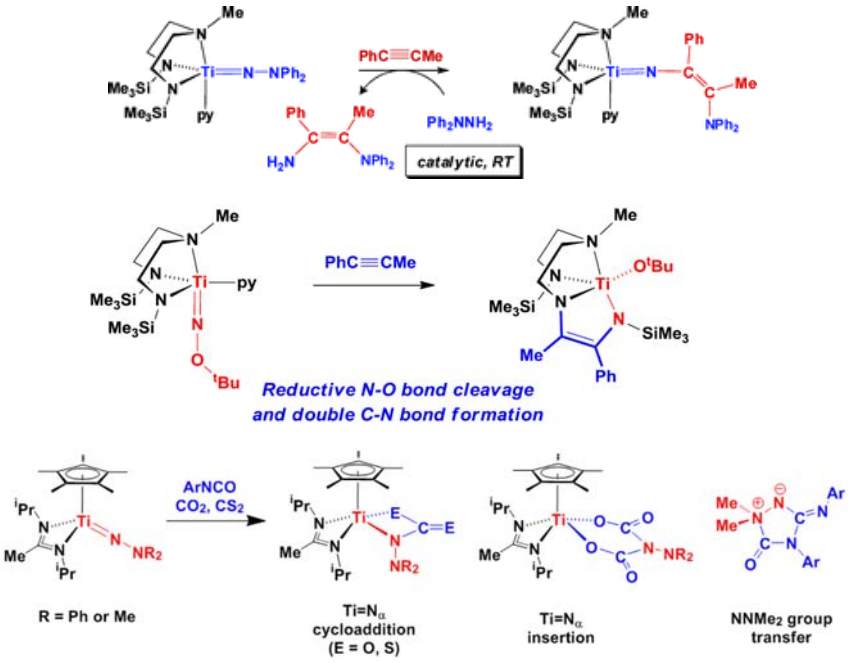
Research

Organometallic Chemistry and Catalysis

The Mountford Group is an international mixture of postdoctoral researchers, PhD and Oxford Masters (Part II) students, and visiting academic fellows. We are working on the synthesis and stoichiometric and catalytic chemistry of organometallic compounds of the transition and lanthanide metals. Please browse the outline information below and then visit the Mountford Group web site for full details, including the latest news from the group, who we are and what we do, along with details of how to join the group. Selected references are given in the next section. Click here for a printable version of this site.

Synthesis, bonding and small molecule activation reactions of transition metal hydrazide complexes

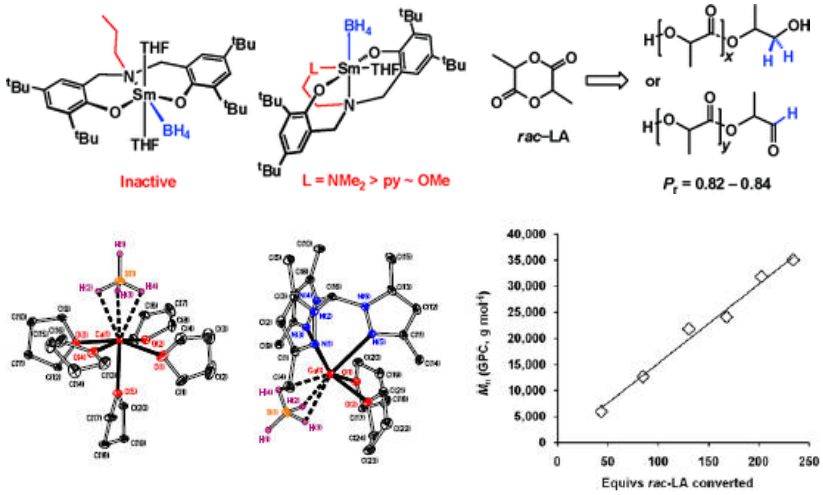
Transition metal hydrazides, (L)M=NNR$_2$, have been of continuing interest because of their relevance to the biological conversion of N_2 to ammonia. Much of the early work was based around Group 6 systems for which M=N-NR$_2$ group small molecule reactivity is minimal.



Group 4 hydrazides have significantly more activated M=NNR$_2$ functional groups. There has recently been a surge in activity in this area with a wide range of hitherto unprecedented new small molecule reactivity. We have been at the forefront of this drive and one example of our new titanium hydrazide chemistry is shown above. Further details

New ring opening polymerisation catalysts for biodegradable and biocompatible green polymers as substitutes for oil-derived materials

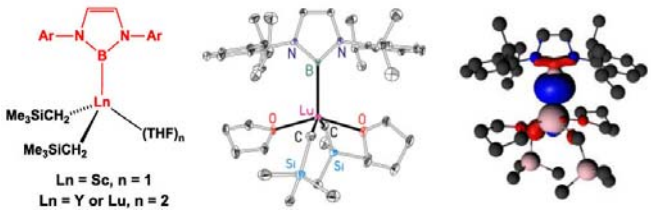
There is a great deal of current interest in the controlled ring-opening polymerization (ROP) of cyclic esters such as e-caprolactone (CL) or lactide (LA) to form biocompatible or biodegradable materials. Lactide (see figure) is in principle infinitely renewable, being derived from corn and is thus an non-oil-derived, renewable resource. The key challenges are the controlled ROP of these cyclic esters allowing control of polymer molecular weight, tacticity.



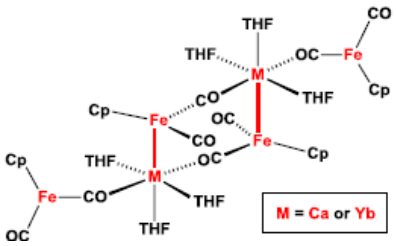
We have been developing three new families of organometallic compounds for the ROP of cyclic esters using either metal-borohydride catalysts (illustrated above), sulfonamide-supported catalysts or amine-co-oinitiated cationic or zwitterionic catalysts. Further details

Synthesis, structure, bonding and reactivity of unusual organometallic complexes

In addition to the three themes summarised above we continue to be interested in fundamental aspects of organometallic synthesis, bonding and reactivity from a "blue skies" exploratory point of view. Recent examples of this type of chemistry are illustrated below. Further details



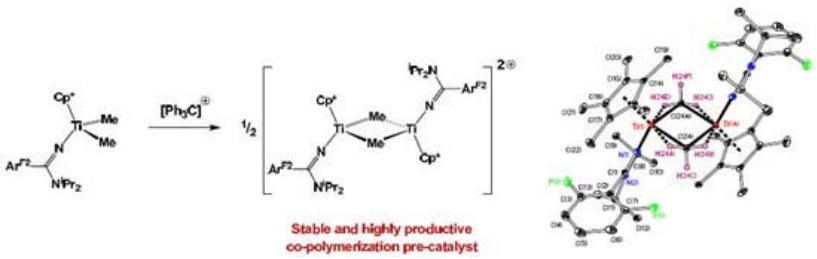
The first Group 3 and lanthanide boryl (metal-boron single bond) compounds



The first calcium-transition metal bond and a comparison with a lanthanide-transition metal counterpart

Fundamental and applied studies of new olefin polymerisation and oligomerisation catalysts

Ziegler-Natta alkene polymerisation catalysis is a very important current area of organometallic chemistry is . Inspired by the early successes of Group 4 metallocene catalysts Cp_2MX_2 (X = alkyl or halide), a huge amount of academic and industrial effort is being spent world-wide on developing new transition metal catalysts that combine very high activities with good control of polymer molecular weight, as well as also understanding the underlying fundamental chemistry.



The catalytically active species in this chemistry are alkyl cations $[(L)M\text{-}R]^+$. In a joint venture between our group, industrial sponsors in the field of catalysis and the UK research councils we

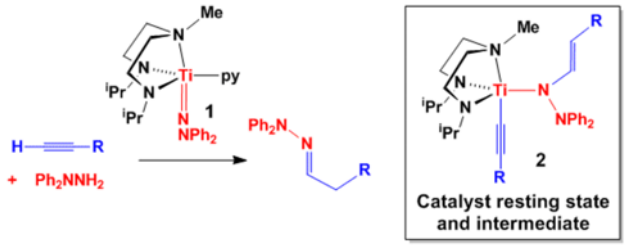
are developing new families of new "post-metallocene" catalysts; a recent example is shown above. Further details

Selected Publications

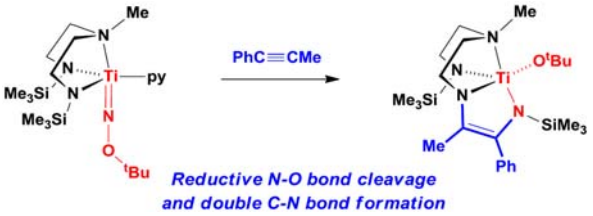
Here are some selected recent publications, including graphical summaries. For a complete publication list click here. Details of our collaborations and funding are given at the end. Click here for a printable version of this site.

Synthesis and small molecule activation reactions of transition metal hydrazide complexes

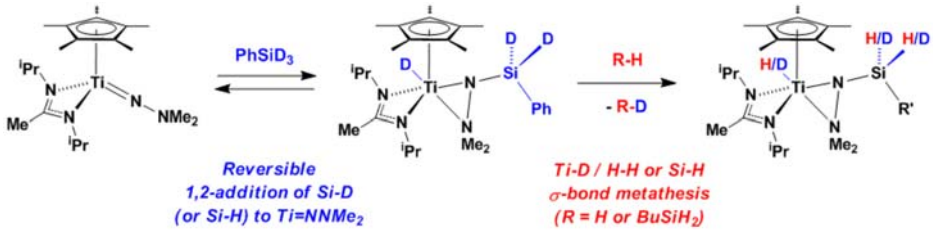
"*A remarkable switch from a diamination to a hydrohydrazination catalyst and observation of an unprecedented catalyst resting state.*" A. D. Schwarz, C. S. Onn and P. Mountford, *Angew. Chem. Int. Ed.*, 2012, **51**, 12298-12302. [link to journal].



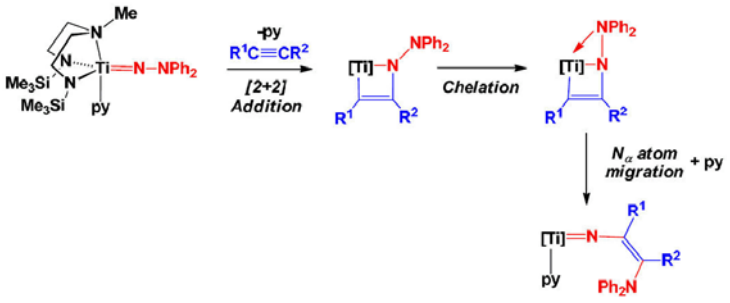
"*Titanium alkoxyimido (Ti=N-OR) complexes: reductive N-O bond cleavage at the boundary between hydrazide and peroxide ligands*". A. D. Schwarz, A. Nova, E. Clot and P. Mountford, *Chem. Commun.*, 2011, **47**, 4926–4928. [link to journal].



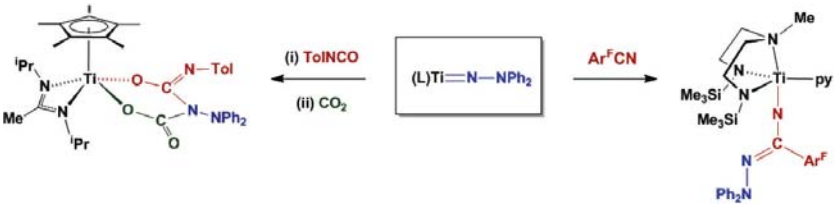
"*Si-H and Si-Cl bond activation of titanium hydrazides with silanes and subsequent Ti-H / E-H (E = Si or H) sigma bond metathesis*". P. J. Tiong, A. Nova, E. Clot and P. Mountford, *Chem. Commun.*, 2011, **47**, 3147-3149. [link to journal].



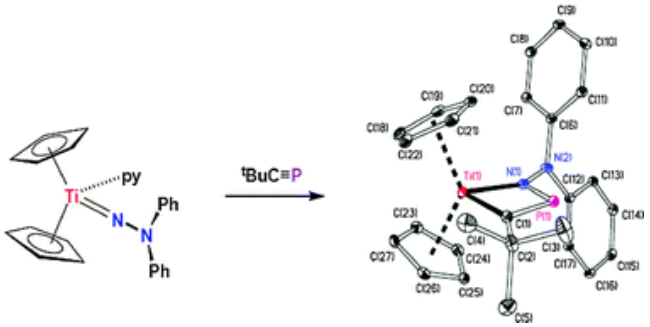
"M=N cycloaddition and N-N insertion in the reactions of titanium hydrazido compounds with alkynes: a combined experimental and computational study".A. D. Schofield, A. Nova, J. D. Selby, C. D. Manley, A. D. Schwarz, E. Clot and P. Mountford, *J. Am. Chem. Soc.*, 2010, **132**, 10484-10497. [link to journal].



"Single and double substrate insertion into the Ti=N bonds of terminal titanium hydrazides". P.-J. Tiong, A. D. Schofield, J. D. Selby, A. Nova, E. Clot and P. Mountford, *Chem. Commun.* 2010, **46**, 85-87. [link to journal].

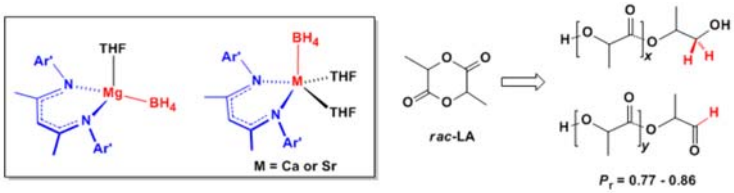


"Cycloaddition reactions of transition metal hydrazides with alkynes and heteroalkynes: coupling of Ti=NNPh$_2$ with PhCCMe, PCCH, MeCN and ^{t}BuCP". J. D. Selby, A. D. Schwarz, C. Schulten, E. Clot, C. Jones and P. Mountford, *Chem. Commun.*, 2008, 5101-5103. Designated a "hot article" by the Editor. [link to journal].

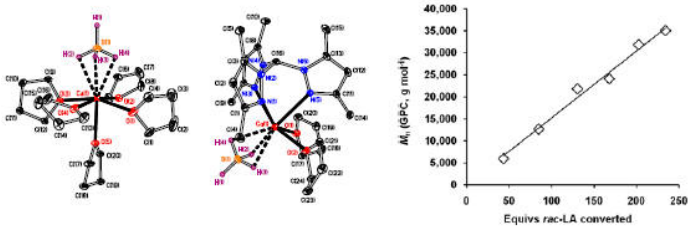


Synthesis and polymerisation studies of new catalysts for the preparation of biodegradable and biocompatible polymers

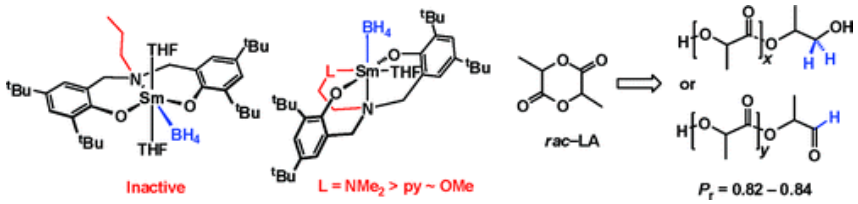
"*Synthesis and rac-lactide ring-opening polymerisation studies of new alkaline earth tetrahydroborate complexes.*" R. A. Collins, J. Unruangsri and P. Mountford, *Dalton Trans.*, 2013, accepted for publication. Invited contribution for a Special Issue on metal borane and borohydride chemistry.



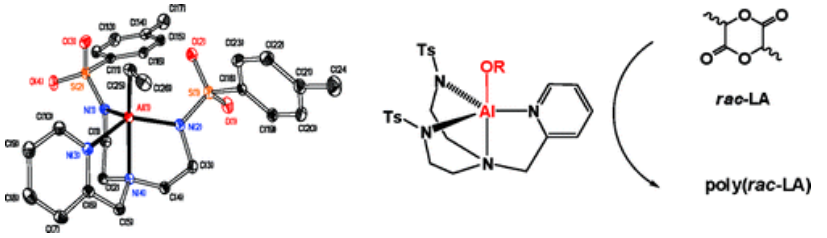
"*Cationic and charge-neutral calcium tetrahydroborate complexes and their use in the controlled ring-opening polymerisation of rac-lactide*." M. G. Cushion and P. Mountford, *Chem. Commun.*, 2011, **47**, 2276-2278. [link to journal].



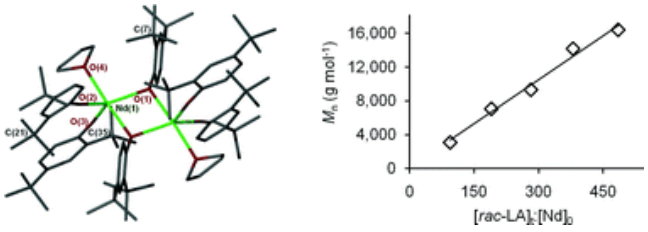
"Ring-opening polymerization of rac-lactide by bis(phenolate)amine-supported samarium borohydride complexes: an experimental and DFT study". H. E. Dyer, S. Huijser, N. Susperregui, F. Bonnet, A. D. Schwarz, R. Duchateau, L. Maron and P. Mountford. *Organometallics*, 2010, **29**, 3602-3621. [link to journal].



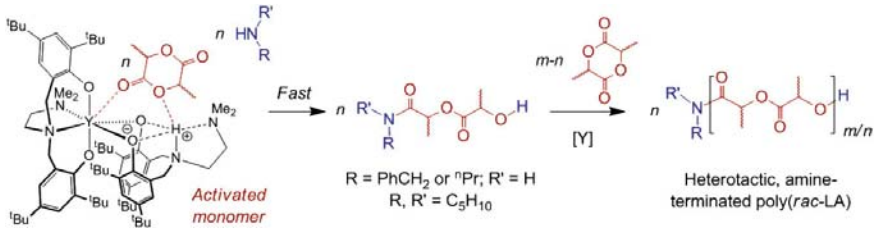
"Sulfonamide-supported aluminum catalysts for the ring-opening polymerization of rac-lactide". A. D. Schwarz, Z. Chu and P. Mountford, *Organometallics*, 2010, **29**, 1246-1260. [link to journal].



"Low-coordinate rare earth complexes of the asymmetric 2,4-di-tert-butylphenolate ligand prepared by redox transmetallation/protonolysis reactions and their reactivity towards ring-opening polymerisation". L. Clark, G. B. Deacon, C. M. Forsyth, P. C. Junk, P. Mountford and J. P. Townley, *Dalton Trans.*, 2010, **39**, 6693-6704. [link to journal].

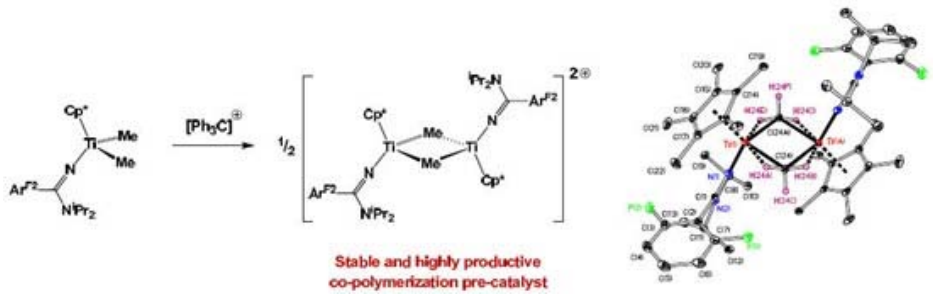


"Dicationic and zwitterionic catalysts for the amine-initiated, immortal ring-opening polymerisation of rac-lactide: facile synthesis of amine-terminated, highly heterotactic PLA". L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateau and P. Mountford, *Chem. Commun*. 2010, **46**, 273-275. [link to journal].

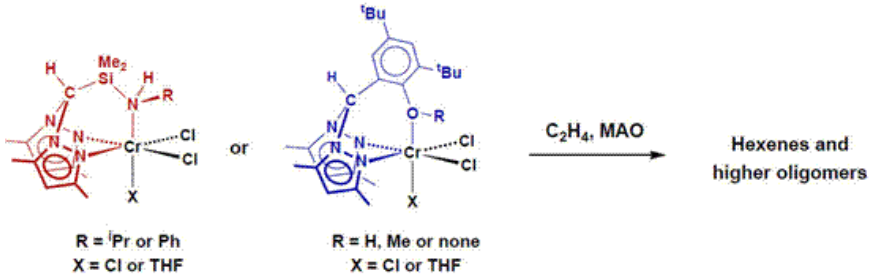


Fundamental and applied studies of new olefin polymerisation and oligomerisation catalysts

"Synthesis, solid state and DFT structure and olefin polymerization capability of a unique base-free dimeric methyl titanium dication". E. G. Ijpeij, B. Coussens, M. A. Zuideveld, G. H. J. van Doremaele, P. Mountford, M. Lutz and A. L. Spek, *Chem. Commun*., 2010, **46**, 3339-3341. [link to journal].

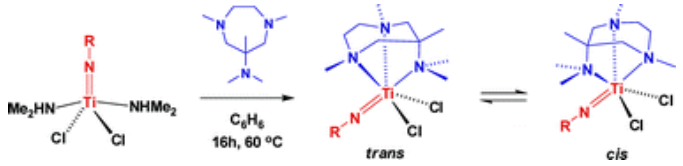


"Synthesis and ethylene trimerisation capability of new chromium(II) and chromium(III) heteroscorpionate complexes". A. F. R. Kilpatrick, S. V. Kulangara, M. G. Cushion, R. Duchateau, and P. Mountford. *Dalton Trans*., 2010, **39**, 3653-3664. [link to journal].

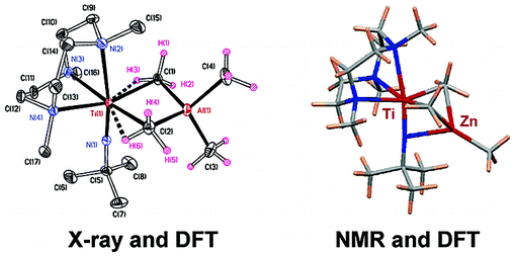


"Imido titanium compounds bearing the 6-dimethylamino-1,4,6-trimethyl-1,4-diazacycloheptane ligand: synthesis, structures, solution dynamics and ethylene polymerisation capability". G. J. Hayday, C. Wang, N. H. Rees and P. Mountford, *Dalton*

Trans. 2008, 3301-3310. Designated a "hot article" by the Editor. [link to journal].

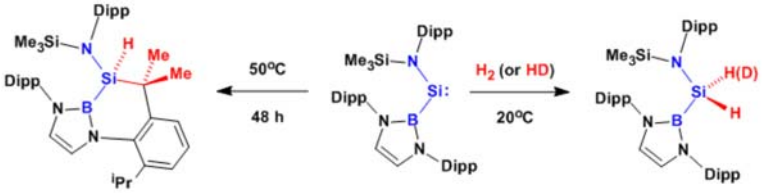


"$AlMe_3$ and $ZnMe_2$ adducts of a titanium imido methyl cation: a combined crystallographic, spectroscopic and DFT study". P.D. Bolton, E. Clot, A. R. Cowley and P. Mountford, *J. Am. Chem. Soc.*, 2006, **128**, 15005-15018. [link to journal].

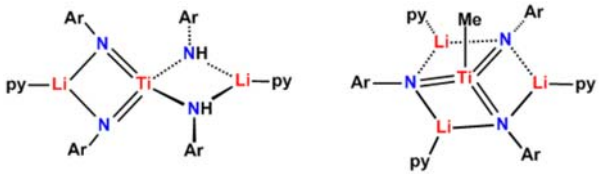


Fundamental aspects of the synthesis, structure, bonding and reactivity of unusual organometallic complexes

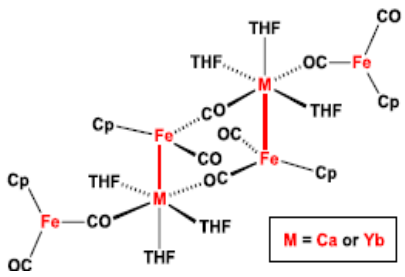
"*A stable two-coordinate silylene*". A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503. [link to journal] Highlighted in *Nature*, 2012, **485**, 49-50 and *Nature Chem.*, 2012, **4**, 525.



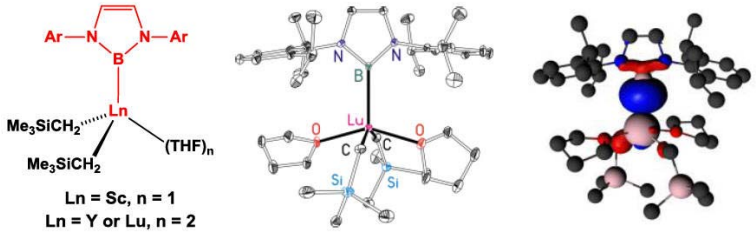
"*The first Group 4 metal bis(imido) and tris(imido) complexes*." A. D. Schwarz, A. J. Nielson, N. Kaltsoyannis and P. Mountford, *Chemical Science*, 2012, **3**, 819-824. [link to journal].



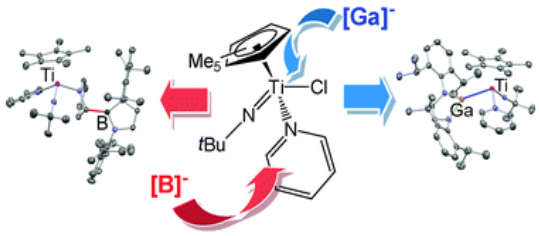
"*Heterobimetallic complexes containing Ca–Fe or Yb–Fe bonds: synthesis and molecular and electronic structures of $[M\{CpFe(CO)_2\}_2(THF)_3]_2$ (M = Ca or Yb)*." M. P. Blake, N. Kaltsoyannis, and P. Mountford, *J. Am. Chem. Soc.*, 2011, **133**, 15359-15361. [link to journal].

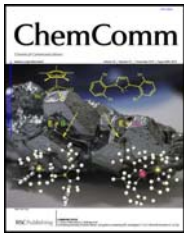


"*Group 3 and lanthanide boryl compounds: syntheses, structures and bonding analyses of Sc–B, Y–B and Lu–B sigma-coordinated NHC analogues*". L. M. A. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, and P. Mountford, *J. Am. Chem. Soc.* 2011, **133**, 3836-3839. [link to journal].



"Contrasting reactivity of anionic boron- and gallium-containing NHC analogues: E-C vs.M-E bond formation (E = B, Ga)". A. V. Protchenko, L. M. A. Saleh, D. Vidovic, D. Dange, C. Jones, P. Mountford and S. Aldridge, *Chem. Commun.*, 2010, **46**, 8546-8548. Designated a "hot article" by the Editor. [link to journal].





Collaborations and Funding

Here are some details of our current principal collaborations and funding

Prof Simon Aldridge (Oxford) and Prof Cameron Jones (Monash University, Australia). Transition and main group boryl and gallyl chemistry.

Dr Eric Clot (University of Montpellier, France) and *Prof. Nik Kaltsoyannis (University College London).* Computational studies of mechanism and electronic structure.

Prof Charlotte Williams (Imperial College London, UK). Ring-opening polymerisation catalysis).

Profs Glen Deacon and Peter Junk (Monash University, Australia). Lanthanide and Group 2 phenolate complexes for the living and immortal ring-opening polymerisation of cyclic esters.

Our work has been funded by grants from the EPSRC, Leverhulme Trust, Nuffield Foundation, China Scholarship Council, EC (Marie Curie), University of Oxford, British Council, Royal Society and the Royal Society of Chemistry. Applied aspects of our research have been supported by DSM Research, DSM Elastomers, Sabic Europe, Cambridge Material Science and Millennium Pharmaceuticals.

Back to the top