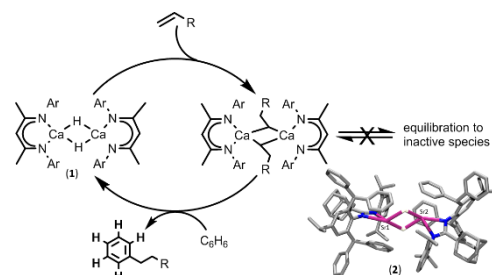


Bath Monash Global PhD Programme in Sustainable Chemical Technologies

Project Title:	Catalytic arene functionalization with nucleophilic heavier alkaline earth reagents
Supervisor at Bath:	Professor Michael Hill (lead)
Supervisor at Monash:	Professor Cameron Jones
Home Institution:	University of Bath
Indicative period at Host Institution:	From April 2021 to April 2022

Project Summary

The direct addition of aromatic C-H bonds to unsaturated substrates (alkenes or alkynes) would provide an atom-economical strategy for the synthesis of valuable functionalised aromatic molecules.¹ Although limited reports of hydroarylation chemistry have appeared since the 1980s, this reactivity typically remains in the realm of precious metal (e.g. Pd, Pt, Ir) catalysis. This PhD project will build directly on the recent discovery in the Hill group that alkyl and hydride derivatives of calcium (e.g. **1**), one the most earth abundant and non-toxic elements, can effect the displacement of hydride from benzene to provide direct nucleophilic access to alkyl benzene derivatives (Scheme 1).² Although, hypothetically, this chemistry may be readily extended to a catalytic regime, the scope this reactivity is limited by the solution instability of the β -diketiminato complexes toward Schlenk equilibration to inactive and/or insoluble species.



Scheme 1: The hydroarylation of benzene catalysed by **1**² and a recently reported stable strontium hydride (**2**).⁴

The Hill and Jones groups have previously reported that the synthesis of unusual 3-coordinate magnesium hydrides may be achieved through judicious ligand design.³ This PhD project will exploit this joint expertise to devise novel heteroleptic hydride derivatives of calcium and its heavier congeners, strontium and barium, (e.g. **2**,⁴ Scheme 1), which will display enhanced stability toward deleterious Schlenk equilibria. The reactivity of the new compounds will be studied to assess and develop their ability to (a) activate sp^2 and sp^3 C-H bonds; (b) enable further completely unprecedented catalytic transformations, including the hydroarylation of hydrocarbon arenes and alkenes and the catalytic synthesis of valuable bi- and polyaryl species. The student will be trained to experimentally investigate the mechanisms of any new transformations, which will be

¹ Catalytic Hydroarylation of Carbon-Carbon Multiple Bonds', eds Lutz Ackermann, T. Brent Gunnoe, Laurel Goj Habgood, **2018**, Wiley-VCH, Weinheim

² Hill, M. S., Mahon, M. F., Wilson, A. S. S., Maron, L. & Dinoi, *Science*, **2017**, 358, 1168-1171;

³ Arrowsmith, M., Maitland, B., Kociok-Köhn, G., Stasch, A., Jones, C. & Hill, M. S. *Inorg. Chem.* **2014**, 53, 10543-10552;

⁴ de Bruin-Dickason, C. N. Sutcliffe, T., Deacon, G. B., Maron, L. & Jones, C. *Chem. Commun.* **2018**, 54, 786-789.

assessed computationally through DFT methods by Prof. L. Maron (University of Toulouse), who has a strong history of collaboration with both the Bath and Monash research groups.

Features of the programme

- PhD researchers will be registered at both institutions and will be awarded a joint PhD degree.
- PhD researchers will be jointly supervised by academics from both Monash and Bath Universities.
- All PhD researchers in the joint programme will also undertake a bespoke advanced training plan covering a range of topics focusing on sustainability.
- Applicants can apply to either Monash University or the University of Bath as their nominated home institution.
- PhD researchers will undertake a period of no less than 12 months at the partner institution.
- Up to four scholarships/studentships will be offered. Additional and suitably qualified applicants who can access a scholarship/studentship from other sources will be also considered. Evidence of funding must be provided.
- The scholarships/studentships include:
 - a *full tuition fee sponsorship* provided by Bath (home or EU students only) or Monash for the course duration (up to a maximum 42 months)
 - a *living allowance (stipend)* provided by Monash or Bath Universities. Note: Overseas Student Health Cover (OSHC) must be paid by the student, unless covered by the university.

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How to apply

Please express interest for up to three projects in order of preference. Please submit your application at the Home institution of your preferred project. However, please note that you are applying for a joint PhD programme and applications will be processed as such.

The deadline to submit applications is Sunday 12 May.

Monash University

Expressions of interest (Eoi) can be lodged through <https://forms.gle/XkC1TKpqVQh4B4N1A>. The Eoi should provide the following information:

CV including details of citizenship, full transcripts of academic records, evidence of English language level (IELTS or TOEFL), nominate your host institution (ie Bath or Monash), two referees and contact details, indication of which projects are of interest.

University of Bath

Please submit an application through the following link:

https://samis.bath.ac.uk/urd/sits.urd/run/siw_ipp_lgn.login?process=siw_ipp_app&code1=RDUCH-MO01&code2=0001

Please make sure to mention in the “finance” section of your application that you are applying for funding through the joint Bath/Monash PhD programme for your specified projects.

In the “research interests” section of your application, please name up to three projects you are interested in and rank them in order of preference. Please also include the names of the Bath lead supervisors.