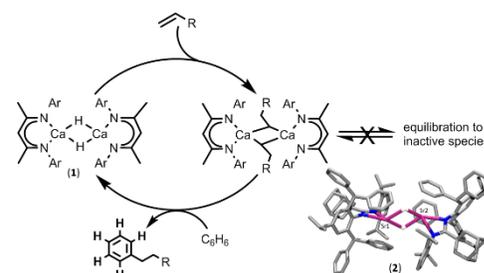


Bath Monash Global PhD Programme in Sustainable Chemical Technologies

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 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.

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.