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## Preface

The field of metal boron chemistry has been an especially active one since the 1960s. Much of the early work centered on the synthesis and structural characterization of polyhedral metallaborane and metallacarborane clusters, which will not be discussed in the current Volume. However, early work on metal boryl complexes by Nöth et al. also appeared during this period, although the first simple metal boryl complexes to be structurally characterized by single-crystal X-ray diffraction were not reported until 1990 (indeed, crystal structures of iridium hydrido boryl complexes were reported nearly simultaneously by Baker, Marder, et al. [1] and by Merola et al. [2]), and this new interest in the area arose specifically as a result of the report by Nöth et al. [3] on the rhodium-catalyzed hydroboration of alkenes using catecholborane. Although there had been previous reports of metal-catalyzed hydroboration employing polyhedral boranes or carboranes as the B–H source [4], the seminal paper by Nöth et al. in 1985 [3] marked the beginning of interest by the organic chemistry community in the application of this reaction in organic synthesis [5]. What ensued was a very rapid increase in the number of metal boryl complexes to be synthesized and structurally characterized, along with studies of their reactivity, in conjunction with an equally rapid growth in the development of catalytic hydroboration chemistry [5] and its asymmetric version [5e]. This was followed by a wide variety of other borylation reactions catalyzed by transition metals including diborations, silylborations, stannylborations, and thiaborations of unsaturated organic substrates [6], borylations of  $\alpha,\beta$ -unsaturated carbonyl compounds [7], borylations of C–halide bonds [8], and most recently, borylations of C–H bonds in alkenes, arenes, heteroarenes, and even alkanes [9,10]. The C–halide and C–H borylation chemistry has been driven by the development and broad application of the Suzuki–Miyaura cross-coupling reaction [11], which is now one of the main C–C bond-forming reactions in the arsenal of the organic chemist. Thus, the synthetic and structural chemistry of metal boryl complexes has grown along with catalytic applications in which metal boryl complexes are key intermediates.

Likewise, the importance of metal borane  $\sigma$ -complexes as intermediates in many catalytic reactions has only recently been recognized [12], and this area is now a rapidly expanding one. This bonding mode is also now known for early, middle, and late transition metals, and is expected to be found more

often (as was the case for dihydrogen complexes) as research continues.

Metal borylene complexes are another recent addition to the library of metal boron compounds, and these are now finding applications in organic synthesis, initially via their role as stoichiometric borylene transfer agents in the synthesis of borirenes from alkynes [13]. It is expected that additional applications of newly discovered metal borylene complexes will emerge as new routes to them are developed.

Borohydride complexes of metals, from across the periodic table, have been known for many years, and represent the other major class of mono-boron systems coordinated to metal centers. They can coordinate via one, two, or three hydrogen bridges to a single metal or can bridge between two metal atoms, and systems involving transition metals as well as lanthanides and actinides are well known [14]. Their structures, bonding, and dynamics have been of interest since their discovery. As the field is rather large, only mononuclear transition-metal complexes with  $\text{BH}_4^-$  ligands will be considered in the current review, although the principles discussed also apply to systems involving  $\text{RBH}_3^-$  and  $\text{R}_2\text{BH}_2^-$  systems [15], for example.

Thus, this Volume brings together the main types of complexes involving single boron units coordinated to metal centers, including examples in which more than one of the boron ligands is involved. A word is required regarding an even more recently developed area of metal boron chemistry involving metal-to-boron dative bonds in complexes now known as “boratranes” [16]. These will be discussed in a future Volume.

Finally, we note that the chapter ordering in the current Volume places borylene complexes before boryl complexes. We have ordered the chapters according to the degree of metal–boron bonding, from highest to lowest, rather than following a historical perspective.

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