Borataalkenes and the $\eta^2$-B,C Coordination Mode in Coordination Chemistry and Catalysis

Maxwell Eaton,$^a$ Yuanzhe Zhang,$^{a,b}$ and Shih-Yuan Liu*$^a$

Borataalkenes are the boron-containing isoelectronic analogues of alkenes. Compared with alkenes, the borataalkene ligand motif in transition metal coordination chemistry is relatively underexplored. In this tutorial review, the synthesis of borataalkene complexes and other transition metal complexes featuring the $\eta^1$-B,C coordination mode are described. The diversity of coordination modes and geometry in borataalkene complexes, and the spectroscopic and structural evidence supporting their assignments are highlighted. The applications of the borataalkene ligand motif in homogeneous catalysis, especially those involving 1,4-azaborines, is discussed. Finally, the use of borataalkene complexes as reactive intermediates in catalysis, usually derived from geminal diboron compounds is summarized.

Introduction

Alkenes are among the most common ligand classes in organometallic chemistry.$^1$ In fact, the first isolated organometallic compound is Zeise’s salt, a platinum complex bearing an ethylene ligand (Figure 1).$^2$ Borataalkenes are the boron-containing isoelectronic and isostructural analogues of alkenes, and are typically synthesized by $\alpha$-deprotonation of alkyl boranes.$^3,^4$ Borataalkenes are nucleophilic species, and find use in boron-Wittig reactions.$^3$ On the other hand, the coordination chemistry of borataalkene ligands is relatively underexplored. Due to the prevalence of alkene ligands in transition metal complexes and homogeneous catalysis, the development of borataalkenes as ligand motifs has attracted increasing attention in recent years.$^5$

![Figure 1](https://example.com/zeise_salt_borataalkene.png)  
**Figure 1** Zeise’s salt and borataalkenes.

In contrast to alkenes which typically bind to transition metals via a symmetrical $\eta^2$-C,C coordination mode,$^6$ borataalkene ligands can bind in unsymmetrical $\eta^1$-B, $\eta^1$-C, and $\eta^2$-B,C coordination modes (Figure 2).$^5$ This phenomenon results from the highly unsymmetrical electronic structure of borataalkenes in comparison with alkenes, in which the C 2p orbital has a much higher contribution to the HOMO, and the B 2p orbital has a much higher contribution to the LUMO. Due to this asymmetry, metal to boron interactions will be favored for electron rich transition metals, and metal to carbon interactions will be favored for electron-deficient transition metals. The correct assignment of coordination mode in borataalkene complexes is therefore largely dependent on X-ray crystal structure analysis.$^{5a}$

![Figure 2](https://example.com/electronic_structure_borataalkene.png)  
**Figure 2** Electronic structure and binding modes of borataalkenes.

Besides borataalkenes, several other ligand motifs feature $\eta^2$-B,C binding, namely boraalkenes,$^7,^8$ aryloboranes (ambiphilic ligands) and borylferrocenes (Figure 3),$^{5a,9,10}$ Ambiphilic ligands containing the aryloborane motif have seen increasing development in recent years. These systems have been applied...
to achieve catalytic small molecule activation often through metal-ligand cooperation.\textsuperscript{9,10}

The Liu group has recently disclosed a series of platinum and palladium complexes of azaborine-containing ligands (SenPhos) which also feature $\eta^2$-B,C coordination resulting from the iminium-borataalkene resonance structure of the 1,4-azaborine.\textsuperscript{11} The phosphino-1,4-azaborine ligands have been applied as supporting ligands for numerous palladium-catalyzed regio- and stereo-selective functionalizations of 1,3-enynes, the selectivity of which is controlled by the unique electronic structure and $\eta^2$-B,C coordination mode of the azaborine ligand.

Borylferrocenes

Boranalkenes

Ambiphilic Arylboranes

1,4-Azaborines

$L = PR_2$

$L = pyr$ or $PR_2$

Figure 3 Other types of complexes featuring $\eta^2$-B,C coordination.

This tutorial review aims to highlight the more recent advances in the synthesis and applications of transition metal borataalkene complexes and other transition metal complexes containing $\eta^2$-B,C interactions. This review outlines: (a) the synthesis of transition metal borataalkene complexes and their typical coordination modes, especially the unique $\eta^2$-B,C coordination mode; (b) other boron-carbon multiply bonded $\pi$ ligands such as borataalkenes, borylferrocenes, aryloboranes, and 1,4-azaborines and their $\eta^2$-B,C bound complexes; (c) the stoichiometric reactions and catalytic applications of $\eta^2$-B,C-bound transition metal complexes; (d) the generation of transition metal borataalkene complexes as reactive catalytic intermediates in coupling reactions. Because a related perspective article was published in 2012,\textsuperscript{5} this review aims to summarize subsequent discoveries. Select citations to reports prior to 2012 are included as reference material to provide context.

$\eta^2$ and $\eta^1$ Borataalkene and Boraalkene Complexes

The first reported transition metal borataalkene complex was isolated in 1999 by Piers and coworkers by reaction of Shrock’s methyl methylene tantalum(V) complex with Piers borane $\text{HB(C}_5\text{F}_3\text{)}_2$ at $-78^\circ\text{C}$.\textsuperscript{11} The resulting cycloaddition product reductively eliminates methane upon warming to $-20^\circ\text{C}$ to generate a green, paramagnetic solution which consists of an equilibrium mixture of singlet 1 and triplet 2 borataalkene complexes as suggested by DFT calculations. Complex 1 can be trapped by oxidative cyclization with 2-butyne to generate 3, whereas complex 2 can be trapped with $\pi$-acidic ligands as the neutral adducts 4a and 4b.

Scheme 1 Piers’ tantalum borataalkene complex.

Crystallographic evidence for the $\eta^2$ formulation for complexes 4a and 4b include Ta–B distances of 2.728(6) and 2.738(6) Å, and B-C distances of 1.508(8) and 1.525(7) Å which are intermediate between typical B–C$_{sp^3}$ bond distances (1.578 Å for BMe$_3$)$^{13}$ and B=C$_{sp^2}$ (1.444 Å in [Mes$_3$B=CH$_2$]$_2$[Li]12-crown-4).\textsuperscript{10} Additionally, the $^{11}$B-NMR chemical shifts of 8.5 and 7.2 ppm are inconsistent with typical three-coordinate boron species.

Owen and colleagues synthesized an $\eta^2$-B,C borataalkene complex of Rh(I) by reaction of norbornadiene Rh(I) chloride dimer with the anionic borane-bound 2-mercaptopyrindine ligand 5 followed by treatment of the resulting complex 6 with excess triphenylphosphine (Scheme 2).\textsuperscript{14} Ligand association and a series of reactions of the bridging hydrides with the norbornadiene ligand furnishes borataalkene complex 7, the $\eta^2$-B,C coordination of which was confirmed by X-ray diffraction analysis.

Scheme 2 Owen’s synthesis of Rh(I) $\eta^2$-B,C borataalkene complex.
After phosphine association with 6 and loss of chelation by norbornadiene, a boron to rhodium hydride transfer occurs to give 8. β-Migratory insertion gives complex 9, which can undergo another phosphine association causing alkyl migration to the borane to yield 10. A second β-migratory insertion yields alkyl bridged intermediate 11, which undergoes β-alkyl elimination to deliver borataalkene complex 7. Dihydrogen undergoes rapid addition to the B=C bond of 7 to give hydride bridged complex 12.

Another example of a rhodium borataalkene complex was reported by the Erker group (Scheme 3). Treatment of phosphino-borane 13 with LiTMP (lithium 2,2,6,6-tetramethylpiperidine) afforded anionic borataalkene lithium salt 14. Complexation with rhodium precursors yields chelated borataalkene complexes 15 featuring η²-B,C coordination. Attempts to prepare iridium analogue 16 only afforded Ir(III) complex 17 due to cyclometallation via C-H insertion into the mesityl group. Complex 15 served as an effective catalyst for hydrogenation of olefins.

The Ozerov group observed a metal η²-B,C borataalkene coordination in iridium complexes derived from boryl PBP pincer ligated iridium complex 18 (Scheme 4). In the presence of excess terminal olefin, conversion to borataalkene complex 19 is observed. The proposed mechanism is outlined in Scheme 4. Olefin association and loss of CO leads to complex 20, which then undergoes C-H insertion with the terminal Csp²-H bond to give Ir(III) complex 21. Alkenyl migration from iridium to boron yields intermediate 22, which undergoes β-migratory insertion to afford borataalkene complex 19. The overall process is reversible, and thermolysis of 19 at elevated temperatures leads to partial conversion back to 18.

Various metal η²-B,C bound azaborataallenes complexes are reported by Nöth and Braunsweg (Scheme 5). Rhodium vinylidene complex 23 undergoes a molybdenum borylene exchange with [OC]Mo=B=N(SiMe₃)₂] to give 24. The ligand motif is best described as a 1-aza-2-bora-cumulene. Interestingly, although there are many different possible coordination modes due to the number of p bonds, the metal selectively coordinates to the B=C bond. η²-B,C coordination was calculated to be ~16 kcal/mol more favorable than coordination to the C=C unit, highlighting the affinity of late transition metals for more polar B=C unit. The bent geometry of the ligand as well as the long B-C distance in 24 (1.489(12) Å) are indicative of significant back-bonding from the metal.

Coordination of azaborataallene 25 with various first-row transition metal carbonyl complexes results in complexes 26, which also feature η²-B,C coordination preferentially in all cases, as opposed to coordination to the B=N bond. MO calculations demonstrated that back-bonding to the B-C π* contributes considerably to the stabilization of such complexes. Martin and coworkers recently disclosed the synthesis of a 9-borataphenanthrene anion by deprotonation of neutral 9,10-
dihydro-9-boraphenanthrene \( \text{27} \) (Scheme 6).\(^\text{19}\) The 9-boraphenanthrene anion \( \text{28} \) can be regarded as having both boratabenzene and borataalkene character, although Clar’s rule predicts the borataalkene resonance form to be the dominant contributor the overall structure. Indeed, DFT calculations predict the HOMO to be localized mostly to the B-C unit, suggesting the possibility for \( \eta^2 \)-B,C coordination to transition metals.

Scheme 6 Martin’s synthesis of 9-boraphenanthrene Cr(0) and Au(I) complexes.

In line with this prediction, anion \( \text{28} \) reacts with Au(PPh\(_3\))Cl to generate \( \eta^2 \)-bound borataalkene complex \( \text{29} \), which is biased towards carbon and away from boron (Au–C = 2.188(7) Å vs. Au–B = 2.427(8) Å). This reflects the high electronegativity of Au(I) and thus its affinity for the more electron rich position in the ligand. Notably, this is the first reported example of a group 11 \( \eta^2 \) borataalkene complex. In contrast, Cr(0) precursor Cr(MeCN)\(_3\)(CO)\(_3\) reacts with \( \text{28} \) to form \( \eta^6 \)-B,C\(_5\)-boratabenzene complex \( \text{30} \) which is isolated as the crown ether-solvated potassium salt (crown = dibenzo-18-crown-6). The preference of Cr(0) for \( \eta^6 \) coordination is likely a consequence of its higher electron richness relative to Au(I). This would make the metal d to ligand LUMO (to which the boron and C1 contribute very little) interaction more important for the overall stabilization of the complex vs the ligand HOMO to empty metal d orbital interaction.

Building upon this work, Martin subsequently reported the complete series of group 11 borataalkene complexes derived from boratabenzene and boraphenanthrene anions.\(^\text{20}\) Boratabenzenzene \( \text{31} \) was reacted with group 11 metal chlorides to give the corresponding \( \eta^2 \)-B,C borataalkene complexes \( \text{32-34} \) (Scheme 7). In all cases the M–C bond distances were shorter than the M–B bond distances, reflecting the high electronegativity of late transition metals. Interestingly, Ag(I) complex \( \text{33} \) exhibits an almost symmetrical binding mode where the Ag-C distance is only slightly shorter than the Ag-B distance (Ag–C = 2.3586(14) Å, Ag–B = 2.3839(16) Å). When ligation of \( \text{31} \) to Cu(PPh\(_3\)) was attempted, the resulting complex had \( \eta^4 \) coordination. Boraphenanthrene \( \text{28} \) could also be ligated to Cu(I) and Ag(I) to generate \( \eta^2 \)-B,C borataalkene complexes \( \text{35 and 36} \).

Scheme 7 Martin’s synthesis of group 11 borataalkene complexes

A new strategy for generating borataalkenes is via B-H deprotonation of an electron deficient, CAAC-stabilized borane (CAAC = cyclic alkyl aminocarbene).\(^\text{21}\) This strategy is in contrast with the more common alpha C-H deprotonation utilized by Erker and Martin. Deprotonation of stabilized borane \( \text{37} \) with KHMDs affords anion \( \text{38} \) (Scheme 8). Anion \( \text{38} \) is described by two resonance forms, a Lewis base-stabilized boryl anion, and a borataalkene. The significant shortening of the CAAC C-B bond in \( \text{38} \) (1.473(2) Å) vs. \( \text{37} \) (1.617(6) Å) and the planar geometry around the boron atom in \( \text{38} \) suggests significant contribution of the borataalkene resonance form. However, complexation with Au(PMe\(_3\))Cl affords \( \eta^1 \)-B Au(I) complex \( \text{39} \). This is in stark contrast with Au(I) borataalkene complexes \( \text{29 and 34} \), which both contain more distal Au-B bonds.

Scheme 8 Bertrand’s borataalkene synthesis via B-H deprotonation strategy.
Since Bertrand’s initial report, CAAC-stabilized boranes have been more widely used as borataalkene precursors. Braunschweig and coworkers were able to synthesize the CAAC-stabilized parent boryl anion 40 (Scheme 9). Complexation of 40 with group 11 metals yields borataalkene complexes 41-43. Like Bertrand’s complex 39, complexes 41-43 all contain shorter M-B distances compared to the corresponding M-C distances. The tendency of CAAC-supported borataalkenes for stronger boron coordination highlights the unique steric and electronic effects of the CAAC moiety as compared with more traditional borataalkenes.

Breher and coworkers reported an α-borylated phosphorus ylide 45 which was synthesized by “trans-ylidation” of triphenylethylphosphonium bromide with diethyl chloroborane (Scheme 10). The calculated Wiberg bond indices (WBI) around the ylidic carbon 45 were determined to be C-B = 1.42 and C-P = 1.25 indicating significant borataalkene character (WBI for C\textsubscript{ethyl}-B = 0.97). Reaction of 45 with gold(I) precursor (SMe\textsubscript{2})AuCl afforded Au(I) borataalkene complex 46 which was structurally characterized. Reaction of 45 with Cu(I) and Ag(I) precursors gave oily products which could not be characterized structurally, precluding any assignment of coordination mode. Complex 46 features an unsymmetrical η\textsuperscript{2}-B,C coordination mode having a significantly shorter Au-C bond. This is in direct contrast to Au(I) complex 43, which borders on η\textsuperscript{1}-B coordination. This again shows the diversity of coordination modes exhibited by borataalkene complexes, and the dependence of the coordination mode on the sterics and electronic properties of the borataalkene ligand.
Braunschweig and coworkers recently reported the synthesis of an unsymmetrical, doubly CAAC-stabilized diborene \( \text{53} \) which served as a versatile precursor to boraalkene and boraalkene complexes (Scheme 12).\(^{27}\) Reaction of \( \text{53} \) with half an equivalent of bis(2-phenylethynyl)mercury (Hg(C(CpH))\(_2\)) resulted in insertion of phenylacetylide into the B=B bond and formation of \( \eta^1 \)-boraalkene complex \( \text{54} \). No Hg-B interaction is observed in \( \text{54} \), consistent with the inability of the low energy Hg d-orbitals to engage in backbonding. Upon heating to 80 °C, diborene \( \text{53} \) undergoes insertion of the carbonic carbon of the non-tethered CAAC ligand into the B=B bond and ring expansion affording boraalkene \( \text{55} \). In addition to the boraalkene resonance form, \( \text{55} \) can also be described by an iminium-boraalkene resonance structure \( \text{55}' \). Complexation of \( \text{55} \) with AgOTf affords \( \eta^2 \)-B,C boraalkene complex \( \text{56} \). Complex \( \text{56} \) bears relatively short and symmetric Ag-C and Ag-B contacts (Ag-C = 2.263(3) Å, Ag-B = 2.364(4) Å).

![Scheme 12 CAAC-stabilized diborane 53 as a precursor to boraalkene complexes](image)

Erker and coworkers reported a deprotonation strategy for the synthesis of boraalkene complexes (Scheme 13).\(^{7}\) From NHC-supported borane \( \text{57a} \) or \( \text{57b} \), protonolysis of the B-H bond with bistriflimidic acid (HNTf\(_2\)) generates a loosely ion paired cationic borenium intermediate followed by deprotonation of the acidic \( \alpha \)-C-H bond using IMes as a bulky base to afford neutral NHC-supported boraalkenenes \( \text{58a} \) and \( \text{58b} \). The base used for the deprotonation had to be selected carefully, presumably to not interact with the highly electrophilic boron center of the borenium-type intermediate.

Treatment of \( \text{58} \) with \((\text{SMe}_2)\text{AuCl} \) affords \( \eta^1 \)-B,C boraalkene complexes \( \text{59a} \) and \( \text{59b} \). Complex \( \text{59a} \) was structurally characterized, confirming the slightly unsymmetrical \( \eta^2 \) coordination mode (Au-C = 2.125(3) Å, Au-B = 2.291(3) Å). The \(^{11} \)B NMR chemical shift of \( \text{59a} \) (δ 14.1) is shifted significantly upfield from \( \text{58a} \) (δ 19.0), suggestive of pyramidalization and/or an increase in electron density at boron due to gold coordination. Reaction of \( \text{58a} \) with [RhCl(CO)]\(_2\) afforded single crystals of rhodium complex \( \text{60a} \). Although \( \text{60a} \) could not be spectroscopically characterized, the structural information derived from its crystal structure is informative. The boraalkene B-C bond in \( \text{60a} \) is significantly lengthened (B-C = 1.502(2) Å) compared to complex \( \text{59a} \) (B-C = 1.476(4) Å) and boraalkene \( \text{58a} \) (B-C = 1.453(3) Å). The B-C bond lengthening is indicative of stronger backbonding in \( \text{60a} \) compared with \( \text{59a} \).

![Scheme 13 Deprotonation pathway to boraalkene complexes](image)

Erker subsequently reported the synthesis of a series of boraalkene complexes derived from NCS-substituted boraalkene \( \text{61} \) (Scheme 14).\(^{8}\) Complexation with group 11 metal precursors yield \( \eta^1 \)-B,C boraalkene complexes \( \text{62} \) and \( \text{63} \). In both complexes the metal-carbon bond distance is significantly shorter than the metal-boron distance. The coordination is more symmetrical in \( \text{63} \), and the long boraalkene B-C bond and upfield \(^{11} \)B NMR signal are both indicative of a higher degree of backbonding than in \( \text{62} \) which can be rationalized as being due to the higher radial projection of Au’s d orbitals relative to Cu. Complexation with \([\eta^1\text{allyl}]\text{PdCl}_2\) affords Pd boraalkene complex \( \text{64} \) which also features a relatively symmetrical \( \eta^2 \)-B,C coordination mode. The B-C bond in \( \text{64} \) is only slightly elongated compared to \( \text{61} \), and the metal-boraalkene contact are the longest in the series.
Several transition metal borataalkene complexes which apparently lack any metal to boron interaction have been reported. Ti(IV), having the $d_0$ electronic configuration, is unable to engage in any stabilizing metal $d \rightarrow$ borataalkene LUMO interaction, which disfavors any coordination to boron. Thus, many examples of Ti(IV) $\eta^1$-C borataalkene complexes have been reported.\(^{28}\) These complexes were universally synthesized by treatment of dimethyl titanium(IV) compounds with tris(pentafluorophenyl)borane ($\text{B(C}_6\text{F}_5)_3$) resulting in methyl abstraction to generate cationic titanium intermediate 66 (Scheme 15). $\sigma$-Bond metathesis and loss of methane generates $\alpha$-boryl alkyltitanium intermediate 67, which then undergoes an intramolecular transmetalation of a C$_6$F$_5$ group generating $\eta^1$-C borataalkene complexes 68a-d. In all cases, the M-B bond distance was determined to be too long for any substantial bonding interaction, and M-C-B bond angles were $>110^\circ$. Interestingly, although there is no appreciable M-B interaction, the borataalkene B-C bond lengths in 68a-d are all quite short at around $\approx 1.50$ Å, suggesting significant double bond character. Further computational work would give more insight into the bonding situations in complexes 68a-68d.

Sadighi also reported the synthesis of a Cu(I) borataalkene complex whose coordination mode is not so straightforwardly assigned (Scheme 17).\(^{30}\) Treatment of borylcopper complex 71 with styrene affords benzylcopper complex 72 after $\beta$-migratory...
insertion of the boryl ligand. Upon heating, 72 rearranges to borataalkene complex 73. This reaction is believed proceed through a β-hyridde elimination to generate olefin complex 74, which can subsequently undergo a β-migratory insertion into the benzylc position to generate 73. Evidence in favor of this pathway is the successful synthesis of 73 from copper hydride precursor 75 and alkenyl boronate 76. The Cu-B distance in 73 of 2.608(3) Å indicates some degree of copper-boron interaction, although it is significantly longer than all of the other copper borataalkene complexes previously mentioned in this review. Additionally, the Cu-C-B angle of 96.3(2)° is significantly more acute than one would expect for a purely Cu-Csp2 bond. Further evidence in favor of an η2-B,C borataalkene ligand formulation is the fact that the Cu-C bond axis is perfectly orthogonal to the O-B-O plane of the Bpin group. However, in solution the assignment is less clear. The 11B NMR chemical shift of 73 is 33.4 ppm is only very slightly upfield from that of 72 (34.7 ppm) which argues against a significant copper to boron interaction in solution. Likely, the presence of two resonance-donating heteroatoms attached to boron raises the LUMO energy of the borataalkene ligand making any metal to boron interaction energetically less favorable.

On the other hand, Group IV borylindenyl complexes show no corresponding metal-boron interaction.32 Hydroboration of dimethylbenzofulvene 79 with Piers’ borane (HB(C5F5)2) followed by deprotonation with LiTMP affords borataalkene 80.32b Complexation with CpTiCl3 yields 81, wherein one of the chloride ligands is bridging. Zirconium analogue 82 features a tricoordinate boron group (11B δ =55.7 ppm), and X-ray diffraction analysis does not indicate there is any significant Zr-B interaction (Zr-B > 3.6 Å).

Pioneered by Bourissou and Peters, ambiphilic ligands are multi-dentate ligands containing both Lewis base(s), such as phosphines, and Lewis acid(s), such as Group 13 elements. As several recent reviews have covered the synthesis and applications of ambiphilic ligands in catalysis, this review will focus more narrowly on those complexes and catalysts involving η2-B,C coordination. To date, a variety of transition metals have been reported to form the η2-B coordination with boron-containing ambiphilic ligands. In some cases such coordination is augmented by an aryl η2-Cipso or η2-CipsoCortho coordination without significantly perturbing the ring aromaticity. These

Other Complexes Featuring η2-B,C Coordination

The metal η2-B,C coordination exists not only in complexes with borataalkene and boraalkene ligands, but also in complexes with B-Caryl moieties containing ligands such as borylferrocene31 and boron-containing ambiphilic ligands9-10. Borylferrocenes can be synthesized by electrophilic aromatic substitution of ferrocene with BBr3, followed by functionalization of the mono- or di-borylated complexes with various nucleophiles to afford complexes 77 or 78 (Scheme 18). X-ray diffraction analyses indicate the Cp (cyclopentadienyl) rings are not coplanar with the boron groups resulting from “bending” of the B-Cipso bond towards the iron center. The degree of bending increases with the Lewis acidity of the boron atom. Additionally, the Cp rings are slightly deformed. The contribution of boron to the ligand binding is supported by DFT calculations which suggest that it is a combination of the p orbitals of the Cp ring and the boron atom which form a bonding interaction with the iron d orbitals, rather than a more localized Fe-B interaction.

Scheme 18 η2-B,Cipso and η2-Cortho interactions in borylmetalocenes

![Scheme 17 Sadighi's synthesis of Cu(I) borataalkene complexes.](image-url)
coordination arrangements can be considered as formal $\eta^2$-B,C binding.

A collection of $\eta^2$-B$_2$C$_{ipso}$ or $\eta^2$-B$_2$C$_{ipso}$C$_{ortho}$ bound ambiphilic ligand complexes of Fe$^{33}$, Co$^{34}$, Rh$^{35}$, Pd$^{36}$, Ni$^{37}$, Cu$^{38}$, and Pt$^{39}$ (83-92) are shown in Scheme 19. Among them, iron shows great coordination diversity. For example, in complex 83 an $\eta^2$-B$_2$C$_{ipso}$ coordination is displayed, whereas in bimetallic iron complex 84, both $\eta^2$-B$_2$C$_{ipso}$ and $\eta^1$-B$_2$C$_{ipso}$C$_{ortho}$ are displayed within the same complex. In solution, only the $\eta^2$-B$_2$C$_{ipso}$ coordination mode in 84 is observed, highlighting the dynamic nature of these ligands. Complex 85 even features an $\eta^1$ coordination mode. Due to the Lewis-acidic nature of the arylborane ligands' boron center, they can act as non-innocent ligands. Most commonly the boron group aids in stabilizing a bridging hydride ligand (Scheme 20).

Scheme 19 Collection of $\eta^n$-bound complexes bearing ambiphilic ligands

When complex 93 is exposed to dihydrogen, the $\eta^2$-B$_2$C$_{ipso}$-M bonding is inert against cleavage by H$_2$. However, the more bulky mesityl substituent in 89 and the resulting $\eta^1$-B$_2$C$_{ipso}$C$_{ortho}$-M bonding is labile enough for facile activation of H$_2$ at room temperature furnishing complex 89-H$_2$. This result highlights that although the coordination mode in these complexes can be fluxional, it has a substantial influence on the reactivity of the metal particularly in cases with ligand cooperation. Complex 89 also serves as a catalyst for the hydrogenation of olefins under mild conditions. Likewise, diphenyl silane (Ph$_2$SiH$_2$) undergoes oxidative addition with ligand cooperation to give silylnickel(II) complex 89-SiH. Complex 89 also serves as a catalyst for hydrosilylation of aldehydes.

Bourissou and coworkers reported the diphosphine-borane ligated palladium(0) complex 94 (Scheme 21). The structural parameters of complex 94 is consistent with $\eta^2$-B$_2$C$_{ipso}$ coordination to the arylborane moiety (Pd-B = 2.294(2) Å, Pd-C$_{ipso}$ = 2.638(2) Å). Although complex 94 does not activate dihydrogen or silanes, it does react with potassium hydride (KH) in the presence of [2.2.2]-cryptand to furnish anionic palladium complex 95. When reacted with chlorobenzene, 94 is reformed.
along with elimination of benzene (PhH) and potassium chloride (KCl). A plausible mechanism supported by experimental and computational evidence is shown in Scheme 21.

Reduction of complex 94 with KH in the presence of [2.2.2]-cryptand first gives 95. Dissociation of PPh3 and subsequent oxidative addition of chlorobenzene (PhCl) gives complex 96 with concomitant release of potassium chloride. Reductive elimination and association of PPh3 regenerates 94 and releases the reduced arene. Interestingly, this catalytic cycle is an “inversion” of a typical palladium-catalyzed cross coupling reaction mechanism with oxidative addition and transmetalation steps having been switched. The cooperative action of the borane ligand allows for transmetallation directly to palladium(0) prior to oxidative addition, likely facilitating the oxidative addition by creating a more nucleophilic metal center.

Peters’ iron dinitrogen complex 84 displays rich and diverse reactivity with E-H bonds (E = O, S, C, N) (Scheme 22).34 Reaction of 84 with two equivalents of phenol (PhOH) results in the formation of Fe(I) phenolate complex 97 along with release of H2 (Scheme 22, top). This process can be considered as a one-electron oxidation of each iron center in 84. The authors suggest as a plausible mechanism the formation of an iron phenolate borohydride intermediate, followed by bimolecular reductive elimination of H2. This mechanism is supported by the isolation of 98 upon reaction of 84 with two equivalents of thiophenol (PhSH). Such a complex could also undergo bimolecular reductive elimination with release of H2, but this was not observed under the applied reaction conditions. When reacted with 8-aminoquinoline, formation of Fe(II) oxidative addition product 99 is observed. Similarly, with benzo[h]quinoline, C-H activation occurs yielding complex 100. X-ray diffraction analysis indicates that complex 100 retains an η2-B,Cipso coordination mode although with a different aryl ring than in 84. The Fe-B and Fe-Cipso contacts are relatively short at 2.3342(9) and 2.3739(9) Å respectively. No such coordination is observed in the crystal structure of 99. Complex 84 also catalyzed the hydrosilylation of aldehydes (Scheme 22, bottom). The Co analogue (complex 86) displays similar reactivity with respect to both E-H bond activation and hydrosilylation catalysis.

**Complexes of 1,4-Azaborine (SenPhos) Ligands**

Although not strictly borataalkenes, 1,4-azaborines can be described by the iminium-borataalkene resonance structure which suggests partial B=C double bond character in the overall electronic structure. Due to this electronic structure, 1,4-azaborine ligands tend to exhibit η2-B,C binding in their transition metal complexes, reminiscent of borataalkene ligands.11a These complexes can be considered as formal...
borataalkene complexes. This phenomenon was first observed in 2014 when the first chelating 1,4-azaborine ligand was synthesized and complexed with various platinum(II) precursors (Scheme 23).\textsuperscript{11a}

![Scheme 23](https://example.com/scheme23.png)

**Scheme 23** Synthesis of pyridine-1,4-azaborine platinum(II) complexes

1,4-azaborine ligand 101 was complexed with trans-[[PtCl(μ-Cl)(PET\textsubscript{3})\textsubscript{2}]] to generate pyridine adduct 102, in which there is no interaction of the platinum center with the azaborine ring. Chloride abstraction with silver triflate (Ag\textsubscript{OTf}) affords cationic platinum complex 103, in which the azaborine ligand adopts a κ\textsuperscript{2}-N-η\textsuperscript{2}-B,C coordination mode. The same coordination mode results from the reaction of 101 with [[PtMe\textsubscript{2}(μ-SMe)\textsubscript{2}] in the neutral platinum complex 104.

The changes in the intraring bond distances of the 1,4-azaborine ring are illustrative of the changes in the electronic structure of the ligand upon coordination with a transition metal. Reference bond distances are provided by the X-ray structure of 102 (Figure 4). Upon coordination to the cationic platinum center of 103, the N1-C2 distance shortens from 1.365(4) Å in 102 to 1.318(8) Å in 103. Concomitantly, the C2-C3 distance lengthens from 1.361(5) Å to 1.415(8) Å. These changes indicate a stronger contribution of the iminium-borataalkene resonance structure to the overall structure of the 1,4-azaborine moiety. The η\textsuperscript{2}-B,C coordination in 103 is asymmetrical, with a much shorter Pt-C distance (2.179(6) Å) than Pt-B distance (2.374(6) Å). Complex 104 follows a similar trend, although the iminium-borataalkene resonance contribution appears less prominent than in 103. Complex 104 features a much longer Pt-C2 distance (2.296(3) Å) and shorter Pt-B distance (2.337(4) Å) vs. 103, likely due to more electron rich neutral platinum, which favors backdonation. Attempts to prepare the corresponding carbonaceous Pt complex with analogous naphthylpyridine ligand failed.

![Figure 4](https://example.com/figure4.png)

**Figure 4** ORTEP illustrations of 102, 103, and 104 with 50% thermal probability ellipsoids. Hydrogens omitted for clarity. Counteranion in 103 omitted for clarity.

Given the unique binding mode of the benzo-fused 1,4-azaborine ligands, it can be inferred that they may confer unique properties upon the transition metal to which they are ligated. These unique properties could then be leveraged in transition metal catalysis to develop new reactivity patterns. To probe the possible effects of the newly discovered coordination mode in transition metal-catalyzed reactions, the selectivity of palladium-catalyzed 1,3-ene hydroboration was investigated as a function of ligand structure (Scheme 24). There are many possibilities for regio-, stereo-, and site selectivity in this reaction but three products predominate. The use of a bisphosphine ligand results in exclusive selectivity for cis-hydroboration product 105. Monodentate phosphines such as triphenylphosphine (PPh\textsubscript{3}) and biarylphosphine 108 furnish allenylborane 107 as the major product. On the other hand, when the 1,4-azaborine analogue 109 was used as the ligand, trans-hydroboration product 106 is furnished as the major product, and in higher overall yield compared with 108.
This discovery was used as the basis for developing a general palladium-catalyzed trans-hydroboration reaction of 1,3-enynes (Scheme 25).\textsuperscript{11b} In the presence of \(\text{Pd}_2\text{dba}_3\) and phosphino-1,4-azaborine ligand \textsuperscript{110}, nick-named “SenPhos”, a wide range of terminal and internal 1,3-enynes could undergo highly selective trans-hydroboration to yield dienyl boronates \textsuperscript{111} after quenching with pinacol. The origin of the high trans selectivity was later revealed by combined computational and experimental mechanistic studies.\textsuperscript{11f} The mechanism most consistent with the evidence from these studies is illustrated in Scheme 25. After the precatalyst reacts with ligand \textsuperscript{111} to generate a monoligated palladium(0) complex (L\textsubscript{n}Pd(0)), this complex could then bind enyne \textsuperscript{112}, which was used as the model substrate for these studies, to generate Pd olefin complex \textsuperscript{113}. The alkyne moiety of \textsuperscript{113} is then attacked electrophilically by the Lewis acidic cat\textsuperscript{h}echolborane (HBCat) anti to the palladium center in a so-called “outer-sphere” oxidative addition process furnishing zwitterionic \(\pi\)-allylpalladium adduct \textsuperscript{114}. Adduct \textsuperscript{114} was determined to be the resting state of the catalytic cycle. Rate-limiting hydride abstraction by a second equivalent of HBCat would then generate ion pair \textsuperscript{115}, and the borohydride ion could then transfer a hydride back to palladium to generate neutral palladium(II) complex \textsuperscript{116}. Inner-sphere reductive elimination at the allenic carbon yields the product \textsuperscript{111} and regenerates the free Pd(0) catalyst.

As the most unusual aspect and defining feature of this mechanism is the outer-sphere oxidative addition process, an analogue of adduct \textsuperscript{114} was prepared independently to verify the feasibility of such an intermediate. In the presence of a strong boron-based electrophile (B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}) and with no external nucleophile to promote reductive elimination, compound \textsuperscript{117} could be isolated upon mixing (1,5-cyclooctadiene)bis(trimethylsilylmethyl)palladium(II) with ligand \textsuperscript{110} and 1,3-enyne \textsuperscript{112}. Complex \textsuperscript{117} is stable enough for structural characterization and features the same \(\eta^2\)-B,C coordination mode observed with the pyridyl 1,4-azaborine ligands in their platinum complexes.

Based on this mechanism, the first general trans-selective cyanoboration of 1,3-enynes was developed (Scheme 26).\textsuperscript{11c} Ligand \textsuperscript{118}, a dialkyl biarylphosphine reminiscent of Buchwald type ligands,\textsuperscript{40} was found to be the optimal ligand. Copper(I) cyanide (CuCN) was used as the cyanide source, and a mechanism similar to the trans-hydroboration reaction is assumed. That is, after outer-sphere oxidative addition and transmetallation resulting in elimination of CuCl, inner sphere C-C reductive elimination would yield tetrasubstituted alkenyl nitriles \textsuperscript{119}. The efficiency and stereoselectivity of the reaction are highly dependent on the structure of the ligand. While dicyclohexylphenylphosphine (PhPCy\textsubscript{2}) is ineffective to promote the transformation, phosphino-1,4-azaborine \textsuperscript{118} delivers the product in 92% yield and >95:5 trans selectivity under the reaction conditions. The all-carbon analogue CC-\textsuperscript{118} is significantly less efficient and selective, giving only 6% yield of
the product and lower stereoselectivity under otherwise the same conditions. This result illustrates the importance of the η2-BC coordination mode, and its substantial influence on reactivity.

Scheme 26 trans-Cyanoboration of 1,3-enynes

Utilizing a rare class of organoboron compounds, C-boron enolates 121, a cis-cyanoboration of 1,3-enynes was developed (Scheme 27). The reaction affords highly substituted alkenylboronates 122. In stark contrast to the Pd/Senphos catalyzed trans hydroboration and cyanoboration reactions, the carboboration is highly cis selective. This surprising result prompted mechanistic investigations, which revealed a unique syn-outer sphere oxidative addition mechanism illustrated in Scheme 27. Free palladium(0) complex 123 first binds enyne 112 to generate enyne complex 124 which was identified as the resting state of the palladium catalyst. Complex 124 is attacked electrophilically by the C-boron enolate in a syn fashion, i.e., with the palladium and boron groups syn to each other, to generate π-allylpalladium intermediate 125. Intermediate 125 then undergoes a B-C to Pd-O enolate isomerization process to 126 enabled by the syn relationship of the Pd and boron groups. The Pd-bound enolate group of 126 is then transferred back to boron to generate the O-boron enolate complex 127. Complex 127 can then undergo an intramolecular, outer-sphere reductive elimination to afford the product 122 and regenerate free palladium catalyst 123.

The performance of ligand 118 and its all-carbon analogue 118-CC were compared using 112 and 121a as model substrates. It was found that while 118 could carry the reaction to completion, the reaction stalls at around ~50% conversion after 4 hours for 118-CC. This result is consistent with the stabilizing effect of the η2-BC coordination imparted by 118 that gives a longer-living catalyst.

Building on the previously discussed revelations with respect to the mechanisms of Pd/Senphos-catalyzed 1,3-enyne functionalizations, a cooperative catalyst system consisting of Pd/Senphos, tris(pentafluorophenyl)borane (B(C6F5)3), copper(I) bromide, and a stoichiometric amount of amine base (2,2,6,6-tetramethylpiperidine, TMP) was devised to effect the trans-hydroalkynylation of internal 1,3-enynes. A variety of alkynes 128 could undergo selective trans-addition to 1,3-enynes to generate cross-conjugated dienynes 129. Whereas previous Pd/Senphos-catalyzed 1,3-enyne functionalizations have relied on an electrophilic borane for activating a palladium enyne complex prior to reductive elimination, the hydroalkynylation catalyst system uses a catalytic Lewis acid to promote outer-sphere oxidative addition followed by quenching of the resulting adduct with an electrophile, here a proton.
A proposed mechanism is shown in Scheme 28 with enyne 112 and phenylacetylene (128a) as model substrates. Enyne complex 124 is activated by $\text{B(C}_6\text{F}_5)_3$ in an anti-outer-sphere oxidative addition process to generate 130. Meanwhile, a combination of copper(I) bromide and TMP generates a copper acetylide and protonated TMPH$^+$ from phenylacetylene (128a) in the same manner as in Sonogashira couplings.41 TMPH$^+$ can then protodeboronate complex 130, liberating free $\text{B(C}_6\text{F}_5)_3$ and TMP, and generating cationic π-allylpalladium complex 131. Copper to palladium transmetalation and concomitant $\eta^3$ to $\eta^1$ allyl isomerization then affords intermediate 132. Intermediate 132 then undergoes reductive elimination yielding the product 129 and regenerating the free palladium catalyst.

Borataalkene complexes as reactive intermediates

Transition metal borataalkene complexes have been used as nucleophiles and catalytic intermediates extensively.3 Indeed, before Sadighi’s report of the structurally characterized copper(I) borataalkene complex 73 (Scheme 17), Knochel reported a general route to copper/zinc stabilized α-boryl organometallic compounds.43 These compounds are known to engage in reactivity with a diverse array of electrophiles and coupling partners under transition metal catalysis. Aryl,44a,b vinyl,44c benzylic,44d and allylic44d electrophiles can be coupled under palladium catalysis (Scheme 30). The reaction follows a typical cross-coupling mechanism with the bis(borinate) being activated by base, typically hydroxide, prior to transmetalation.

More recently, geminal bis(boronates) 137 have emerged as readily accessible, bench stable precursors to α-boryl organometallic compounds.43 These compounds are known to engage in reactivity with a diverse array of electrophiles and coupling partners under transition metal catalysis. Aryl,44a,b vinyl,44c benzylic,44d and allylic44d electrophiles can be coupled under palladium catalysis (Scheme 30). The reaction follows a typical cross-coupling mechanism with the bis(borinate) being activated by base, typically hydroxide, prior to transmetalation.
Similarly, geminal bis(pinacolatoboronates) 140 undergo copper-catalyzed coupling with a somewhat complementary array of electrophiles (Scheme 31) including alkyl halides,\(^{45a}\) allylic halides/pseudohalides in an \(\text{S}_2^2\) fashion,\(^{45b}\) imines,\(^{45c}\) epoxides and aziridines.\(^{45d}\) These reactions involve a copper(I) source, typically copper(I) chloride (CuCl), and an alkoxide base, most commonly lithium tert-butoxide (LiOr-Bu). A simplified mechanism is presented in Scheme 31. The copper halide complex first undergoes a salt metathesis with the alkoxide base to generate a copper(I) alkoxide. The copper(I) alkoxide then undergoes a transmetalation with the bis(boronate) complex to afford the corresponding electrophile 141 to the product 142.

![Scheme 31 Cu-catalyzed couplings of geminal bis(boronates)](https://example.com/scheme31)

**Conclusions**

The recently developed strategies for synthesizing transition metal borataalkene complexes and other complexes featuring the rare \(\eta^3\)-B,C coordination mode, as well as their role in transition metal catalysis have been described in this review. The diversity of coordination modes and the unique reactivity induced by borataalkene ligands and other boron-containing π ligands are leveraged to develop new catalytic activity. As the use of borataalkenes as ancillary ligands is only just emerging, we anticipate this active area of research will continue provide fertile ground for new discoveries in the future.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

We are very grateful to the many co-workers in the Liu laboratory who have contributed to the results described in portions of this review. This work was supported by the National Institutes of Health NIGMS (R01-GM136920). M.E and Y.Z. were supported as LaMattina Graduate Fellows in Chemical Synthesis at Boston College.

**Notes and references**

A. Vargas and H. Braunschweig,

D. Martin,

G. Linti, H. Nöth, S. Channareddy and P. Hofmann,

Angew.


