

Cluster Preface: Modern Boron Chemistry: 60 Years of the Matteson Reaction

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James P. Morken (left) was born in Concord, California (USA) and obtained his B.S. in chemistry in 1989 from UC Santa Barbara (USA) working with Prof. Bruce Rickborn. He obtained his Ph.D. from Boston College (USA) in 1995 with Prof. Amir Hoveyda and was an NSF Postdoctoral Fellow with Prof. Stuart Schreiber at Harvard University (USA). In 1997, he became an Assistant Professor of Chemistry at the University of North Carolina at Chapel Hill (USA). He was promoted to Associate Professor in 2002 and in 2006 joined the faculty of Boston College (USA). In 2014, he was named the Louise and James Vanderslice and Family Chaired Professor of Chemistry at Boston College. Professor Morken's research focuses on the development of transition-metal-catalyzed asymmetric processes and their use in complex molecule synthesis. He is particularly interested in the study and development of catalytic enantioselective reactions involving organoboron reagents.

Varinder K. Aggarwal (right) studied chemistry at Cambridge University and received his Ph.D. in 1986 under the guidance of Dr. Stuart Warren. After postdoctoral studies under Prof. Gilbert Stork at Columbia University (1986–1988), he returned to the UK as a lecturer at Bath University. In 1991, he moved to Sheffield University, where he was promoted to professor in 1997. In 2000, he moved to Bristol University, where he holds the Chair in Synthetic Chemistry. His research interests include the development of new catalytic processes for asymmetric synthesis, the development of chiral carbenoids and their use and subsequent applications in catalysis and synthesis, and the development of new methodology and its applications in synthesis and the total synthesis of biologically important targets.

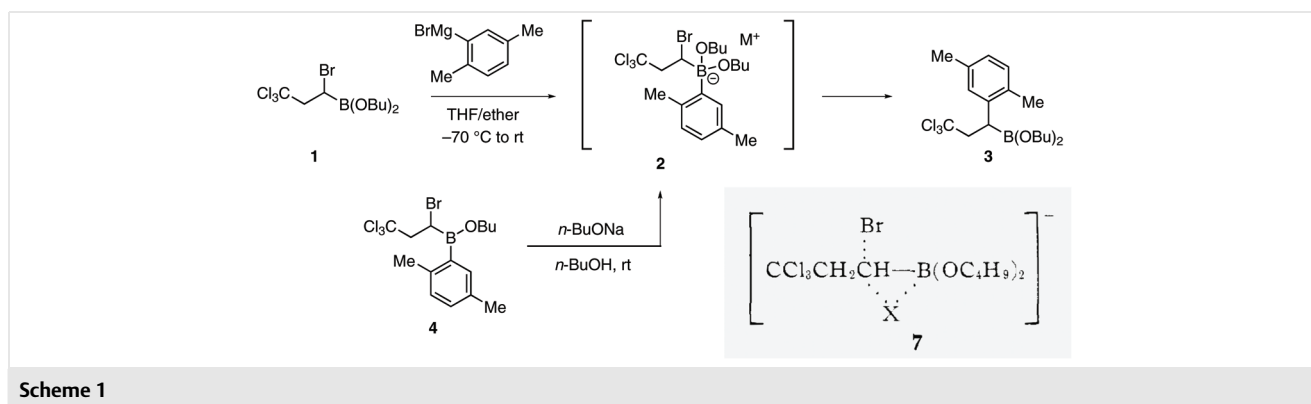
We are thrilled to present this *Special Issue* of SYNLETT to commemorate the 60th anniversary of Professor Donald Matteson's publication entitled 'Neighboring Boron in Nucleophilic Displacement'.¹ This seminal report describes the discovery of the 1,2-boronate rearrangement reaction. Prof. Matteson is currently emeritus Professor of Chemistry

at Washington State University in Pullman, WA. It was in his laboratories there that a wealth of organoboron chemistry was discovered, including the work that inspires this *Special Issue*. Prof. Matteson completed his bachelor's degree under the tutelage of Henry Rapoport at UC Berkeley in 1954 and his Ph.D. in 1957 with Harold R. Snyder at the University of Illinois at Urbana-Champaign. In 1958, after a short appointment at the du Pont Central Research and Development Laboratories, he joined the faculty at Washington State University. Over the course of his career, he has authored >200 publications that have shaped the field of organoboron chemistry. While Prof. Matteson's publication back in 1963 is not his most cited work, this publication clearly has inspired the development of numerous new synthetic methods and it continues to inspire many scientists in our community today.

To give the 1963 discovery of the Matteson rearrangement some context, it was discovered at a time when new carbonyl compounds were most often characterized by elemental analysis of their hydrazone derivatives, when starting annual salaries for an assistant professor were \$5700,² and when analysis of compounds by state-of-the-art 60 MHz NMR might require collaboration with Varian. The discovery of the 1,2-boronate rearrangement was enabled by the recently developed (1957) synthesis of vinylmagnesium bromide by Normant,³ which provided access to vinylboronic esters. In 1959, Matteson employed the latter compounds in an atom-transfer radical addition reaction to furnish the first α -bromoboronic ester **1** (Scheme 1).⁴ While Mikhailov had shown that β -bromo organoboranes undergo elimination in the presence of nucleophiles,⁵ and Hawthorne had shown that γ -bromo organoboranes ring-close to cyclopropanes,⁶ the reactivity of α -bromo organo-

boranes was uncharted territory. As Prof. Matteson himself describes,⁷ “With a very naive idea of what might be done with the product (**1**), I suggested to Raymond Mah, my first graduate student, that he phenylate the boron atom with the Grignard reagent...”. They found that α -bromo boronic ester **1** was converted into the substitution product **3**, presumably through the intermediacy of four-coordinate borate **2**, a proposal that was supported by the reaction between **4** and sodium butoxide to furnish **3**. The conversion of boron ‘ate’ complex **2** into boronic ester **3** was proposed

to occur through a transition state represented by **7** in the original paper.¹ As they say, “The rest is history.” The involvement of **7** suggested a reaction that is stereospecific with respect to both the migrating group (X) and the electrophilic carbon atom. These features would later be verified, and they continue to be employed in the development of important strategies for asymmetric synthesis. In addition, with appropriate reaction design, strategies that employ ensembles such as **7** for asymmetric catalysis also continue to emerge.



Scheme 1

While much has changed in the field of chemistry since the process in Scheme 1 was elucidated 60 years ago, that the inner workings of the Matteson rearrangement continue to be employed in creative new ways points to the impact of this fundamental reaction. As you read through the collection of invited articles in this *Special Issue*, we hope that you too will be inspired to employ 1,2-boronate rearrangements in innovative ways or be captivated by other exciting new directions in boron chemistry reported herein.

James P. Morken
Varinder Aggarwal
October 2023

Conflict of Interest

The authors declare no conflict of interest.

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