

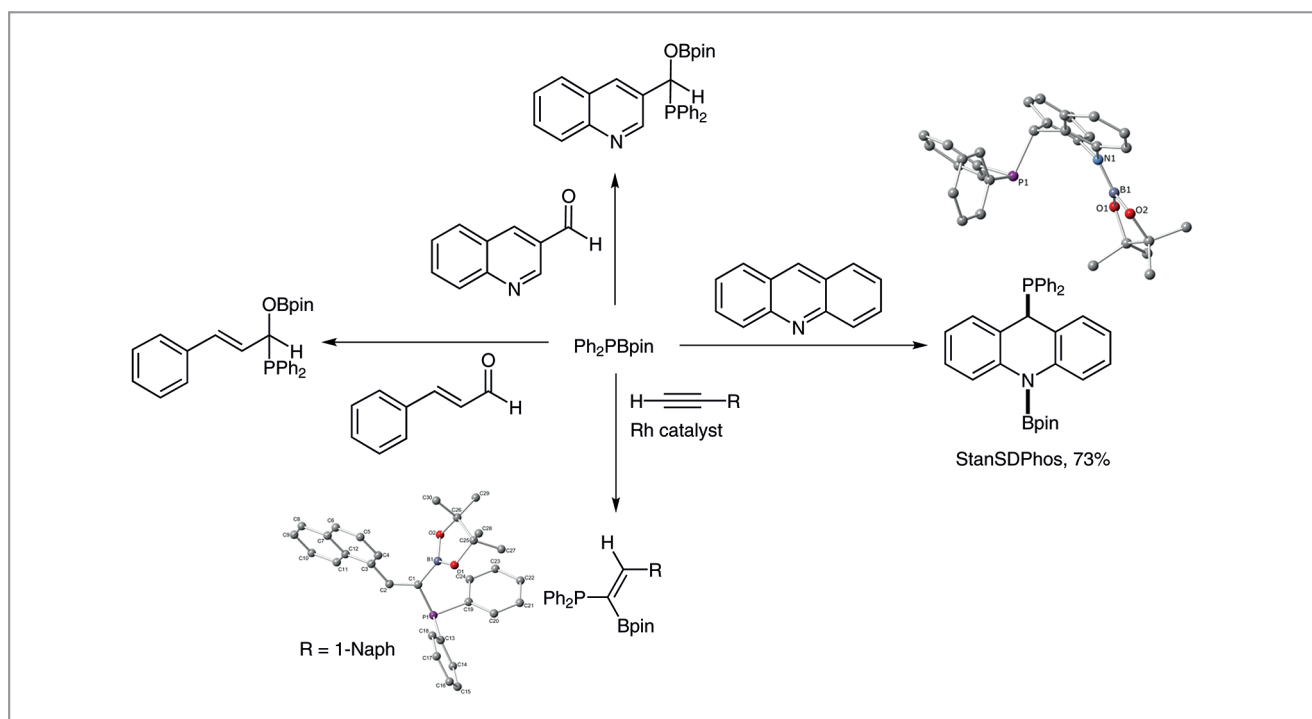
# The Phosphinoboration Reaction

*Angew. Chem. Int. Ed.* **2015**, *54*, 2121–2125

The addition of boron–element bonds (where element = H, B, Sn, Si, Se, S) to organic substrates has become a fundamentally important reaction in organic synthesis over the past few decades. Classic examples are the hydroboration reaction (element = H) or diboration/borylation reactions (element = B), but many more reactions of this type are becoming an integral part of the arsenal of reactions available to organic chemists. Recently, the research group of Professor Stephen Westcott at Mount Allison University (New Brunswick, Canada) reported on a unique phosphinoboration reaction where compounds with a single P–B bond add readily to unsaturated bonds. Professor Westcott said: “Although research associate Chris Vogels initially made the starting phosphinoboronate esters several years ago, the project didn’t really take off until we assembled a remarkable group of people to conduct this research.” He continued: “Erika was an undergraduate student at the time and initiated the reactivity studies as part of her Honours thesis work. Chris Vogels and Dr. Steve Geier rocked this project and helped design the substrate scope, finished

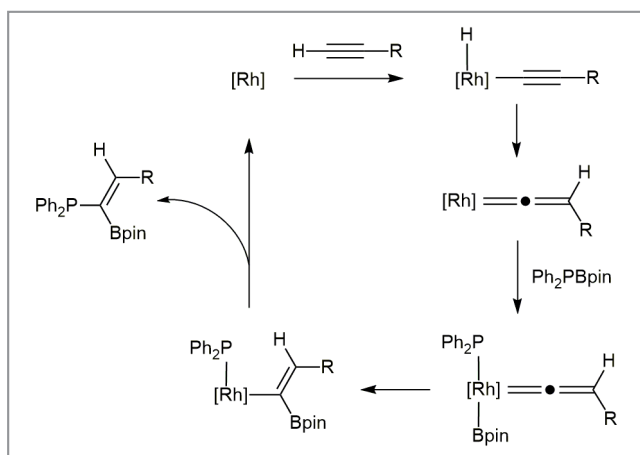
the addition reactions, isolated products and carried out the catalytic work. Dr. Andreas Decken was crucial in solving the challenging molecular structures using X-ray diffraction studies and confirming the nature of the resulting addition products, which was key to our understanding of the 1,1-addition product observed in the unusual reaction with terminal alkynes. Dr. Simon Doherty investigated the computational aspects of this project, provided fundamental insights into the chemistry and co-wrote the publication. The editor of the journal and anonymous reviewers were also exceedingly helpful. It really has been a great team effort all around and everyone played a critical role in the success of this work.”

Highlighted in Scheme 1 are some of the more remarkable reactions covered in this initial study. “Surprisingly, addition of  $\text{Ph}_2\text{PBpin}$  to acridine proceeded at room temperature to give the corresponding 1,4-addition product, named StanSDPhos here because we plan to expand this chemistry by investigating its use as an ambiphilic ligand and in Frustrated Lewis Pair (FLP) chemistry,” said Professor Westcott, who



**Scheme 1** Reactions of  $\text{Ph}_2\text{PBpin}$

continued by explaining that the reduction of pyridine derivatives with other boron agents usually requires the use of a transition metal to facilitate the addition. "Chemoselective reduction of the aldehyde group was observed in reactions with 3-quinolinecarboxaldehyde and one equivalent of  $\text{Ph}_2\text{PBpin}$ ," he continued. Interestingly, the reaction of *trans*-cinnamaldehyde with  $\text{Ph}_2\text{PBpin}$  gave only the corresponding 1,2-addition product, even though 1,4-addition products are observed predominantly in other borylation reactions. "Finally, the first example of a metal-catalyzed phosphinoboration reaction was reported with terminal alkynes," said Professor Westcott, "which presumably proceeds via a vinylidene-type mechanism (Scheme 2), to give unusual 1,1-addition products."

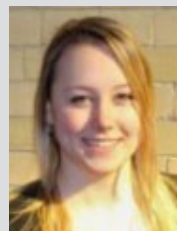


**Scheme 2** Possible mechanism for the phosphinoboration of terminal alkynes

Professor Westcott concluded: "We are excited this work has received such positive attention, especially from the groups of Doug Stephan (University of Toronto, Canada) and Elena Fernández (University Rovira i Virgili, Spain), who are now interested in helping us develop this unique reaction. We hope others will want to expand this chemistry and are looking forward to seeing what else these new phosphinoboronate esters can do!"

*Matthew Farnish*

## About the authors



*E. N. Daley*

**Erika N. Daley** was born and raised in Halifax, Nova Scotia (Canada). She obtained her BSc (Hons) in chemistry from Mount Allison University (Canada) in 2014. Erika is currently a PhD student at the University of Toronto (Canada) under the guidance of Professor Douglas W. Stephan. She holds an Ontario Graduate Scholarship and was recently awarded the BASF Canada Graduate Student Award. Her current research focuses on investigating the synthesis and reactivity of novel Group 13 cations for hydrogenation catalysis. Erika is also an executive member of the U of T Green Chemistry Initiative and a Science Ambassador at Pueblo Science.



*C. M. Vogels*

**Christopher M. Vogels** received his BSc from Mount Allison University (Canada) in 1993 and his MS from New Mexico State University (USA) in 1996 under the supervision of Professor Michael Johnson, studying reactions between potassium ferrate and a variety of arsenic compounds. He has been working with the Wild Toads since 1997 as a Research Associate and Lab Manager and has helped

training hundreds of remarkable undergraduate students. His current research interests include the synthesis of novel transition-metal complexes and the biological activity of boron-containing compounds.



*Dr. S. J. Geier*

**Stephen J. Geier** is a native of Sackville, New Brunswick (Canada). He completed his BSc at Mount Allison University (Canada) and went on to pursue his PhD at the University of Windsor (Canada) under the supervision of Dr. Douglas W. Stephan. His PhD work focused on Frustrated Lewis Pair (FLP) chemistry. He accompanied Dr. Stephan in his move to the University of Toronto (Canada). Following the completion of his PhD in 2010, he spent two years as an NSERC Postdoctoral Fellow in the lab of Dr. Jeffrey R. Long at the University of California, Berkeley (USA). He then returned to Sackville to help old man Westcott and has been a Research Associate with the Wild Toads at Mount Allison University since January 2013. His research interests include all things boron.

>>



Dr. A. Decken

**Andreas Decken** was born in Germany in 1964 and received his Diplom from the University of Duisburg (Germany) in 1989. He obtained his PhD from McMaster University (Canada) under the guidance of Michael J. McGlinchey in 1993. He continued his work at UT Austin (USA) as a Postdoctoral Fellow with Alan H. Cowley and in 1995 joined the Chemistry Department at the University of New Brunswick (Canada), Fredericton. He is currently Senior Research Associate focusing on small-molecule crystallography.



Dr. S. Doherty

**Simon Doherty** was awarded first class honors in Chemistry in 1987 and a PhD in 1990 with Professor A. J. Deeming at University College London (UK). He then conducted postdoctoral research with Professor Arthur J. Carty at the University of Waterloo (Canada) and with Professor Malcolm Chisholm at Indiana University (USA). In 1995, Simon was appointed as a Lecturer in Chemistry at Newcastle University (UK) and after a three-year appointment at Queens University Belfast (UK) (2000–2003) he returned to Newcastle where he is currently a

Senior Lecturer in Organometallic Chemistry and Catalysis and Director of Newcastle University Catalysis (NUCAT). His research interests are wide-ranging in organophosphorus and boron chemistry. More recent endeavors have been exploring the concept and applications of polymer-immobilized ionic-liquid-phase (PIILP) catalysis.



Prof. S. A. Westcott

**Stephen A. Westcott** was born in the sixties somewhere around Tecumseh and received his PhD from the University of Waterloo (Canada) under the joint supervision of Drs Todd B. Marder (now at Universität Würzburg, Germany) and R. Tom Baker (now at the University of Ottawa, Canada). He was an NSERC postdoctoral fellow, where he spent one year working with Dr. Lanny Liebeskind (Emory University, USA) and then another year working with Dr. Maurice Brookhart (University of North Carolina, USA). He has been at Mount Allison University (Canada) since 1995 and is currently a Canada Research Chair in Boron Chemistry. His research interests include catalysis and the synthesis and development of biologically active boron and transition-metal compounds. His research group is called the Wild Toads and it is best not to ask why.