Chapter 1. Background and context for the development of (phosphino)borate ligands

1.1. Introduction

Anionic phosphine ligands templated on a borate are emerging as a new class of ligands with unique properties.[1-5] These ligands, termed (phosphino)borates, have been successfully used in coordination, reaction, and catalytic chemistry of transition metals in groups 7 through 11.[1-4,6] Almost all of the (phosphino)borates that have appeared in the literature contain an anionic borate covalently bound through a methylene link to one or more dialkyl or diaryl phosphines (Figure 1.1A-C). This structure type has also been described in the literature as a (dialkylphosphinomethyl)borate[7] or as a (phosphanyl)borate,[2c] both of these names being more reflective of the presence of a carbon-based link between the boron and phosphorus atoms. Recently, the use of an aryl link between the borate and phosphorus atom also has been introduced (Figure 1.1D). Regardless of the nomenclature, all of these species contain the same significant feature: a phosphine and a borate covalently bound together through an organic link.

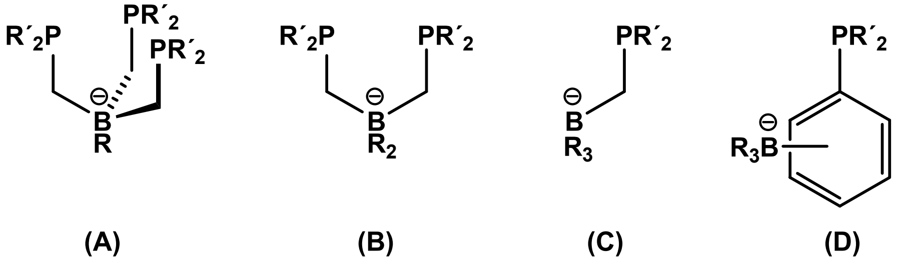

Figure 1.1. Structural representations of known tris(phosphino)borates (A), bis(phosphino)borates (B), and mono(phosphino)borates (C and D).

The importance of (phosphino)borates is directly related to the importance of phosphine donors in transition metal chemistry. As ligands for metals, phosphines have a long history, playing significant roles in basic coordination chemistry as well as being at the leading edge of catalytic reaction development.[8] The potential to modify the electronic and steric properties of a phosphine allows the chemist control over their effects on a transition metal. For example, small changes in the steric characteristics of a chiral phosphine can lead to greater enantioselectivity in catalysis.[9] Consequently, the development of new synthetic methods for the preparation of new phosphines is of continuing importance. In this light, (phosphino)borates represent an advancement in phosphine synthesis due to the ease of their steric and electronic modification as well as to the fundamentally new properties that are inherent to this class of molecules.

1.2. Neutral ligands/cationic complexes versus anionic ligands/neutral complexes

Examination of the literature of phosphine-supported transition metal chemistry shows an abundance of cationic complexes that are used for spectroscopic studies, stoichiometric transformations, and catalytic conversions.[10,11] Many of these cationic complexes result from multidentate, *neutral* phosphine ligands. An example of one such cationic square planar complex is shown in Figure 1.2A. One of the primary results of the *anionic* (phosphino)borate ligands is their ability to render an analogous transition metal complex neutral (Figure 1.2B). At the outset of these studies, it was envisioned that the development of neutral complexes coordinated by an anionic (phosphino)borate would have several consequences. First, tethering the anion into the backbone of the ligand framework ought to reduce or eliminate metal-counterion interactions. The importance of transition metal-anion interactions is evident in the significant efforts made towards developing weakly coordinating and unreactive anions.[12] Additionally, we hypothesized that by generating neutral metal complexes using (phosphino)borate ligands, increased solubility in non-polar, hydrocarbon solvents would result. As has been observed in the study of cationic transition metal complexes, solubility in less polar solvents is usually poor and is directly affected by the anion. By removing these anion-based effects, we hypothesized that the (phosphino)borate ligands would provide a formally zwitterionic transition metal complex that would demonstrate similar reactivity patterns to structurally similar cationic systems. As will be shown in the following chapters, we have synthesized several new phosphine ligands based on an anionic borate backbone and have studied their properties upon coordination to a metal center. Much of this work is devoted to the development and understanding of bis(phosphino)borate ligands whose general structure is shown in Figure 1.1B.

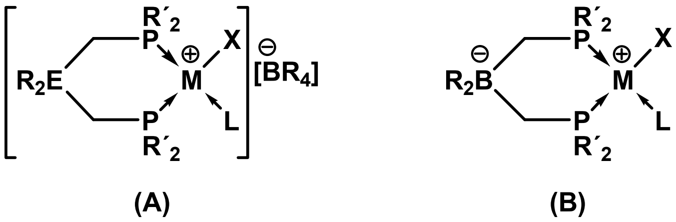

Figure 1.2. Generalized representations of a group ten (A) cationic metal complex with a borate counteranion coordinated by a neutral bis(phosphine) and (B) neutral metal complex coordinated by a bis(phosphino)borate.

1.3. Comparison to other ligands

When we began exploring the chemistry of (phosphino)borate ligands, we noted the limited examples of previously described anionic phosphines in the literature. Figure 1.3 depicts the examples of which we are aware.[13-18] Several different structure types have been described for anionic phosphines, ranging from Fu's monodentate triphenylphosphine analogue containing a boratabenzene (Figure 1.3F) to Mathey's sterically encumbered η^5-phospholide ligands (Figure 1.3B). Of the examples that are bidentate bis(phosphine) ligands, the work of Karsch is most structurally related to (phosphino)borates (Figure 1.3C). Similar to the borate-based ligands, Karsch has provided examples of aluminate-centered anionic phosphines; however, their transition metal chemistry has not been explored. Another somewhat related class of anionic phosphines are templated on a carborane anion (Figure 1.3A). Unlike the other anionic phosphines in Figure 1.3, the anionic charge of the ligand can be considered to be highly delocalized away from the phosphine donors.

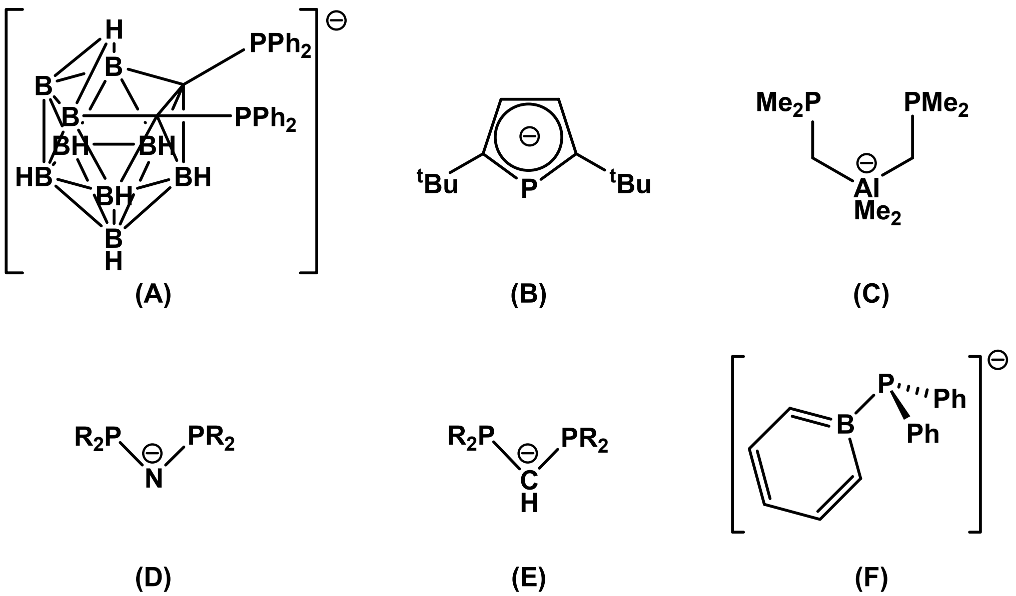

Figure 1.3. Previously described monoanionic phosphines.

In addition to the known examples of anionic phosphines, several other bidentate donors templated on an anionic borate have been described in the literature.[19-22] The first and most well known of these borate ligands are the (pyrazolyl)borates introduced by Trofimenko (Figure 1.4A). The coordination chemistry of this ligand class has been heavily explored in both bidentate and tridentate forms with a wide variety of substitutions on the pyrazole rings. Many related derivatives exploiting five-membered nitrogen heterocycles such as imidazole and indazole also have been used for transition metal chemistry. One interesting derivative that has received scant attention is the bis(pyridyl)borate ligand shown in Figure 1.4C. This ligand is related to the highly successful bipyridine family of ligands; however, its coordination chemistry has been explored only briefly. In addition to (pyrazolyl)borates and their derivatives, Riordan and coworkers have developed the (thioether)borate ligands depicted in Figure 1.4C. These sulfur donor ligands have been effective in expanding the chemistry of late transition metals. Like the (phosphino)borates, the donor atom is covalently bound to the borate through a methylene unit. Similar to both the (thioether)borates and the (phosphino)borates, an example of a bis(amino)borate ligand has recently been introduced by Betley and Peters. This amine donor ligand expands the range of available donors templated on the borate anion.

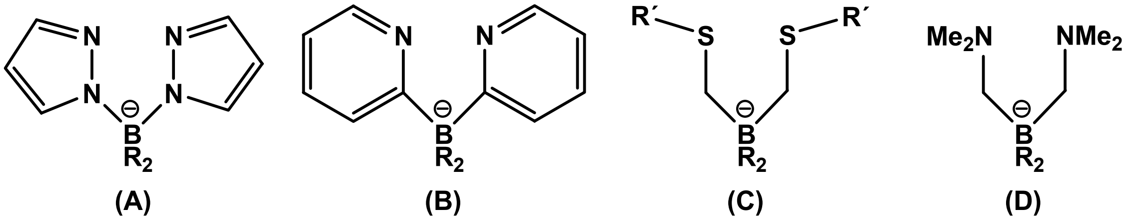

Figure 1.4. Structural representations of other borate based ligands.

1.4. The zwitterionic description of (phosphino)borate-metal complexes

From an electron-counting perspective using a covalent model, metal complexes supported by bis(phosphino)borates can be regarded as zwitterionic complexes containing a cationic metal center chelated by an L_2, four-electron, donor ligand.[8b,23] This electronic description is distinct from that offered by Trofimenko for the related families of bis- and tris(pyrazolyl)borates. Electron-counting schemes typically designate bis(pyrazolyl)borates as LX-type, three-electron donors in contrast to bis(phosphino)borates.

The difference in electron-counting results from the presumption that the borate charge in a (pyrazolyl)borate is more uniformly distributed due to important resonance contributors that fully delocalize the borate charge. For comparison, some resonance structures for a bis(pyrazolyl)borate are shown in Figure 1.5A. These resonance forms were first highlighted by Trofimenko in his early work on poly(pyrazolyl)borates.[24] Delocalization of the anionic borate charge through the aromatic ring allows the anionic charge to reach the metal through a pyrazolate anion. Electronic delocalization through an aromatic system is an understood phenomenon and thus provides a rational mechanism for interaction between the borate charge and the metal center.

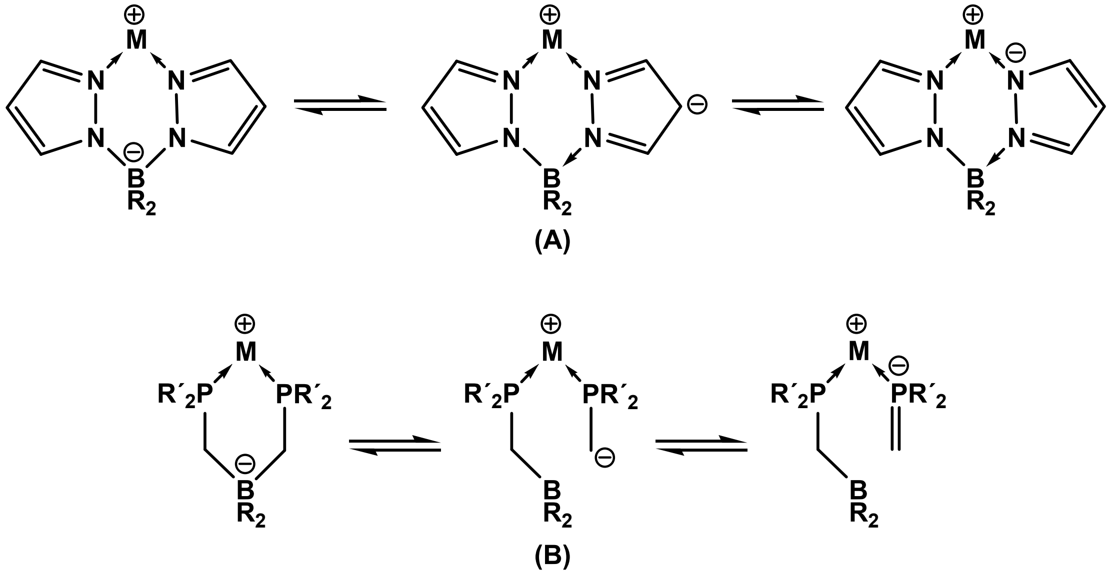

Figure 1.5. Selected resonance forms for (A) bis(pyrazolyl)borates and (B) bis(phosphino)borates.

In contrast to (pyrazolyl)borates, (phosphino)borates do not have an accepted means for delocalizing the charge of the borate by resonance. In Figure 1.5A, some possible resonance structures of a (phosphino)borate ligand are presented. These resonance forms include a borate centered anion, a carbanion, and a phosphorus ylide structure. Note that for two of the resonance structures, there is no B-C interaction. This suggests that these forms may be less valid resonance contributors. As a result, the (phosphino)borate class of ligands is intuitively considered as providing a zwitterionic complex when coordinated to a metal, in that the charges are well separated.

An important issue that is examined in the following chapters is the relevance of the zwitterionic description for transition metals coordinated by (phosphino)borate ligands. In a zwitterionic formulation, the anionic charge of the ligand resides completely on the borate center, while a cationic charge is placed on the metal (Figure 1.2A). If this discrete charge separation were an accurate depiction of the electronics of (phosphino)borate-ligated metal complexes, no significant differences would be expected between a (phosphino)borate-coordinated metal center and a metal coordinated by a structurally analogous neutral ligand. However, other relevant models can also be considered. One important model concerns the ability of the anionic borate charge to be delocalized through σ-bond interactions. In this case, the phosphine donors would receive an additional amount of electron density, thus making them more electron-rich. A third possibility is that the borate anion and a cationic metal center will interact in an electrostatic manner. This model suggests that the proximity of the borate center to the transition metal will play a significant role in the electrophilicity of the metal. It is perhaps most reasonable to expect that all three of these models will contribute to the electronic description of a (phosphino)borate coordinated to a transition metal. The following chapters will in part attempt to address the significance of each of these models by considering the spectroscopic characteristics, coordination chemistry, and reaction pathways of (phosphino)borates and their transition metal complexes.

1.5. Chapter summary

This chapter has introduced the (phosphino)borate class of ligands. Several key aspects of the (phosphino)borates with regard to their coordination to metals include the ability to form neutral complexes, the potential removal of anion effects including solubility and metal-anion interactions, and the zwitterionic description of a (phosphino)borate-metal complex. Anionic (phosphino)borates are one of the few examples of anionic phosphines in the literature. They can be compared with other borate-templated donor ligands such as (pyrazolyl)borates, (thioether)borates, and (amino)borates. In this context, the (pyrazolyl)borates are best regarded as three-electron LX-type donors due to the significant delocalization of the anionic charge through several resonance structures. In contrast, (phosphino)borates are better considered as anionic four-electron L_2 donors with less significant resonance delocalization of the anionic charge. This results in a zwitterionic description for transition metals coordinated by (phosphino)borates. The zwitterionic nature of these metal complexes will be a target for consideration as we attempt to understand the properties of (phosphino)borates and their transition metal complexes.

In Chapter 2, the synthetic protocols for preparing various substituted bis(phosphino)borates are presented along with spectroscopic and structural information for these compounds. Emphasis is placed on the relatively general methodology of reacting phosphine-containing carbanions with borane electrophiles that is successful for constructing various alkyl and aryl phosphine ligands. The formation of different salts is also discussed, as the diverse countercations provide different metalation reactivity.

The electronic effects resulting from coordination of a transition metal by a bis(phosphino)borate are explored in Chapter 3. The influence of electron-donating and electron-withdrawing groups substituted onto a bis(phosphino)borate are examined through NMR and infrared spectroscopic studies for a series of platinum(II) complexes. Spectroscopic and structural comparisons are also made between neutral and cationic platinum complexes coordinated by structurally similar bis(phosphine) ligands. These studies are used to draw conclusions about the electronic impact of (phosphino)borates on a transition metal.

Chapter 4 presents a mechanistic inquiry into structurally similar cationic and neutral platinum(II) complexes that both undergo a benzene C-H activation process. Ligand exchange mechanisms, reaction pathways, reaction kinetics, and isotope effects are all considered in an attempt to probe the similarities and differences between the charge-differentiated complexes. We describe subtle distinctions in the reaction mechanisms that differentiate these platinum systems that result from changes in the ligand electronics.

The application of a phenyl-substituted tris(phosphino)borate ligand to platinum coordination chemistry is the subject of Chapter 5. Octahedral Pt(IV) and square planar platinum(II) alkyl and hydride complexes are discussed. Where possible, comparisons are made to analogous tris(pyrazolyl)borate species.

Chapter 6 describes the nickel coordination chemistry of an isopropyl-substituted tris(phosphino)borate. Examples of three-, four-, and five-coordinate complexes in the Ni(II), Ni(I), and Ni(0) oxidation states are included. A theoretical study using DFT methods emphasizes the possibility of forming high-valent Ni(III) and Ni(IV) species containing metal-ligand multiple bonds.

Finally, Chapter 7 contains introductory coordination studies of bis(phosphino)borates on copper(I). Both aryl and alkyl bis(phosphino)borates are used to prepare a family of copper(I) complexes. The primary focus of this work is the development of several well-defined three-coordinate species coordinated by a sterically encumbered *tert*-butyl-substituted bis(phosphino)borate ligand.

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