

Transmetalation of Unsaturated Carbon Nucleophiles from Boron-Containing Species to the Mid to Late d-Block Metals of Relevance to Catalytic C–X Coupling Reactions (X = C, F, N, O, Pb, S, Se, Te)

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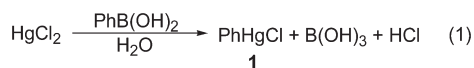
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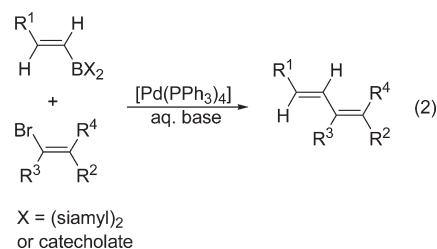
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Scheme 1



Scheme 2



1. INTRODUCTION

Though often perceived as the simple metaphorical hybrid of synthetic inorganic and organic chemistry, synthetic organometallic chemistry continues to vigorously differentiate itself from its more firmly established progenitor subdisciplines of chemistry. Organometallic complexes are commonly synthesized by a transmetalation reaction, a process by which one organometallic compound transfers its organic group to the metal of interest. In the cases of transition metals, a variety of transmetalating reagents, including organolithium compounds,^{1–27} organomagnesium compounds (Grignard reagents),^{28–53} and organostannanes,^{54–70} have been utilized with great success in the synthesis of organo-transition metal compounds. However, the air and water sensitivity of organolithium and Grignard reagents demands caution from the user, while the toxicity of tin makes organostannanes less than ideal for the purposes of transmetalation reactions.

Organoboron compounds^{71–73} have also been utilized as stoichiometric transmetalation reagents in the syntheses of organometallic compounds of the d-block metals (boron is actually not a metal but a metalloid, but historically the term transmetalation has been used for organoboron compounds), although it has only been in recent years that the number of stoichiometric transmetalation reactions which utilized organoboron compounds have not been overwhelmed by the number which did not. Organoboronic acids are only marginally toxic and can be routinely handled in air. Thus, it is not particularly surprising that Michaelis and co-workers demonstrated the utility of organoboronic acids in the synthesis of organomercurials by 1882,⁷⁴ an early account of a successful transmetalation protocol using phenylboronic acid (Scheme 1). Later work by Challenger and co-workers further corroborated the utility of arylboronic acids in the synthesis of isolable organometallic complexes of mercury(II) and thallium(III). Several reports of transmetalations from organoboron compounds to mercury salts continued to emerge in exclusion to any other d-block metals until the 1960s, after which reports of organometallic compounds of nickel, platinum, ruthenium, and palladium synthesized by transmetalation from organoboron compounds began to appear in the literature.

In 1979, Professor Akira Suzuki published the first of a series of seminal papers on what is now called the Suzuki–Miyaura

cross-coupling reaction,^{75,76} a carbon–carbon bond forming methodology in which an organoboron compound (the nucleophile) and an organohalide or pseudohalide (the electrophile) couple in the presence of a transition-metal catalyst and base (Scheme 2). The influence that this class of catalytic coupling reactions^{77–90} had on (ironically) catalyzing the development of transmetalation chemistry via organoboron compounds cannot be overstated. From this point forward, the number of investigations involving transmetalations from organoboron compounds to mid to late d-block metals exploded, the product of a synergistic coevolution between stoichiometric and catalytic transmetalations that together came to include almost every mid to late d-block metal. The well-established organoboron-mediated transmetalation steps of the 1,4-conjugate addition,^{91–96} oxidative homocoupling,⁹⁷ and Chan–Lam–Evans cross-coupling⁹⁸ (to name a few) putative catalytic cycles were all arguably influenced by the precedent set by the Suzuki–Miyaura cross-coupling reaction.

In this review, transmetalation reactions from organoboron compounds to catalytically relevant mid to late d-block metals (that is, all d-block metals from group 6 to group 12 with the exceptions of Tc and Os) are discussed. For the purposes of this review, *transmetalation* will be defined as a chemical transformation that is the result of one or more elementary steps in which a B–C_A bond is cleaved and, in the same or a subsequent elementary step, a M–C_A bond (or M–C_A bonds) is formed, where C_A is the same carbon atom. Note that M–C bond formation need not be coupled to M–X bond cleavage.

Investigations which feature transmetalation reactions to form either isolable organometallic products or proposed organometallic intermediates as part of a catalytic cycle are included in this review. However, investigations which feature transmetalation of alkyl groups (i.e., sp³-hybridized carbon) from organoboron compounds^{99–105} are excluded from this review, as the vast majority of transmetalations (both in stoichiometric reactions and in catalysis) from organoboron compounds transfer unsaturated carbon nucleophiles (i.e., aryl, heteroaryl, alkenyl, or alkynyl groups) to the transition metal. Note that cyclopropylboronic acids (and derivatives) are also excluded from consideration, even though there has been much discussion about the sp²-hybridized character of the carbon atoms of cyclopropane.¹⁰⁶ In addition, there have been several examples reported in the literature of transmetalation reactions from organoboron compounds to metals earlier than group 6 (Sc,¹⁰⁷ Y,¹⁰⁸ Ti,^{109,110} Zr,¹¹¹ Hf,¹¹² V,^{110,113} Nb¹¹⁴). However, these metals are excluded from this review since the overwhelming majority of coupling reactions which utilize organoboron compounds are catalyzed by d-block metals to the right of group 5. A relatively broad period of time (from 1965 to 2010) will be covered, from the first reports of transmetalation reactions between organoboron compounds and mid to late d-block metals other than mercury. Note that organomercurials are somewhat exceptional in the context of this review, as organomercurials synthesized by transmetalation reactions from organoboron compounds were reported as early as 1882.⁷⁴

2. PRELIMINARY CONSIDERATIONS

2.1. Scope of Transmetalating Agents

Competence in transmetalation reactions with the mid to late d-block metals has been demonstrated by a great variety of

Table 1. Organoboron Compounds Typically Used in Transmetalation Reactions and Catalysis

transmetalation reagent	abbreviated notation	general comments
diorganoboronic acids	R_2BOH	rarely used in cross-coupling
organoboronate esters	$RB(OR')_2$	usually more stable to protodeboronation and more soluble in organic solvents than organoboronic acids
organoboronic acids	$RB(OH)_2$	most common commercial organoboron compounds
organoboroxines	$(RBO)_3$	equilibrate with organoboronic acids in the presence of water
organotrialkoxyborates	$RB(OR')_3^-$	commonly formed in situ when used in cross-coupling reactions
organotrifluoroborates	RBF_3^-	usually more stable to protodeboronation than organoboronic acids, but B–F bonds can be hydrolyzed
organotrihydroxyborates	$RB(OH)_3^-$	historically studied in solution but recently isolated as solids for cross-coupling
tetraorganylborates	BR_4^-	commonly used as water-soluble, nucleophilic aryl sources
triorganoboranes	R_3B	strong Lewis acid for alkyl abstraction when $R = C_6F_5$

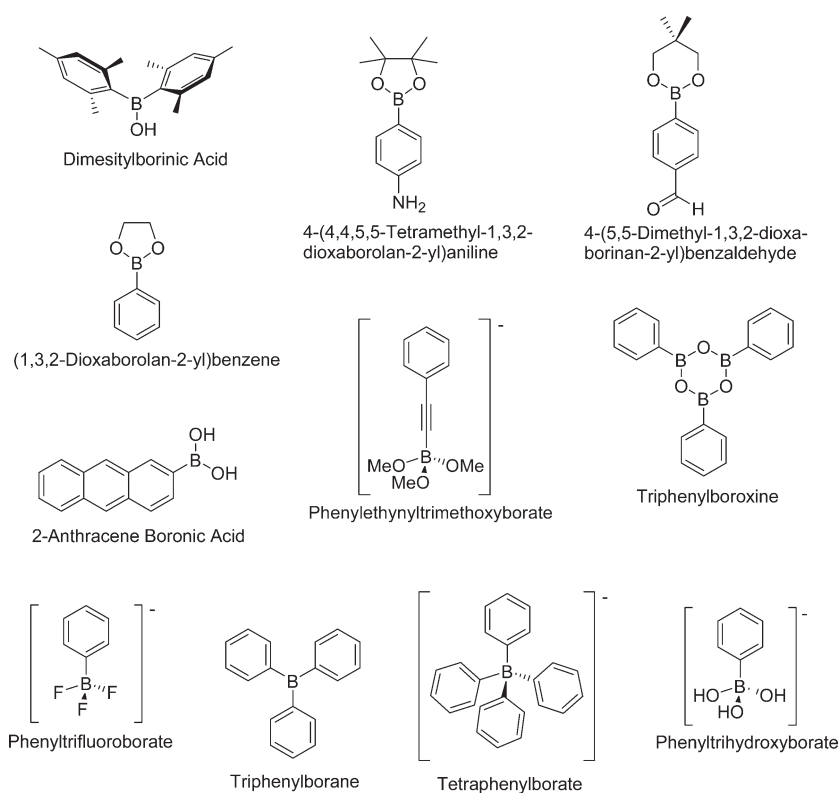
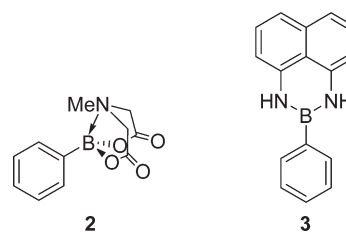


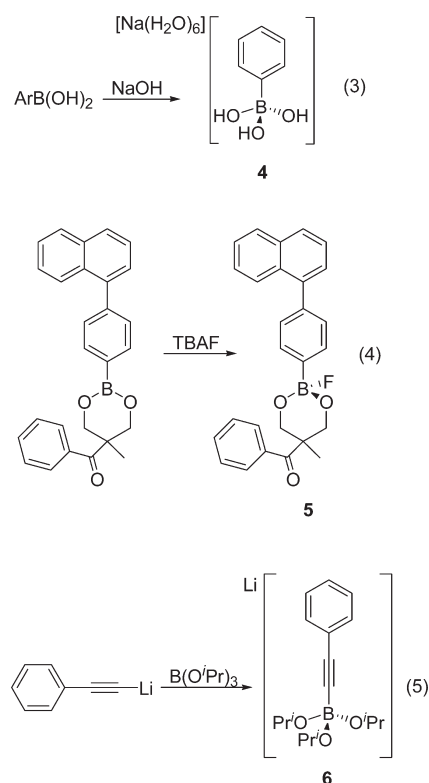
Figure 1. Representative examples of the types of organoboron compounds listed in Table 1 and routinely employed in synthesis.

organoboron compounds. While initial transmetalation reactions were performed exclusively with organoboronic acids ($RB(OH)_2$),^{74,115–118} it was later shown that organoboronic acids (R_2BOH), organoboroxines ($(RBO)_3$), organotrifluoroborates (RBF_3^-),^{119–121} tetraorganoborates (BR_4^-), organoboronate esters ($RB(OR')_2$), triorganoboranes (BR_3), organotrialkoxyborates ($RB(OR')_3^-$), and aryltrihydroxyborates ($ArB(OH)_3^-$) are all capable of transmetalation, transferring organic nucleophiles from boron to transition-metal substrates to form isolable organometallic compounds or transient organometallic intermediates (the latter are most frequently involved in catalytic cycles). Figure 1 shows examples of each type of organoboron compound listed in Table 1. Recently, *N*-methyliminodiacetic acid^{122–124} and 1,8-diaminonaphthalene^{125–131} have been exploited as organoboron protecting groups, deactivating or even rendering the compounds inactive to transmetalation under typical Suzuki–Miyaura cross-coupling conditions

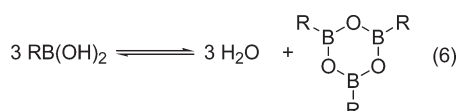
Figure 2. Example of *N*-methyliminodiacetic acid-protected (left) and 1,8-diaminonaphthalene-protected (right) $PhB(OH)_2$.

(Figure 2). Deprotection under basic or acidic conditions yields an organoboronic acid, which is now competent for catalytic coupling reactions. As part of the orthogonal functionalization strategy in synthesis, the B(dan) group has recently garnered much attention. However, as reagents inactive or deactivated to

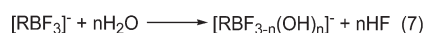
Scheme 3



Scheme 4



Scheme 5



transmetalation, compounds of the type shown in Figure 2 are outside the scope of this review.

2.2. Chemical Changes of the Transmetalating Agent in Situ

Under certain reaction conditions, the organoboron compound used in a transmetalation reaction (including a transmetalation step in a catalytic transformation) may undergo a chemical change, such that the identity of the transmetalating agent in situ is not the same as that from which one started. Three of the most common chemical changes are briefly discussed below.

2.2.1. Base-Mediated Formation of Borate Anions.

Three-coordinate boron in compounds such as $\text{RB}(\text{OH})_2$ and BR_3 can become four-coordinate, forming tetrahedral borate anions in the presence of a base. The coordination geometry of four-coordinate boron was established initially by Raman spectroscopy¹³² and later by thermodynamic analysis,¹³³ pK_a analysis,^{134,135} ^{11}B NMR spectroscopic analysis,^{99,136,137} mass

spectrometry,¹³⁸ and X-ray crystallography.^{123,139,140} In the context of transmetalation reactions, RO^- ,^{99,139} F^- ,¹⁴¹ and C-nucleophiles^{142–147} are most commonly responsible for the formation of four-coordinate boron as a borate anion (Scheme 3).^{146,148,149} The binding of $\text{PhB}(\text{OH})_2$ to small nucleophiles (HO^- , F^-) has been the subject of theoretical calculations recently.¹⁵⁰ Glaser and Knotts described the B–C bond in $[\text{PhB}(\text{OH})_2\text{Nu}]^-$ as coordinate covalent and calculated ΔG_{298} for the reaction $\text{PhB}(\text{OH})_2 + \text{Nu}^-$ to be negative in all cases. Furthermore, they calculated the strength of the B–C bond in $[\text{PhB}(\text{OH})_2\text{Nu}]^-$ ($\text{Nu} = \text{HO}^-$ or F^-) as less than 50 kcal/mol.

2.2.2. Boronic Acid–Boroxine Equilibrium. In solution in the presence of water, boronic acids and boroxines can be in equilibrium (Scheme 4). This equilibrium has been the subject of several spectroscopic and crystallographic studies.^{151–155} In the systems discussed below, the most relevant instances of this equilibrium are found in Cu-catalyzed (mediated) and Rh-catalyzed systems. In some systems, molecular sieves have been used to remove water from the system, driving equilibrium (reaction 6 in Scheme 4) to the right.

2.2.3. Hydrolysis of the Transmetalating Agent in Situ (without B–C Cleavage). Organoboronate esters and organotrifluoroborates are known to undergo hydrolysis reactions to generate organoboronic acids in situ (Scheme 5). Early in the development of alternatives to organoboronic acids in Pd-catalyzed cross-coupling reactions, the possible involvement of species of the type $[\text{RBF}_{3-n}(\text{OH})_n]^-$ was hypothesized by several investigators.^{156–160} However, mechanistic investigations by Molander,¹⁶¹ Perrin,¹⁶² and Lloyd-Jones¹⁶³ determined that solvolysis of the B–F bonds of the trifluoroborate is complete, with formation of B–O bonds in their stead. In the investigation of Perrin,¹⁶² a Hammett plot indicated the rate of aryltrifluoroborate solvolysis correlates with the electron-richness of the aryl group. In the investigation of Lloyd-Jones,¹⁶³ it was also determined the B–F bonds of the aryltrifluoroborate hydrolyzed in the presence of a base, yielding arylborate species $\text{ArB}(\text{OH})_3^-$ (significantly, a small amount of an intermediate hydrolysis species, $\text{ArBF}_{3-n}(\text{OH})_n^-$, was detected by ^{19}F NMR spectroscopy). The arylborate species was ascertained to be the more potent transmetalation reagent, as supported by calculations (vide infra).

3. STOICHIOMETRIC TRANSMETALATION REACTIONS

In this section, only reactions in which a B–C bond has been broken concomitantly (but not necessarily simultaneously) with the formation of a M–C bond to form an isolable organometallic product(s) are considered. Each metal will be considered in its own subsection, highlighting the stark contrast between leaders and laggards and ultimately suggesting where the largest frontiers in this chemistry may be. For example, the contrast between platinum (several investigations) and manganese (few investigations) becomes obvious. These transmetalation reactions will be presented in chronological order per metal so that the reader may trace the development of transmetalation methodology for a particular metal. For example, the transmetalation chemistry of gold (section 3.15), originally explored with tetra-arylborates as the transmetalation reagent, has come to be dominated by arylboronic acids. Except in a few cases, the focus of this section will be on reactions in which a transmetalated product has been isolated.

Noteworthy in this context are the inorganic starting materials for these reactions, which frequently feature metal–oxygen bonds (that is, *O*-bonded ligands either are present in the starting materials or become bound to the metal at some point during the reaction before transmetalation occurs). Transmetalation reactions of this type (i.e., organoboron compound plus *M*–OR compound) are the most commonly observed. Relevant to this point but outside the scope of this review is the review by Brynzda and Tam,¹⁶⁴ in which the reactivities of hydroxides, alkoxides, and amides of the late transition metals have been thoroughly discussed. Other common transmetalation archetypes are organoboron plus *M*–*X*, where *X* typically is Cl or Br, and *Ar*₃B plus *M*–*R'*, where *Ar* = aryl group and is usually C₆F₅. In the latter archetypical reaction, the organoborane typically abstracts an alkyl group, quaternizes to a borate anion, and is then activated to transfer an aryl group to the metal. This latter class of transmetalation reactions is most frequently observed for iron and zinc.

Also noteworthy is the particularity of the organoboron compound for the reaction conditions (especially the metal-based reaction partner and reaction medium). An “analogy-based” approach to transmetalation frequently proves fruitless, as seemingly minor changes of solvent or on the coordination sphere of a metal can be important enough to overwhelmingly favor a different reaction pathway (this point was recently made by Molander with respect to the choice of organoboron reagent in cross-coupling reactions).¹⁶⁵ Examples of the importance of these factors will be emphasized when relevant.

Side reactions are a consideration for some stoichiometric transmetalation protocols, the most common of which are protodeboronation (section 6.4, *vide infra*) and “arrested” transmetalation (section 4, *vide infra*). Protodeboronation is a chemical change by which a B–C bond of an organoboron compound is cleaved with subsequent formation of (for the purposes of this review) a H–C (not M–C) bond. Arrested transmetalation describes a process by which an organoboron “ligand” forms a M–C bond, but the B–C bond is not cleaved.

Finally, some experimental and theoretical data have been gathered to better understand the mechanism(s) by which organoboron compounds transmetalate to metal complexes. To supplement the discussion in this section, some experimental and theoretical evidence for mechanisms by which transmetalation reactions proceed will also be included.

3.1. Chromium

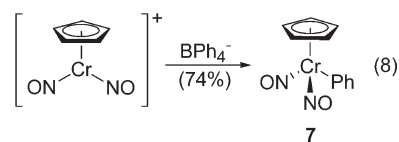
Legzdins and co-workers have exploited the electrophilicity of the cationic organometallic complex [CpCr(NO)₂](BF₄) to yield a variety of addition products when treated with nucleophiles, as the Cr complex can accept additional ligation due to coordinative unsaturation.¹⁶⁶ Treating [CpCr(NO)₂](BF₄) with NaBPh₄ in an essentially noncoordinating solvent (CH₂Cl₂) gave the phenylchromium product **7** in 74% yield (Scheme 6).

3.2. Molybdenum

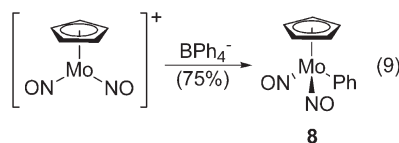
Legzdins and co-workers used the same strategy for Mo as they did for Cr (Scheme 6) to generate a phenylmolybdenum species.¹⁶⁶ Treating the electrophilic, coordinatively unsaturated complex [CpMo(NO)₂](BF₄) with NaBPh₄ in CH₂Cl₂ gave the phenylmolybdenum product **8** in 75% yield (Scheme 7).

In an exploration of the reactivity of Ph₄Cp-ligated Mo and W complexes, Legzdins and co-workers subsequently reported an interesting example of the use of a reactant to activate a metal complex to electrophilic substitution by both oxidation and

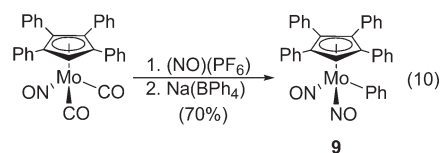
Scheme 6



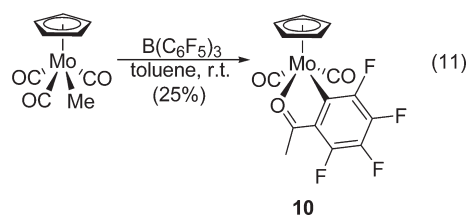
Scheme 7



Scheme 8



Scheme 9



ligand substitution.¹⁶⁷ The Ph_4Cp -ligated Mo complex was treated sequentially with the one-electron oxidant $(\text{NO})(\text{PF}_6)$ and NaBPh_4 to yield **9** (in 70% isolated yield), in which both of the original CO ligands had been displaced (Scheme 8).

Green and co-workers reported another example of transmetalation for Mo and speculated on the elementary steps (including methyl migration) to form the final product.¹⁶⁸ The chelated product **10** is formed in much lower yield (25%) than its heavier W congener (Scheme 9).

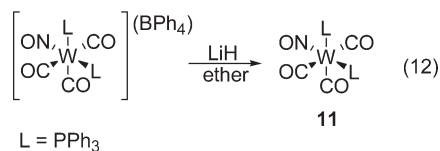
3.3. Tungsten

There have been a few reports of arylation of electrophilic tungsten species, similar to the examples of chromium and molybdenum. In an initial report, Hundel and Berke witnessed the collapse of a BPh_4^- ion pair to yield a neutral phenyltungsten product, **11**, in the presence of LiH (Scheme 10).

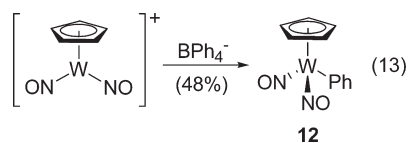
The electrophilicity of the cationic tungsten species $[\text{CpW}(\text{NO})_2](\text{BF}_4)$ was made evident by Legzdins and Martin, in which the phenyltungsten derivative **12** was synthesized in 48% yield by treatment of $[\text{CpW}(\text{NO})_2](\text{BF}_4)$ with NaBPh_4 (Scheme 11).¹⁶⁹

In a subsequent report, Green and co-workers also used a CpW species for transmetalation.¹⁶⁹ In this case, similar to the reaction reported by the same group for a CpMo species (Scheme 9, *vide supra*), the transmetalated product **13**, produced

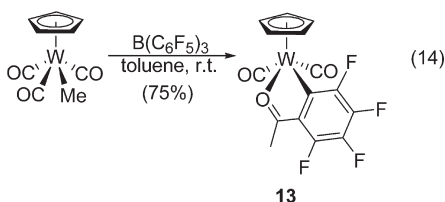
Scheme 10



Scheme 11



Scheme 12



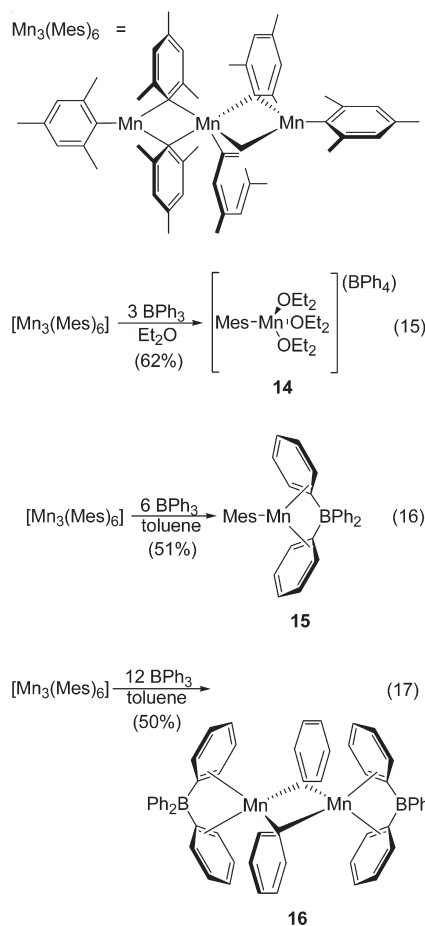
in 75% yield, is probably the end result of several elementary steps, including methyl migration (Scheme 12).

3.4. Manganese

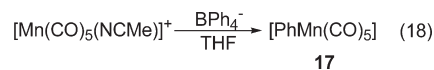
In one report by Solari et al.,¹⁷⁰ the phenylation of a trinuclear organomanganese complex, Mn₃Mes₆ (featuring terminal and bridging mesityl ligands), by BPh₃ in a solvent- and stoichiometry-dependent set of reactions was demonstrated and is shown in Scheme 13. In diethyl ether, using a 3:1 ratio of BPh₃ to Mn₃Mes₆, 1 equiv of mesityl per manganese atom has been abstracted (a large amount of MesBPh₂ was identified by GC–MS in the mother liquor of the recrystallized product) to yield a mononuclear product, **14**, in good yield. However, in a less coordinating solvent (toluene), a 6:1 ratio of BPh₃ to Mn₃Mes₆ yields a BPh₄[−]-ligated mononuclear product, **15**, in which one mesityl ligand has been abstracted per manganese (GC–MS detected large amounts of BPh₂Mes) while a 12:1 ratio of BPh₃ to Mn₃Mes₆ gives a BPh₄[−]-ligated dinuclear complex, **16**, featuring bridging phenyl ligands. Note that the phenyl ligands in the latter are the result of formal transmetalation of phenyl groups from boron to manganese. Furthermore, the BPh₄[−] ligands bind to Mn via the π -face of a phenyl ring, a well-known binding mode that has been reviewed by Strauss.¹⁷¹

The reactivity of the borate anions BMe₄[−], BMePh₃[−], and BPh₄[−] with [Mn(CO)₅L]⁺ (L = MeCN, py, PPh₃, PPh₂Me) was explored by Kochi and Zhu.¹⁷² All three borate anions are capable of transferring their R groups to Mn to form products of the type [RMn(CO)₅], and in general, the authors found BPh₄[−] to be the least reactive of the borate anions. Thus, in the mixed borate BMePh₃[−], it was the methyl group that was found to be the transferable R group. In the case of BPh₄[−] (as the Na⁺ salt) plus [Mn(CO)₅(NCMe)]⁺,

Scheme 13



Scheme 14

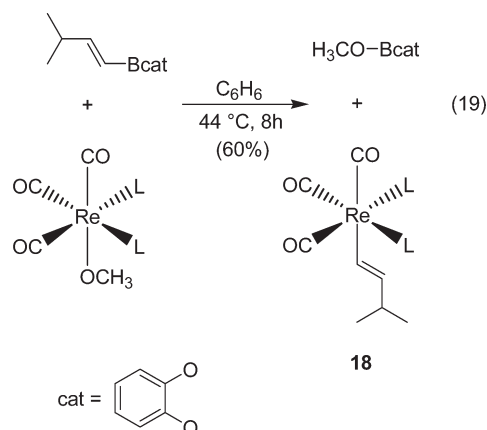


[PhMn(CO)₅] (**17**) was cleanly formed, quantified by IR spectroscopy (Scheme 14).

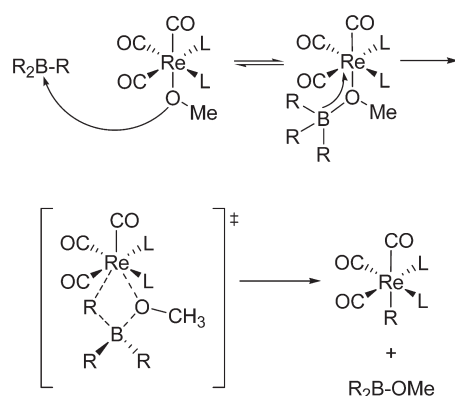
3.5. Rhenium

Bergman and co-workers reported one example of a transmetalation reaction from an organoboron compound to rhenium.¹⁷³ In an exploration of the reactivity of rhenium(I) alkoxide complexes with various Lewis acids, it was demonstrated that the reaction of a vinylborane with [Re(CO)₃(dppe)(OCH₃)] gave a vinylrhenium product, **18**, in 60% yield along with methoxycatecholborane (Scheme 15). Interestingly, the similar substrates [Re(CO)₃(dppe)Cl] and [Re(CO)₃(dppe)(OC₆H₄CH₃)] did not react at all with the vinylborane, suggesting that the electron-rich methoxide ligand was necessary for transmetalation. In addition, the transmetalation reaction was sensitive to steric parameters, as an α -substituted vinylborane formed very little product under the same conditions. These data are consistent with the proposed reaction mechanism, the first step of which involves the nucleophilic attack of alkoxide on the borane to form an “ate” complex, which rearranges to form the observed products (Scheme 16).

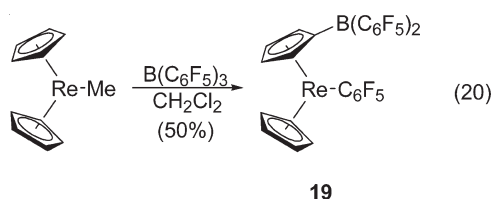
Scheme 15



Scheme 16



Scheme 17

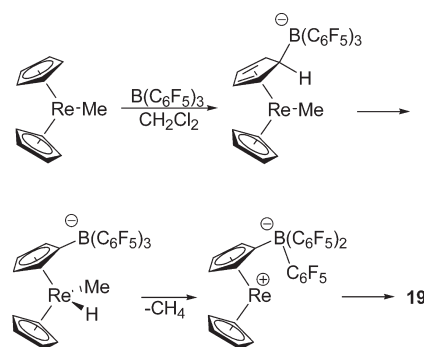


Green and co-workers were able to exploit the alkyl abstraction ability of $\text{B}(\text{C}_6\text{F}_5)_3$ with an organorhenium complex to effect transmetalation of C_6F_5 to Re (Scheme 17).¹⁷⁴ The product **19**, formed in approximately 50% yield, was hypothesized by the authors to be the result of initial electrophilic attack at a Cp ring, migration of a proton to the metal center, and reductive elimination of CH_4 to generate a cationic Re species, which is then arylated by a C_6F_5 group in close spatial proximity to the metal center (Scheme 18).

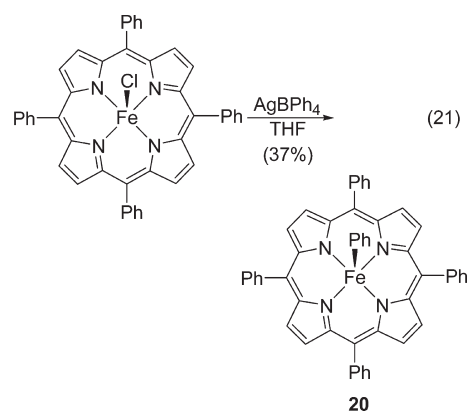
3.6. Iron

Isolated reports from different laboratories have emerged since the 1970s on the formation of organometallic iron complexes via transmetalation from organoboron compounds. In two of the earliest reports, transmetalation appeared to occur as an

Scheme 18



Scheme 19

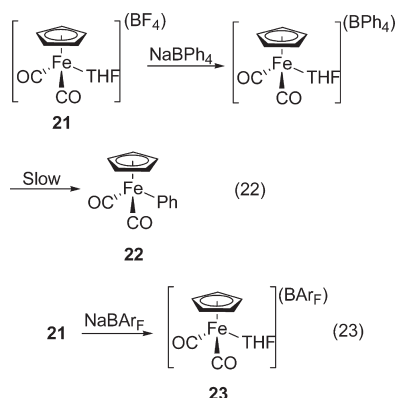


undesired reaction. In one early report, Lang and co-workers investigated the intermediate spin states of Fe^{III} complexes of the type $[\text{Fe}(\text{tpp})\text{Y}]$ (tpp = *meso*-tetraphenylporphyrin).¹⁷⁵ To prepare $[\text{Fe}(\text{tpp})\text{Ph}]$, the authors treated $[\text{Fe}(\text{tpp})\text{Cl}]$ with $\text{Ag}(\text{BPh}_4)$; **20** was isolated in 37% yield (Scheme 19). The product **20**, which was structurally authenticated in a subsequent investigation,¹⁷⁶ was compositionally consistent with microanalytical data and yielded the expected product (i.e., the $\text{FeCl}(\text{TPP})$ starting material by UV-vis spectroscopy) when treated with concentrated HCl.

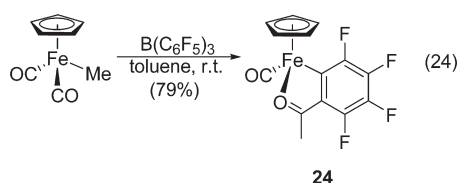
In another early study, Lewis acid catalyzed Diels-Alder transformations (in which the catalysts were complexes of low-valent metals) were studied by Hersh and co-workers.¹⁷⁷ To prepare a cationic Fe^{II} catalyst, the authors attempted to execute an anion exchange of BPh_4^- or $[\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]^-$ (that is, BAR_F) for BF_4^- . The anion exchange was successful in both cases, but once prepared, **21** was slowly phenylated, although a procedure and yield were not specified (Scheme 20). This is one of many examples of the enhanced inertness to B-C cleavage for BAR_F relative to other tetraarylborates.

Mehnert and co-workers investigated the reaction of $[\text{CpFe}(\text{CO})_2\text{Me}]$ with $\text{B}(\text{C}_6\text{F}_5)_3$, the product of which, according to the authors, was unexpected.¹⁷⁸ In a subsequent report, the procedure to produce **24** in 79% yield was refined (Scheme 21).¹⁶⁸ Several elementary steps were posited to account for the observed product, including (initially) formation of an acetyl ligand by methyl migration, B-C bond cleavage concomitant with oxidative addition of the C-F bond and

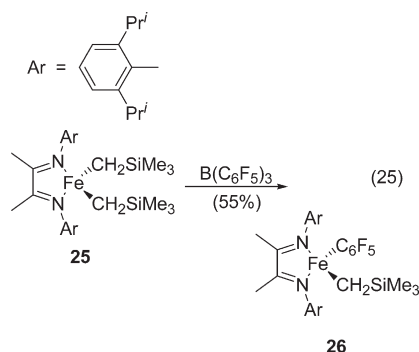
Scheme 20



Scheme 21



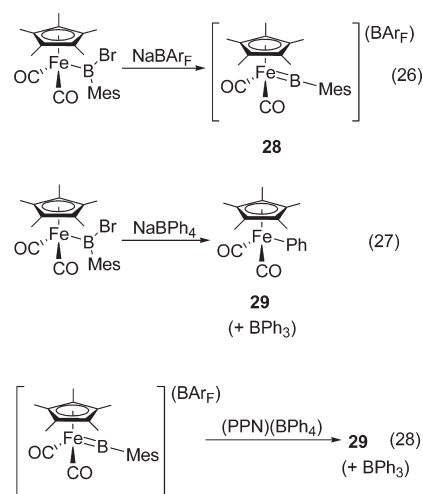
Scheme 22



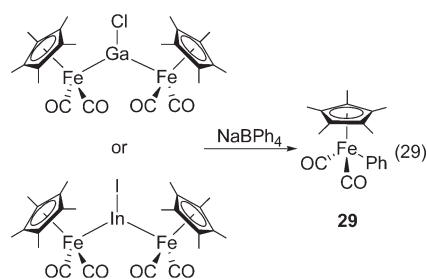
benzynes formation, and migration of the resulting fluoride ligand from Fe to B. As evidence for the proposed mechanism, the authors cited the detection (by ¹¹B NMR spectroscopy) of BF(C₆F₅)₂, BF₂(C₆F₅), and BF₃ formed during the reaction.

Four-coordinate N[^]N-chelated dialkyliron(II) and dialkylmanganese(II) complexes were the targets of an investigation by Chirik and co-workers, the reactivity of which would be probed via treatment with ethylene, CO, and B(C₆F₅)₃.¹⁷⁹ The reactions of the dialkyliron(II) complexes with ethylene and B(C₆F₅)₃ were especially of interest, relevant to ethylene polymerization. The reaction between a diimine-ligated dialkyliron(II) complex, **25**, and B(C₆F₅)₃ not only abstracted CH₂SiMe₃ from the coordination sphere of Fe, but transferred C₆F₅ from the borane to form **26** in 55% yield (Scheme 22). The byproduct B(C₆F₅)₂(CH₂SiMe₃) was detected by ¹H and ¹⁹F NMR spectroscopies. Similar to the reactivity of **25**, B(C₆F₅)₃ abstracted an alkyl group from the (–)-sparteine-ligated analogue of **25**, but arylation did not follow alkyl group abstraction. The

Scheme 23



Scheme 24

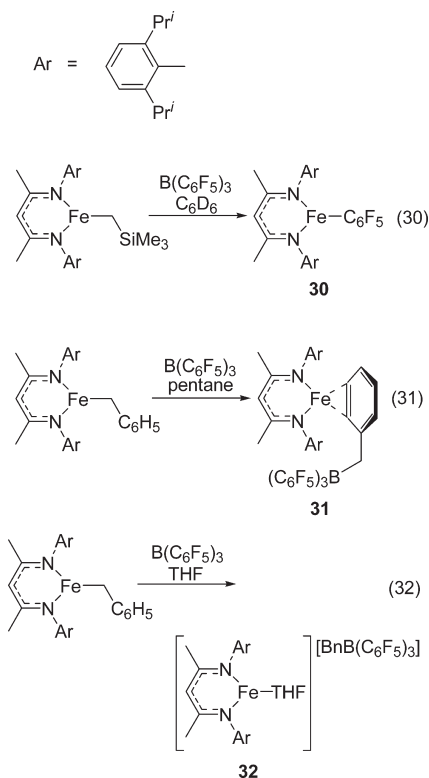


final product was a contact ion pair, [(–)-(sparteine)Fe(CH₂SiMe₃)]⁺[B(C₆F₅)₃(CH₂SiMe₃)]⁻ (**27**), an excellent example of the sensitivity of transmetalation to the coordination sphere of the metal.

Aldridge and co-workers explored the reactivity of a haloboryl-ligated iron(II) complex, Cp^{*}Fe(CO)₂(BBrMes), to determine its synthetic utility as an iron–borylene precursor.¹⁸⁰ Once again, NaBPh₄ was shown to be a useful phenylating reagent, forming the same aryliron(II) product in two separate reactions (Scheme 23). The authors did not report a yield for the two transmetalation reactions, but in both cases identified a resonance at δ 66.0 ppm in the ¹¹B NMR (confirming the presence of BPh₃) and isolated orange crystals that were confirmed to be **29**. The first two reactions underscore the sensitivity of the iron complexes to the tetraarylborate that was used. That is, while NaBARF dehalogenates the haloboryl ligand to form the terminal iron–borylene complex, NaBPh₄ phenylates iron, displacing the haloboryl ligand.

Aldridge and co-workers followed up their Fe–B study¹⁸⁰ with a study (both experimental and theoretical) of Ga and In systems featuring single and multiple bonds to Fe, an exploratory foray into the coordination chemistry of these heavier congeners of B.¹⁸¹ In one set of reactions, GaCl- and InI-bridged Cp^{*}Fe(CO)₂ fragments reacted with NaBPh₄ to yield (in both cases) the known complex [Cp^{*}Fe(CO)₂Ph] (**29**), in contrast to the behavior of NaBARF, which simply abstracted halide from the Ga or In atom (Scheme 24).

Scheme 25

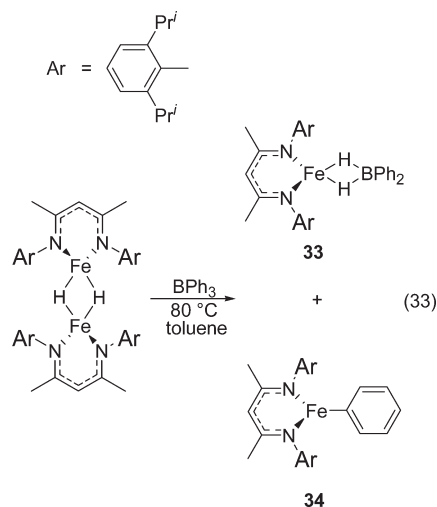


The importance of solvent choice and metal coordination sphere were highlighted in an investigation by Hessen and co-workers, in which $\text{B}(\text{C}_6\text{F}_5)_3$ was examined as a possible activator of three-coordinate alkyliron(II) complexes for use in olefin polymerization.¹⁸² The supporting ligand in each case was a bulky β -diketiminate (L), but two different alkyl groups on Fe^{II} were examined ((trimethylsilyl)methyl, or CH_2SiMe_3 , and benzyl, or $\text{CH}_2\text{C}_6\text{H}_5$). In the case of $\text{LFeCH}_2\text{SiMe}_3$, reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 gave the alkyl-abstracted, aryl transfer product **30**. However, in the case of $\text{LFe}(\text{CH}_2\text{C}_6\text{H}_5)$, the same reaction gave only the alkyl abstraction product as a solvent-separated ion pair in THF (**31**) and as a contact ion pair (**32**) in pentane (Scheme 25). The contact in **32** was an η^2 -interaction between the arene (of the benzyl group) and Fe.

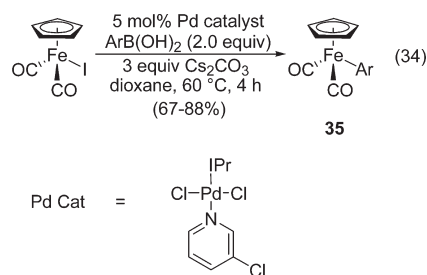
In a study of the reactivity of iron(II) hydride-bridged dimers,¹⁸³ Holland and co-workers exploited the sterically encumbered and strongly binding ligand 2,4-bis((2,6-diisopropylphenyl)imino)pent-3-yl (NacNac) in the reaction of the dimers with BPh_3 . The isolated material was a mixture of a BH_2Ph_2^- -chelated iron(II) complex (**33**) and a phenyliron(II) complex (**34**) (Scheme 26). The authors reported that the phenyliron(II) complex was more cleanly synthesized using PhMgCl as a phenylating reagent.

In an unprecedented set of transmetalation conditions, Oshima and co-workers *catalytically* synthesized a series of aryliron(II) complexes using a carbene-ligated Pd^{II} complex as the catalyst and arylboronic acids as the stoichiometric transmetalation reagents¹⁸⁴ (Scheme 27). A variety of substituted arylboronic acids (with the notable exceptions of hydroxyl- and amino-substituted arylboronic acids) formed products **35** in good to excellent isolated yields. Yields were improved in some cases by

Scheme 26



Scheme 27



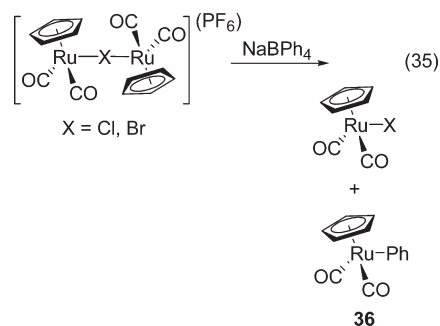
the addition of substoichiometric amounts of copper(I) iodide; the authors speculated that the formation of an arylcopper species *in situ* may enhance the efficiency of transmetalation to palladium, as in other systems.^{185,186}

3.7. Ruthenium

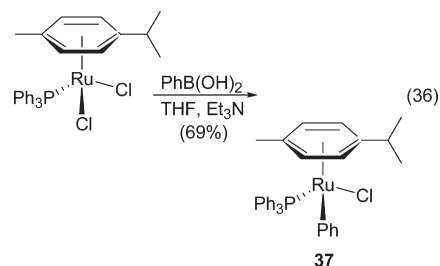
Reports of formation of organoruthenium compounds via organoboron transmetalation reactions began to emerge in the 1970s. In the initial set of reports,^{187,188} Haines and du Preez exploited the potent electrophilicity of the cation $\{[\text{CpRu}(\text{CO})_2]_2\text{X}\}^+$ ($\text{X} = \text{Cl}, \text{Br}$) to demonstrate phenylation by BPh_4^- (Scheme 28). However, a second set of reactions in the same report called attention to the importance of the coordination sphere of the metal in transmetalation reactions. Whereas $[\text{CpRu}(\text{CO})_2\text{Cl}]$ reacted with BPh_4^- to form $[\text{CpRu}(\text{CO})_2\text{Ph}]$ (**36**), B–C cleavage for the less electrophilic ruthenium(II) complex $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ was not observed. Instead, the authors proposed the product to be a “half-sandwich” complex, $\{\text{CpRu}[(\eta^6\text{-Ph})\text{BPh}_3]\}$, in which transmetalation was arrested upon binding to the π -electrons of one phenyl ring of the BPh_4^- ligand.

In a study of the intermediates of the ruthenium-catalyzed oxidative Heck coupling of olefins and arylboronic acids, Brown and co-workers established that the reaction of a ruthenium–arene complex, (*p*-cymene)(PPh_3) RuCl_2 , and $\text{PhB}(\text{OH})_2$ yielded a stable transmetalation product, **37**, in 69% yield, the identity of which was authenticated by X-ray crystallography¹⁸⁹ (Scheme 29).

Scheme 28



Scheme 29



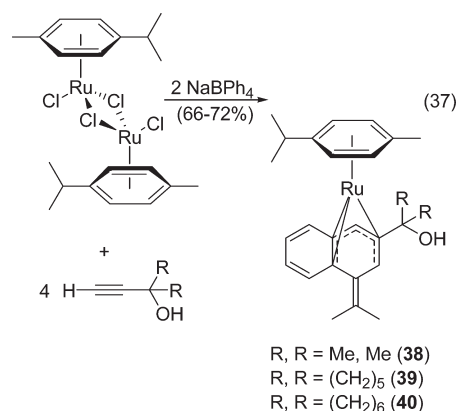
Starting with a Ru-*p*-cymene complex, a very unusual ligand was reported by Winter and co-workers.¹⁹⁰ The ligand, an η^5 -1-methylene-1,2-dihydronaphthalenide, spontaneously formed in the presence of NaBPh_4 , an excess of a butynol, and the Ru complex (Scheme 30). Note that this is a transmetalation reaction. The B-C bond of BPh_4^- has been cleaved to provide a phenyl scaffold, which through a series of insertion reactions with alkyne forms a naphthalenide ligand, to which the original phenyl ring (the left ring of the naphthalenide ligand drawn in Scheme 30) has a bonding interaction with Ru.

3.8. Rhodium

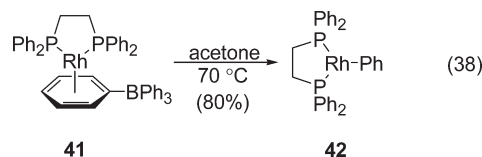
In a study aimed at the activation of CO_2 , Aresta and co-workers focused their attention on a thermally stable (at room temperature) complex, **41**, that is capable of coordinating CO_2 at pressures higher than 10 atm.^{191,192} However, at temperatures approaching 70 °C in acetone (in a sealed tube), **41** thermally decomposed to yield the transmetalated product **42** in 80% yield (Scheme 31). The authors noted that halogenated solvents needed to be avoided under the reaction conditions, since they produced undesired byproducts. Although **42** was confirmed to be monomeric, was found to insert CO_2 to form a benzoate complex, and was compositionally consistent with microanalytical data, the authors conceded that **42** needed to be authenticated by X-ray crystallography as a three-coordinate Rh complex. The utility of reaction 38 in Scheme 31 was underscored by the inability of the authors to generate **42** in a yield greater than 15% using more “traditional” transmetalation reagents (such as PhMgBr or PhLi) with Rh-X ($\text{X} = \text{Cl, Br}$) starting materials.

A study of the redox properties of $[(\text{triphos})\text{Rh}(\text{S}_2\text{C-O})](\text{BPh}_4)$, a dithiocarbonate complex of Rh^{III} , yielded an unexpected result in the presence of $[\text{Cu}(\text{PPh}_3)_3](\text{ClO}_4)$ (Scheme 32).¹⁹³ Complex **43** is stable as a BPh_4^- salt, but in the presence of $[\text{Cu}(\text{PPh}_3)_3](\text{ClO}_4)$, **43** undergoes a transmetalation

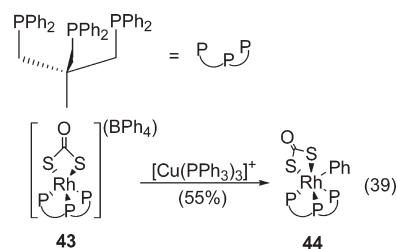
Scheme 30



Scheme 31



Scheme 32

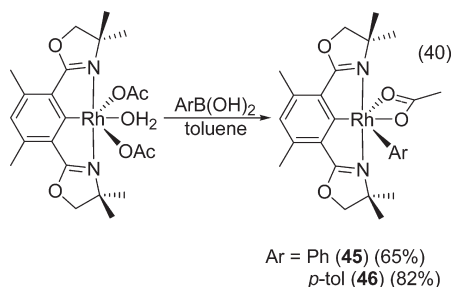


reaction, producing the phenylated product **44** in 55% yield. The authors conceded that the role of the copper salt is unclear, as the ^{31}P NMR spectrum does not change during the course of the reaction. However, $[\text{Cu}(\text{PPh}_3)_3]^+$ is clearly necessary for the transmetalation to occur, as the PF_6^- salt of **43** does not form **44** when treated with $[\text{Cu}(\text{PPh}_3)_3](\text{ClO}_4)$ but *does* form **44** when treated with $[\text{Cu}(\text{PPh}_3)_3](\text{BPh}_4)$.

Carbon-hydrogen bond activation of arenes was the topic of study for Nishiyama and Ito, who used the Phebox-coordinated complex $[(dm\text{-Phebox-dm})\text{Rh}(\text{OAc})_2(\text{OH}_2)]$ ($dm\text{-Phebox-dm} = 2,6\text{-bis}(4,4\text{-dimethyloxazolynil})\text{phenyl}$) as the C-H activating reagent.¹⁹⁴ Several substituted benzene derivatives were successfully activated to form Rh-Ar complexes; however, to provide an alternative route to the Rh-Ar complexes, two substrates were synthesized by a transmetalation reaction with arylboronic acid (Scheme 33). This alternative route was effective, giving products **45** and **46** in 65% and 82% yields, respectively.

The details of the mechanism by which organoboron compounds transmetalate to late-transition-metal complexes is generally not well-known. This was the rationale by which Hartwig and co-workers approached and reported the reaction of $\{\text{Rh}(\text{PET}_3)_2[(\text{N}(\text{SiMe}_3)_3)]\}$ with arylboronic acids.¹⁹⁵ Initially,

Scheme 33



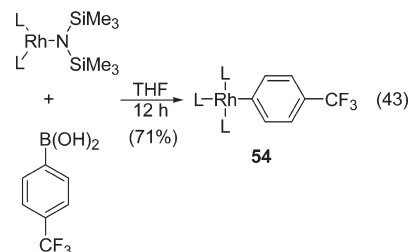
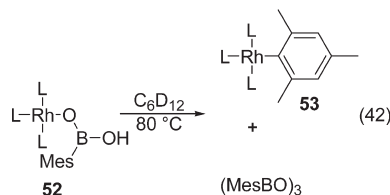
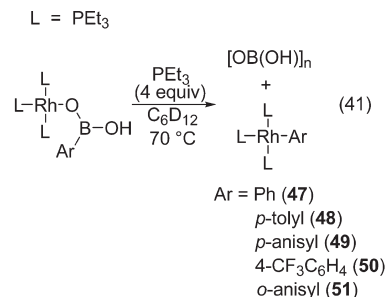
the reaction yields a series of boronate-ligated Rh^{I} complexes or a borinate-ligated complex, **52**, in solution which, upon heating, yields the transmetalated products and (presumably) boroxine byproducts (Scheme 34). Using these solution data, a procedure for synthesis of an arylrhodium(I) complex, **54**, in 71% isolated was developed from the reaction of $\{\text{Rh}(\text{PEt}_3)_2[\text{N}(\text{SiMe}_3)]\}$ with 4-(trifluoromethyl)phenylboronic acid. Stirring for an extended period of time ensured full conversion of the intermediate arylboronate-ligated Rh^{I} complex.

In a report that gave only the second example of B–C cleavage from a BAR_{F} anion ($\text{BAR}_{\text{F}} = [\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$), Milstein and co-workers exploited BAR_{F} for an efficient transmetalation reaction with Rh^{196} (Scheme 35). The transmetalation reaction was very sensitive to the reaction conditions. For example, both sets of products ($\text{R} = ^i\text{Pr}$ or ^tBu) were formed in nearly quantitative yields when the solvent was either noncoordinating (fluorobenzene, CH_2Cl_2) or weakly coordinating (acetone, Et_2O). However, when MeCN (a strongly coordinating solvent) was used, only the less bulky starting material **55** formed product, whereas the bulkier starting material **56** only formed a solvent-substituted Rh^{II} analogue of **56**. Furthermore, the oxidizing Ag^+ salt of BAR_{F} was a necessity, as treating **56** with 1 equiv of AgBAR_{F} followed by treatment with 1 equiv of NaBAR_{F} did not yield any of the solvated products **58**, **60**, or **62**, but rather the same solvent-substituted Rh^{II} analogue of **56**. It seems that 2 equiv of Ag^+ was necessary to oxidize Rh^{I} to Rh^{III} and invoke B–C bond cleavage; however, no evidence for $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3]$ was found by ^{19}F NMR spectroscopy.

Arylated dinuclear paddlewheel complexes of rhodium were recently prepared via transmetalation by Doyle and co-workers. In their initial paper,¹⁹⁷ an aquo-substituted dirhodium caprolactamate (cap) complex was treated with Cu^{II} (generated in situ) as the oxidant and NaBPh_4 as the stoichiometric phenylating agent to yield a two-electron-oxidized complex, $\text{Rh}_2\text{-(cap)}_4\text{Ph}_2$ (**63**), in 77% yield (Scheme 36). The authors speculate that this reaction occurs stepwise, beginning with a one-electron oxidation of the diaquo starting material (this product was isolated) followed by the first phenylation, a second one-electron reduction, and finally the second phenylation to form **63**.

The same laboratory subsequently reported an expansion of the transmetalation substrate scope to various substituted arylboronic acids as stoichiometric arylating agents (Scheme 37).¹⁹⁸ No reaction was observed in the absence of copper or using NaBF_3Ph as the stoichiometric arylating reagent, and the presence of a base aided product formation, presumably by activating the arylboronic acid to a tetracoordinate species. A low yield of product was obtained when the 1,3-propylene glycol ester of

Scheme 34



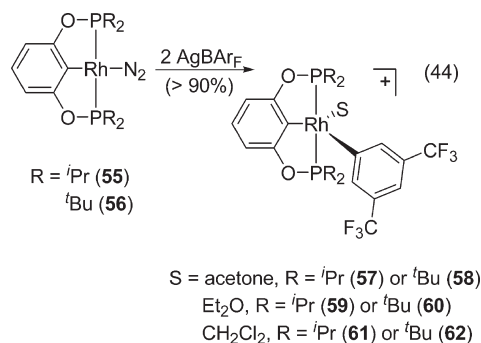
phenylboronic acid was used or when the reaction medium was a solvent other than methanol. Furthermore, *ortho*-substituted arylboronic acids, ferrocenylboronic acid, nor 2-furanylboronic acid yielded any organorhodium product. The authors believed the role of the copper catalyst was to oxidize $\text{Rh}^{\text{II}} \rightarrow \text{Rh}^{\text{III}}$. A mechanism was proposed in which the aryl group of an intermediate borate ligand bonded to rhodium is activated to aryl transfer (Scheme 38). The electronic structures of complexes (using bridging pyrrolidinate ligands) similar to **64**, phenylated by treatment with NaBPh_4 , were explored by an integrated XPS, electrochemical, and computational approach.¹⁹⁹

In a follow-up investigation from the same laboratory,²⁰⁰ Doyle and co-workers treated the same dirhodium starting material **64** with a mixture of $\text{Ar}^1\text{B(OH)}_2$ and $\text{Ar}^2\text{B(OH)}_2$ (under conditions similar to those previously used¹⁹⁸ except for the stoichiometric oxidant, which was $\text{Cu}(\text{SO}_4)$ in this case) to synthesize mixed diaryldirhodium complexes $\text{Ar}^1\text{Ar}^2\text{Rh}_2\text{-(cap)}_4$ (Scheme 39). Note that each reaction produced a mixture of three diarylated products, including $\text{Ar}^1\text{Ar}^1\text{Rh}_2\text{-(cap)}_4$, $\text{Ar}^1\text{Ar}^2\text{Rh}_2\text{-(cap)}_4$, and $\text{Ar}^2\text{Ar}^2\text{Rh}_2\text{-(cap)}_4$. The electronic and electrochemical properties for this set of compounds were recorded.

3.9. Iridium

There is one report of the synthesis (in 61% isolated yield) of an irylidium(I) complex, **67**, via transmetalation,²⁰¹ and not surprisingly, the starting material is an iridium(I) hydroxide (Scheme 40), recalling the generally high reactivity of late-metal alkoxides as reviewed by Tam.¹⁶⁴ The authors do not discuss the

Scheme 35



role or necessity of either the amine base or phosphine ligand for this reaction. However, they posit the likelihood of **67** as an intermediate in the tandem cyclization catalytic cycle, as treatment with dienes gives the expected organic product of the iridium-catalyzed reaction in high yield.

3.10. Nickel

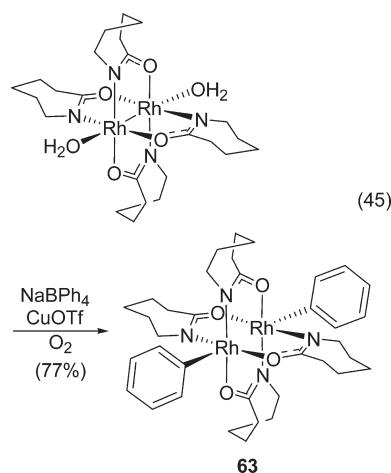
Transmetalation reactions to nickel from organoboron compounds were first observed as a side reaction in the reaction of CpNi(PPh₃)Cl with NaBPh₄ in benzene/EtOH, the primary product of which was the ionic compound [CpNi(PPh₃)](BPh₄).²⁰² In a subsequent report by Treichel and Shubkin,²⁰³ changing the solvent from benzene/EtOH to THF favored the exclusive formation of the phenylated nickel complex CpNi(PPh₃)Ph (**68**) (Scheme 41). The identity of this compound was later authenticated by X-ray crystallography.²⁰⁴

Sacconi and co-workers utilized a tripodal (but potentially tetradentate) ligand, tris(2-(diphenylarsino)ethyl)amine, as a supporting ligand for the observation of stable, trigonal bipyramidal nickel(I) complexes formed via transmetalation from BPh₄[−] (Scheme 42).²⁰⁵ Two other ligands, bidentate *o*-phenylenebis(dimethylarsine) (DAS) and potentially tetradentate tris(*o*-(diphenylarsino)phenyl)arsine, were also used as supporting ligands in transmetalation reactions, although the products **73** and **74** were not structurally authenticated by X-ray crystallography (Scheme 43).

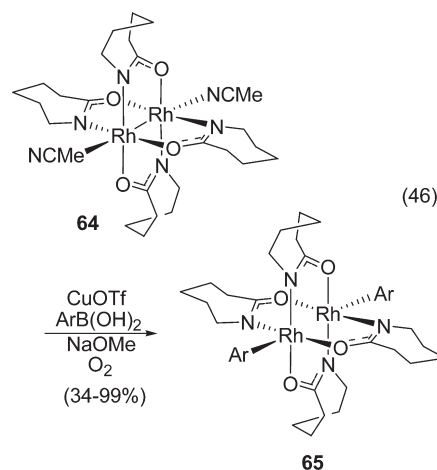
Rhodes and co-workers demonstrated the utility of B(C₆F₅)₃·3H₂O in a transmetalation reaction that was accompanied by protonation and protodeboronation²⁰⁶ (Scheme 44). Protonation of the β -carbon atom of the phosphine-substituted enolate ligand of the starting Ni complex, proposed as the first step, is made possible by the high Brønsted acidity of B(C₆F₅)₃·3H₂O. This is followed by intramolecular proton transfer from the borate ligand [B(C₆F₅)₃(OH)][−] to the phenyl ligand (to form benzene, observed by ¹H NMR spectroscopy) and successive transfers of the pentafluoroaryl group from boron to the nickel to give **75**. Protodeboronation of the third pentafluoroaryl group bonded to each boron forms C₆F₅H (which was detected by ¹⁹F NMR spectroscopy) and boric acid as byproducts. The authors note that this transmetalation reaction is the first example of the transfer of two pentafluorophenyl groups from B(C₆F₅)₃ to a transition metal.

Benzyne complexes have been studied for decades, but in an unusual route to metal–benzyne complexes (M = Ni, Pd), Wenger and co-workers utilized an *ortho*-borylated arylmetal(II) species as a precursor.²⁰⁷ In the case of nickel, the reactions proceeded rapidly at room temperature (Scheme 45), much

Scheme 36



Scheme 37



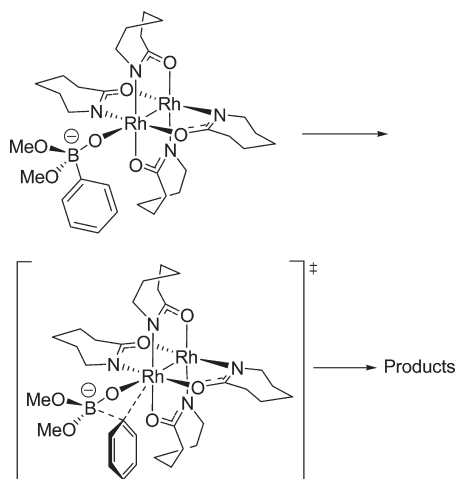
more rapidly than their Pd analogues. The authors referred to this reaction series (and its Pd analogue) as an “intramolecular version of the Suzuki cross-coupling reaction”. Similar to the Suzuki–Miyaura cross-coupling reaction, addition of base was necessary for the reaction to proceed; the authors speculated the base attacks the boron of the boropinacolate ester, forming a more reactive “ate” complex which formally eliminates [Bpin-(O^{*t*}Bu)Br][−] to form the metal–benzyne product.

3.11. Palladium

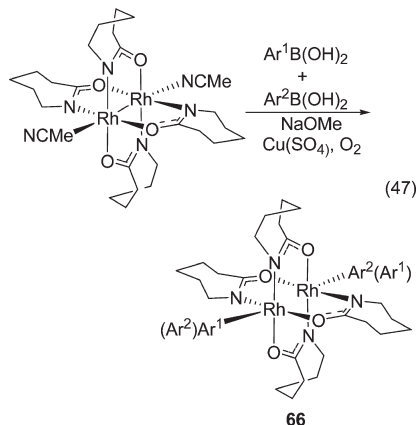
Unlike its heavier congener Pt, which has been the subject of more transmetalation reactions with organoboron compounds than any other d-block metal with the exception of Hg, transmetalation reactions with Pd and organoboron compounds have not been as frequently reported, perhaps due to the generally lower stability of organopalladium complexes relative to organoplatinum complexes. However, developments in organoboron-mediated transmetalation reactions with Pd have nearly as long of a history.

As one example, Hartley and Chin used a strategy similar to that previously developed for Pt (vide infra) to synthesize a phenylpalladium(II) species in nearly quantitative yield²⁰⁸

Scheme 38



Scheme 39

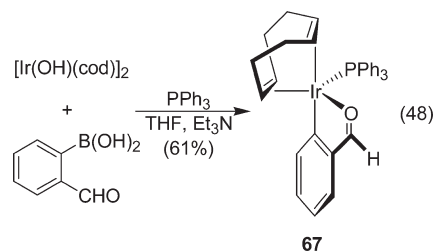


(Scheme 46). The product was confirmed by IR and NMR spectroscopies and compositionally consistent with microanalytical data, but was not structurally authenticated by X-ray crystallography. The presence of BPh₃ in the product mixture, the strict 2:1 stoichiometry of BPh₄[−] to **80**, and the nearly quantitative yield of **81** confirmed BPh₄[−] as the stoichiometric transmetalation agent.

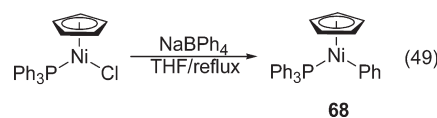
An uncommon variation of a cyclometalation reaction was demonstrated by Westcott and co-workers using amino-substituted arylboronic acids/arylboronates.²⁰⁹ In the more common variation of cyclometalation forming a C[^]N chelate (typically the chelate ring which includes M is five-membered), a C–H bond is broken in tandem with M–X bond cleavage to form a M–C bond; a neighboring N atom forms the M–N bond of the chelate. In this example, it was not a C–H bond that was broken but a C–B bond, forming the cyclometalated product **82** in 75% isolated yield (Scheme 47). [PdCl₂(coe)]₂ (coe = *cis*-cyclooctene) was also a suitable source of Pd for this reaction.

In a series of reactions similar to those previously discussed with Ni (Scheme 45, *vide supra*), a series of *ortho*-borylated arylpalladium(II) complexes behaved similarly to their Ni analogues in the presence of KO^tBu, forming Pd–benzyne complexes provided that the supporting ligand on Pd was a monodentate

Scheme 40



Scheme 41



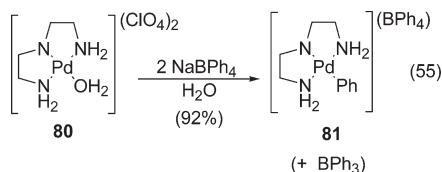
phosphine (Scheme 48).²⁰⁷ However, when the supporting ligand on Pd was a chelating phosphine, the reaction was more complex than the analogous reaction with Ni (Scheme 49). Only when R = cyclohexyl was a Pd–benzyne transmetalation intermediate observable by ³¹P NMR spectroscopy. However, in both cases, transmetalated decomposition product(s) **85–87** were ultimately produced.

It is commonly believed that, in the catalytic cycle of the Suzuki–Miyaura cross-coupling reaction, reductive elimination of the diorganopalladium(II) intermediate occurs from the *cis*-isomer, and therefore, a *trans*-diorganopalladium(II) complex that was hindered from achieving the *cis*-configuration would reductively eliminate slowly. In fact, this point was made clearly by Osakada and co-workers, who prepared such a complex, *trans*-[Pd(PET₃)₂(C₆F₅)(2,4,6-C₆F₃H₂)] (**88**).²¹⁰ The Pd complex was prepared by treating *trans*-[Pd(PET₃)₂(C₆F₅)I] with 2,4,6-trifluorophenylboronic acid in the presence of Ag₂O (Scheme 50).

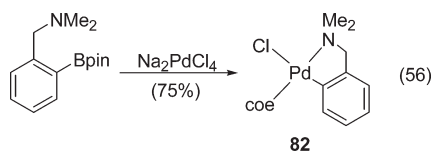
The authors believed the role of the Ag₂O plus H₂O was to dehalogenate the Pd–I starting material to form an intermediate Pd–OH species which is activated to transmetalation. Isolated **88** was found to be stable in air for months and did not reductively eliminate after being heated at 100 °C for 24 h in toluene-*d*₇. The authors noted that the rate of reaction of 2,4,6-trifluorophenylboronic acid with a series of complexes, *trans*-[Pd(C₆F₅)I(PR₃)₂] (PR₃ = PET₃, PMe₂Ph, PMePh₂), was inversely proportional to p*K*_a, with PET₃ (8.65) < PMe₂Ph (6.50) < PMePh₂ (4.65).²¹¹ Noting that the phosphine cone angles are also inversely proportional to the reaction rate, these data suggest the rate-limiting step is more sensitive to electron deficiency on the metal center than it is to steric congestion at the metal center.

A rare report of *cis*-diaryl palladium(II) complexes relatively stable to reductive elimination was made by Osakada and co-workers.²¹² To synthesize the diaryl palladium(II) complexes **89** and **90**, an iodide-ligated complex, [Pd(tmen)(*p*-anisyl)I] (tmen = *N,N,N',N'*-tetramethylethylenediamine), was treated with a di- or trifluorinated arylboronic acid in the presence of Ag₂O (Scheme 51). Ag₂O had two suggested roles, including the activation of the Pd–I bond and the activation of the boron to B–C cleavage. The reaction time in the synthesis of **89** had to be monitored carefully, as reductive elimination of biaryl began after approximately 3 h at room temperature. In the case of **90**, biaryl

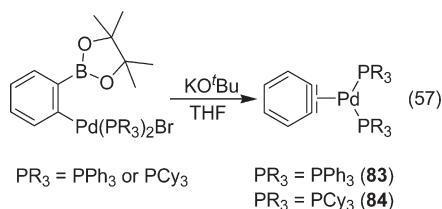
Scheme 46



Scheme 47



Scheme 48

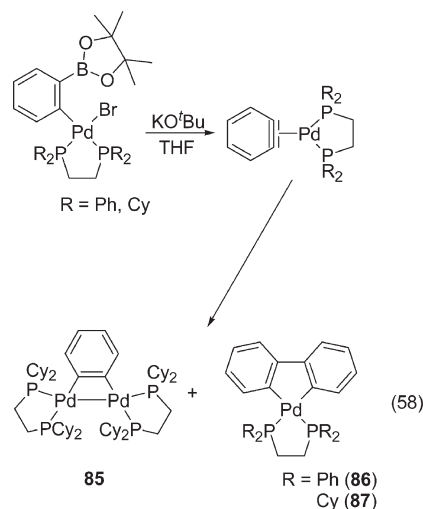


counterion. This is an example of the delicate role the coordination sphere of the metal plays in negotiating whether transmetalation or some other reaction will occur in the presence of an organoboron compound.

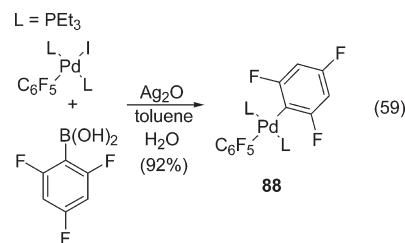
In an investigation of the NMR spectra of cationic Pt^{II} complexes, Clark and Ruddick attempted to use BPh₄[−] as a counterion for [Pt(Me)(PMe₂Ph)(L)]⁺ (L is a neutral ligand) generated in situ, but instead formed a diphenylplatinum complex in 80% yield (Scheme 56).²¹⁸ This reaction is an uncommon example of a transmetalation reaction in which an alkyl ligand is substituted from the Pt coordination sphere (for the mid to late d-block metals, this occurs most commonly with Fe and Zn). A similar result by Clark and Manzer was reported the following year,²¹⁹ in which a series of cationic, acetonitrile-ligated complexes of the type *trans*-[PtMe(NCMe)(L)₂](X) (X = BF₄[−] or PF₆[−]; L = phosphine or arsine) yielded a similar set of products, **103**, when treated with NaBPh₄ in MeOH (Scheme 57).

In a separate investigation of cationic Pt^{II} complexes,²²⁰ Rogers and co-workers investigated the aquo complex [Pt(dien)(H₂O)](ClO₄)₂. All attempts to exchange BPh₄[−] for ClO₄[−] using NaBPh₄ in EtOH failed, but instead instantaneously formed the transmetalated product [Pt(dien)Ph](BPh₄) (**104**), a product the authors were not expecting (Scheme 58). As NMR and IR spectroscopic evidence did not suggest a π -bonded BPh₄[−] ligand, the authors speculated on the existence of a π -bonded, BPh₄[−]-ligated Pt intermediate **105** in an electrophilic aromatic substitution mechanism (Scheme 59). As a side note, Rogers and co-workers tried to use BPh₄[−] as a phenylating agent with *trans*-[Rh(en)₂I(H₂O)](ClO₄)₂, which like the [Pt(dien)(H₂O)](ClO₄)₂ system had a labile aquo ligand.²²¹ Relevantly, the authors made a point of justifying their rationale

Scheme 49



Scheme 50



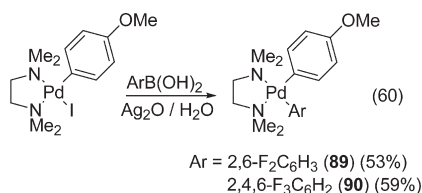
for the attempted transmetalation, explaining how the conditions worked for the [Pt(dien)(H₂O)](ClO₄)₂ system. However, the only product isolated was the anion-exchanged product *trans*-[Rh(en)₂I(H₂O)](BPh₄)₂, which is an excellent example of how an analogy-based approach is not valid for transmetalation reactions with organoboron compounds.

Lewis and co-workers, attempting to probe the reactivity of a platinum–hydrido complex with ethylene, dienes, and electron-deficient olefins, reported an unexpected transmetalation reaction.²²² In one reaction, an ethylene-ligated product, [PtH(C₂H₄)(PEt₃)₂](BPh₄), was formed by bubbling ethylene into a methanolic solution of [PtH(NO₃)(PEt₃)₂] (*cis*- or *trans*-stereochemistry not specified). [PtH(C₂H₄)(PEt₃)₂](BPh₄) was determined to be unstable in solution, slowly decomposing to the transmetalated product *trans*-[PtPh₂(PEt₃)₂] (**101**). This result was followed up by a more deliberate route, the transmetalation reaction of [PtH(NO₃)(PEt₃)₂] with NaBPh₄ to give **101** (Scheme 60).

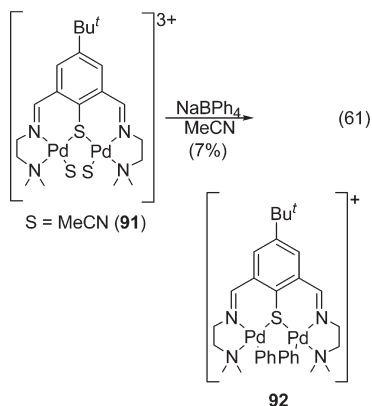
Shul'pin and Nizova used PhB(OH)₂ and NaBPh₄ as phenylation reagents in a reaction with H₂PtCl₆·6H₂O under acidic conditions (Scheme 61).²²³ Both reactions were low yielding, 15% and 7% for PhB(OH)₂ and NaBPh₄, respectively. The NH₄⁺ cation presumably comes from the chromatographic conditions, which included NH₃-containing silica gel.

In an investigation into the mechanism of phenylation of Pt^{II} complexes, Venanzi and co-workers studied the reactions of cationic Pt complexes **107–109** of the type *cis*-[Pt(solvent)₂(PR₃)₂]²⁺ with tetraarylbates (Scheme 62).²²⁴ An exception

Scheme 51



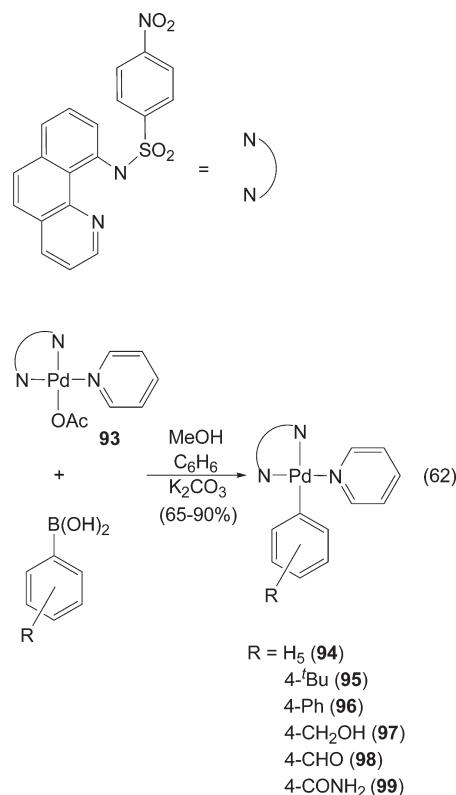
Scheme 52



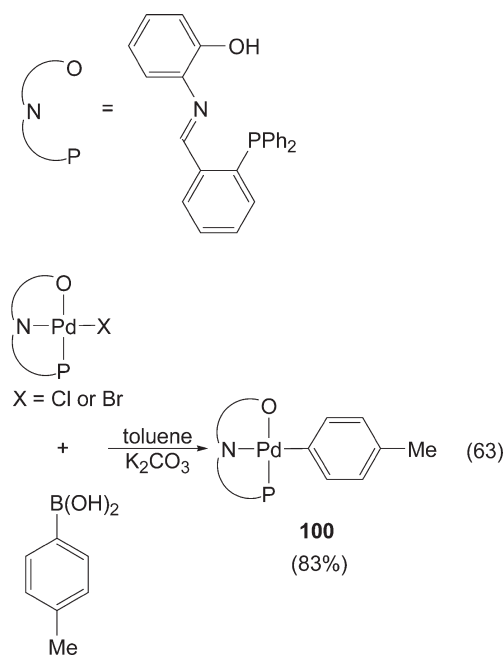
was the reaction with sodium tetrakis(3-fluorophenylborate), which only reached approximately 50% conversion in 20 h (the reactions with the tetraarylborates in Scheme 62 were complete in approximately 30 min). In addition, phenylborane derivatives Ph_3B , $\text{PhB}(\text{OH})_2$, $\text{PhB}(\text{OMe})_2$, and Ph_2BOMe were all found to be effective phenylating agents of the cationic Pt complexes. The phenylation reactions were complete within about 10 min at room temperature, but took 30 min at 0 °C and did not proceed at −70 °C. Noteworthy was the *trans*-stereochemistry of the products, in contrast to the starting materials. As the presumed *cis*–*trans* metalated intermediate was not observed at room temperature by ^{31}P NMR spectroscopy, the authors concluded that the *cis*–*trans* isomerization in this system was faster than the phenylation reaction itself. Notably, when using CD_3CN as a cosolvent (1:1 with MeOH), the complex *cis*-[Pt(CH_3CN) $_2$ -(PEt_3) $_2$](BPh_4) $_2$ slowly decomposed to the transmetalation products *cis*-[Pt(Ph)(S)(PEt_3) $_2$](BPh_4) (**113**) and *trans*-[Pt(Ph)(S)(PEt_3) $_2$](BPh_4) (**114**) (S could be CD_3CN or MeOH) (Scheme 63). Due to the reduced lability of the acetonitrile ligand, the *cis*-complex **113** was observable by NMR spectroscopy; the *cis* to *trans* ratio was 44:56 after 27 h, and only after 100 h was the *trans*-isomer **114** exclusively present.

In what was promulgated to be the first example of transition-metal-mediated decomposition of a BAR_F anion, [B(3,5-($\text{C}-\text{F}_3$) $_2\text{C}_6\text{H}_3$) $_4$], Kubas and co-workers reported the arylation of a methylplatinum(II) complex (Scheme 64).²²⁵ When stored in ether solution at −30 °C, complex **115** was reported to be stable for weeks and indefinitely in the solid state, but when kept in benzene solution at room temperature for 5 days or refluxed in toluene for 20 min, **116** is synthesized and isolated in 63% yield. Interestingly, when the ether ligand in **115** was exchanged with either MeOH or MeCN to form the solvento complexes *trans*-[Pt(S)(Me)(PPh_3)](BAR_F), reflux in toluene or benzene

Scheme 53

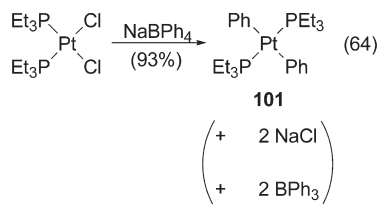


Scheme 54



formed product for S = MeOH but not for S = MeCN. The authors suggested that a labile ligand was necessary for formation of product, which corroborated their speculation that electrophilic attack of the Pt cation upon an aryl group of BAR_F initiated formation of product. The authors also retried this

Scheme 55



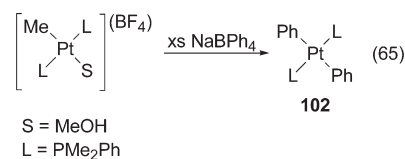
transmetalation reaction with a larger and smaller cone angle phosphine ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ or PEt_3 , respectively) in place of PPh_3 . In the case of P^iPr_3 , no reaction occurred in refluxing toluene, but for PEt_3 , a mixture of products formed, including $[\text{B}(3,5\text{-}(\text{C-F}_3)_2\text{C}_6\text{H}_3)_3]$, the B–C cleavage of which suggested transmetalation was possible only with phosphines that were not too bulky.

In an investigation of the coordination chemistry of cyanamides and cyanoguanidines with Pt^{II} complexes, including *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$, Pombeiro and co-workers isolated some phenylplatinum(II) cyanamide and cyanoguanidine complexes using BPh_4^- as the phenylating reagent (Scheme 65).²²⁶ The authors also reported that, in the synthesis of **117**, a diphenylated byproduct, *trans*- $[\text{PtPh}_2(\text{PPh}_3)_2]$, was isolated, which is not surprising considering the investigation of Clark and Dixon²¹⁶ (Scheme 55, *vide supra*). Intriguingly, a reaction similar to reaction 75 in Scheme 65, that is, the reaction of *cis*- $\{\text{PtCl}[\text{NCNC}(\text{NH}_2)_2](\text{PPh}_3)_2\}(\text{BF}_4)$ (**119**) with $\text{NCNC}(\text{NH}_2)_2$ in the presence of NaBPh_4 , abstracted Cl^- from and exchanged anions with **119** over 5 days, but gave no evidence for phenylation of **119**, showing once again how sensitive the transmetalation reaction is to the coordination sphere of the metal and the reaction conditions.

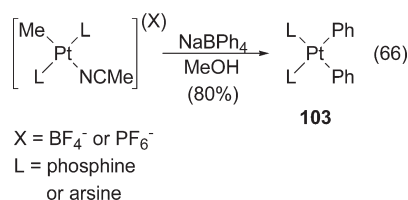
Aldridge and co-workers, as part of an exploration of the highly electrophilic boranes $\text{ClB}(\text{C}_6\text{F}_5)_2$ and $[\text{HB}(\text{C}_6\text{F}_5)_2]_n$, investigated the reactivity of these boranes with several transition-metal complexes, including the reaction of zerovalent complex $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)]$ with $\text{ClB}(\text{C}_6\text{F}_5)_2$.²²⁷ A mixture of products resulted, but unexpectedly, one of the products was an arylplatinum(II) complex (**120**), a transmetalated species that was confirmed by X-ray crystallography by separation from the product mixture (Scheme 66). No boron-containing products were detected by ^{11}B NMR spectroscopy, so the authors subsequently repeated the reaction with $[\text{HB}(\text{C}_6\text{F}_5)_2]_n$ and were able to detect $\text{EtB}(\text{C}_6\text{F}_5)$ by ^{11}B NMR spectroscopy. To account for the formation of the arylplatinum(II) complex in Scheme 66, the authors speculated that an intermediate Pt–boryl complex is formed (presumably by dissociation of a labile ethylene ligand to yield a coordinatively unsaturated Pt^0 complex which then undergoes oxidative addition with $\text{ClB}(\text{C}_6\text{F}_5)_2$ to yield the Pt–boryl species), followed by insertion of ethylene into the Pt–B bond. The intermediate Pt–boryl complex then transfers one of its C_6F_5 groups to Pt to form **120** (Scheme 67).

Osakada and co-workers prepared mixed diarylplatinum(II) complexes **121** and **122** by treating *trans*- $[\text{Pt}(\text{PMe}_2\text{Ph})_2(\text{Ph})\text{I}]$ with arylboronic acid in the presence of Ag_2O (Scheme 68).^{228,229} The authors speculate that Ag_2O may have two roles, including the deiodination of the Pt starting material and activation of the arylboronic acid to B–C bond cleavage. Interestingly, the arylated products **121** and **122** were exclusively observed after relatively long periods of stirring (24–72 h), but at much shorter time intervals (4–6 h), an intermediate

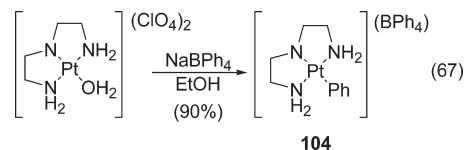
Scheme 56



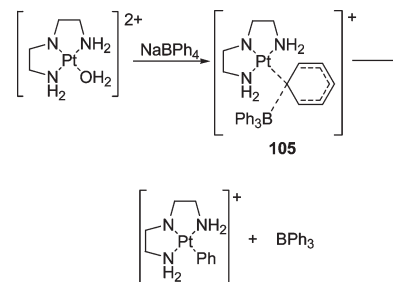
Scheme 57



Scheme 58



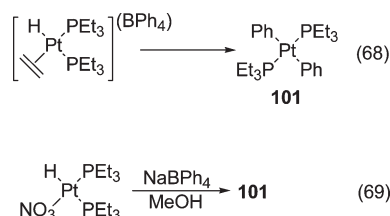
Scheme 59



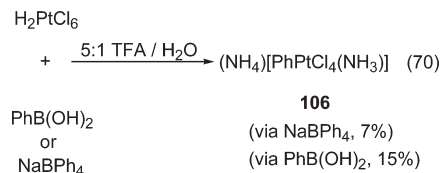
arylboroxide complex (**123**) was isolated, an example of arrested transmetalation (see section 4). The authors used this Pt–arylboroxide complex to illustrate the greater effectiveness of Ag_2O versus $(\text{Bu}_4\text{N})\text{OH}$ as a base in this reaction (Scheme 69). When the $\text{123}:\text{ArB}(\text{OH})_2:(\text{Bu}_4\text{N})\text{OH}$ ratio was 1.0:1.5:1.6, the **123**:**124**:**122** ratio after 48 h was 40:60:0 (that is, no product was formed). When the $\text{123}:\text{ArB}(\text{OH})_2:(\text{Bu}_4\text{N})\text{OH}$ ratio was 1.0:1.5:10, the **123**:**124**:**122** ratio after 36 h was 0:25:75. Ag_2O is clearly a more effective base for this system.

Clarke and Heydt compared the rates of transmetalation in three different transmetalation systems to determine which one was fastest for use in subsequent transmetalation reactions.²³⁰ The platinum substrate was $[\text{Pt}(\text{dppe})(\text{Ph})\text{Br}]$, while the three transmetalation systems used were (i) $\text{PhSi}(\text{OMe})_3/\text{TBAF}$, (ii) $\text{PhB}(\text{OH})_2/\text{TBAF}$, and (iii) PhZnBr . The general reaction is shown in Scheme 70. The reaction with PhZnBr was fastest, with 100% conversion after 15 min at room temperature. In contrast, the transmetalation with $\text{PhB}(\text{OH})_2$ did not proceed at all after

Scheme 60



Scheme 61



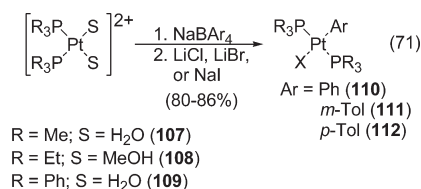
15 min at room temperature, while after 15 min at 75 °C only 33% conversion was observed along with 22% unknown product.

In a unique example of a transmetalation reaction with a Pt^{III} complex, Matsumoto and co-workers utilized a dinuclear Pt–Pt bonded complex as a precursor to arylated complexes.²³¹ The reaction of PhB(OH)₂, *o*-hydroxyphenylboronic acid, *m*-hydroxyphenylboronic acid, or *p*-hydroxyphenylboronic acid with this dinuclear Pt–Pt complex formed in each case stable, isolable organoplatinum species (Scheme 71). Notably, phenol also reacted with the dinuclear Pt complex to give the same product as *o*-hydroxyphenylboronic acid, but much less cleanly as several byproducts were also observed. Not surprisingly, it is again a M–O bond that is cleaved at the expense of M–C bond formation. The phenylplatinum(III) species did not react with nucleophiles such as Cl[–] even at elevated temperature, in contrast to a Pt^{IV} species cited by the authors.^{232,233}

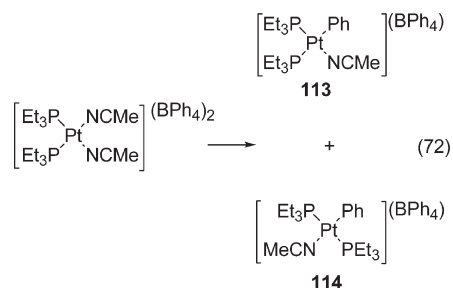
Osakada and Suzaki studied the reactivity of a dinuclear, hydroxide-bridged system and found that, in the presence of water, the dinuclear complex split into two mononuclear Pt complexes (one ligated by hydroxide and the other by water).²³⁴ The hydroxide ligand is highly nucleophilic, as treatment of { [Pt(cod)Ph]₂(μ-OH) } (BF₄) with aqueous NH₄Cl protonated the hydroxide to form [Pt(cod)PhCl] (2 equiv). It was the Pt–OH complex that the authors believed to be the transmetalation-active species in the presence of arylboronic acids (Scheme 72). The formation of B(OH)₃ as a byproduct in the syntheses of **132** and **133** was detected by ¹¹B NMR and suggested that attack of hydroxide on boron was a part of the reaction sequence (for a mechanistic discussion, vide infra). As a further indication of the nucleophilicity and reactivity of platinum-bound hydroxide ligands, the authors treated [Pt(cod)₂I₂] with PhB(OH)₂ in the presence of hydroxide, followed by aqueous workup, to generate the diphenylated complex **134** in 51% yield (Scheme 73). In contrast, the authors did not observe any reaction of the solvato complex [Pt(cod)(THF)₂](BF₄)₂ with PhB(OH)₂.

Under a set of conditions similar to those used in a 2005 report by the same research group,²²⁸ Osakada and Pantcheva extended their arylation methodology to a chelate-enforced *cis*-Pt^{II} system, [Pt(dppe)I₂].²³⁵ In contrast to the *trans*-bisphosphine investigated in their prior report, the treatment of [Pt(dppe)I₂] with

Scheme 62



Scheme 63



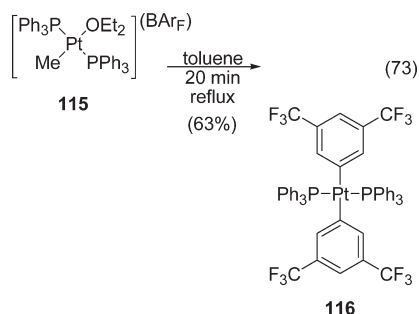
arylboronic acid in the presence of Ag₂O for relatively short periods of time (3–6 h) gave dehydro(arylboronic anhydride)-chelated Pt complexes in good to excellent yield (an example of arrested transmetalation; see section 4). To complete the transmetalation, the dehydro(arylboronic anhydride)-chelated Pt complexes were treated with arylboronic acid in THF for an additional several hours (Scheme 74). In the case of 4-methoxyphenylboronic acid, **137** was formed in 85% yield. The protodeboronation byproduct (anisole) was detected by ¹H and ¹³C NMR spectroscopies, while ¹¹B NMR and IR spectroscopies confirmed the production of the boric acid byproduct. The same reaction occurs for the analogous reactions with PhB(OH)₂ and 4-acetylphenylboronic acid (confirmed on the NMR scale). Interestingly, in “mixed” systems where the arylboronic acid does not correspond to the aryl group of the dehydro(arylboronic anhydride) ligand, scrambling of aryl groups was observed.

In an unusual instance of intramolecular transmetalation, Vedernikov and co-workers explored the reversibility of methyl group transfer from a dimethylborate ligand, [BMe₂(2-pyridyl)₂][–], to Pt^{II}.²³⁶ As part of their investigation, the transfer of a phenyl group (to form **138**) was demonstrated to occur from an analogous borate ligand, [BPh₂(2-pyridyl)₂][–], in the presence of alcoholic solvent and oxygen (Scheme 75). The phenyl transfer was coupled to the oxidation of Pt^{II} to Pt^{IV}. The sixth coordination site on Pt^{IV} was filled by the oxygen atom of the borate ligand.

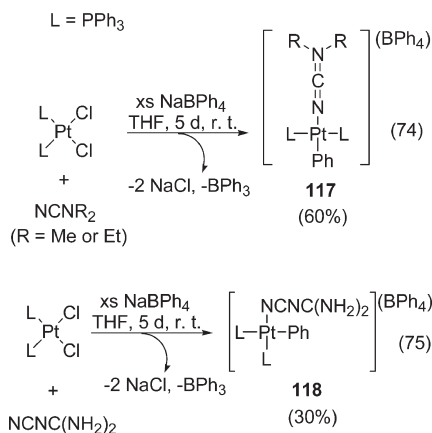
3.13. Copper

The copper-catalyzed carboxylation of neopentyl glycol esters of arylboronic acids using CO₂ in the presence of a base (KO^{*t*}Bu was used) was recently explored by Hou and co-workers.²³⁷ As part of a thorough exploration of the catalytic cycle, the authors suggested the potential intermediacy of a transmetalated, two-coordinate arylcopper(I) species. A transmetalation reaction of [(IPr)Cu(O^{*t*}Bu)] and an arylboronate ester was used to synthesize the desired compound **139** (which was structurally authenticated by X-ray crystallography) in 91% yield (Scheme 76).

Scheme 64



Scheme 65



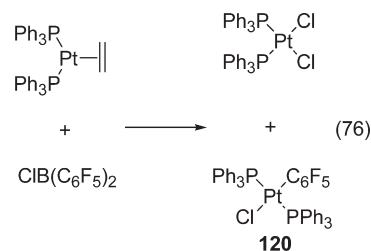
Interestingly, the chlorinated complex $[(\text{IPr})\text{CuCl}]$ did not undergo transmetalation with the arylboronate ester, suggesting that one of the roles of KO^tBu in the catalytic cycle is to form the transmetalation-active complex $[(\text{IPr})\text{Cu}(\text{O}^t\text{Bu})]$ in situ. In a subsequent report, Lalic and co-workers utilized an almost identical route (except IMes was used instead of IPr) to synthesize **140** (a *p*-tolyl analogue of **139**) in 61% yield.²³⁸ Note that the enhanced reactivity and high-basicity of late-transition-metal alkoxides have been well-documented.^{164,239–241}

3.14. Silver

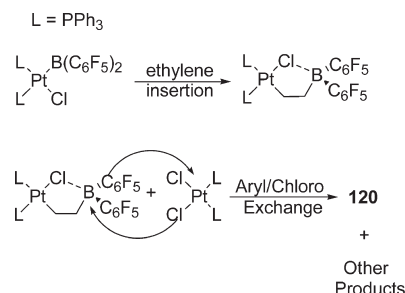
In an early report of the reaction of phenylboroxine and AgNO_3 in the presence of aqueous NaOH , Coutts et al. isolated what they believed was a “phenylsilver” complex, **141**, represented as $[\text{AgPh}]_2 \cdot [\text{Ag}_2\text{B}_4\text{O}_7]$, which was compositionally consistent with microanalytical data.²⁴² As further evidence for a phenylsilver complex containing a $\text{Ag}-\text{C}$ bond, the complex decomposed in boiling water to give benzene in nearly quantitative yield based on the formula $[\text{AgPh}]_2 \cdot [\text{Ag}_2\text{B}_4\text{O}_7]$.

Decades later, the silver(I)-mediated fluorination of aryl-, heteroaryl- and alkenylboronic acids using an electrophilic fluorinating reagent (F-TEDA-BF_4) was recently explored by Ritter and Furuya.²⁴³ As part of their investigation, an arylsilver(I) complex, **142**, was isolated in 50% yield by the transmetalation of 4-fluorophenylboronic acid with AgOTf and characterized by ^1H and ^{19}F NMR, but was too unstable for further characterization. $\text{MesB}(\text{OH})_2$, a more sterically hindered transmetalation reagent, was subsequently utilized under the same

Scheme 66



Scheme 67



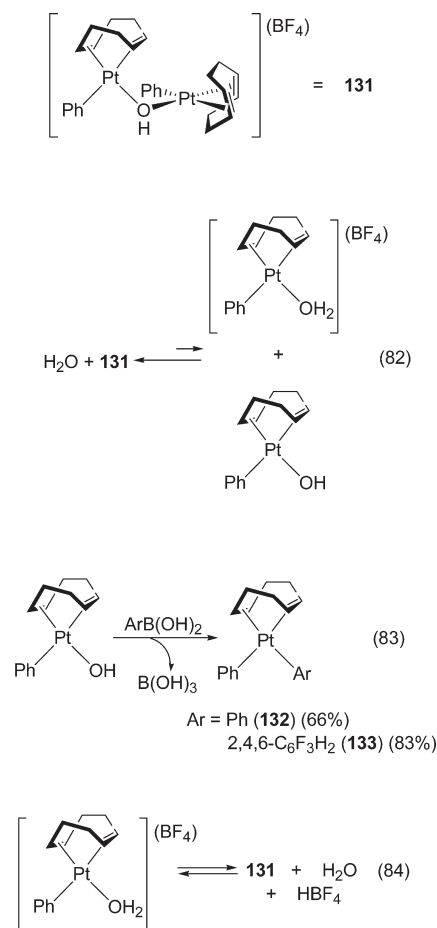
conditions to isolate a more stable, tetrameric arylsilver(I) product, **143**, in 67% yield (Scheme 77).

Another example of the arylation of a silver(I) precursor was recently reported in the literature.²⁴⁴ In an investigation into the synthesis of lithium and silver tetrakis(pentafluorophenyl)borate salts, an unusual solvent dependence was noted for the silver-containing observed products. In toluene and diethyl ether, treatment of AgNO_3 with the lithium salt $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ yielded the respective solvent-coordinated silver salts $[\text{Ag}(\text{solvent})_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (solvent = toluene or diethyl ether) in which no $\text{B}-\text{C}$ bond cleavage is observed. However, in the less coordinating solvent dichloromethane, the reaction of $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ and AgF yields $\text{Ag}(\text{C}_6\text{F}_5)$ (in 90% yield); recrystallization in acetonitrile gives a crystallographically characterized arylsilver(I) polymer, **144** (Scheme 78). The authors state that, in the poorly coordinating solvent dichloromethane, the initial product $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$ is not stable, as the unsolvated Ag^+ is a stronger Lewis acid than $\text{B}(\text{C}_6\text{F}_5)_3$, leading to $\text{B}-\text{C}$ bond cleavage and $\text{Ag}-\text{C}$ bond formation.

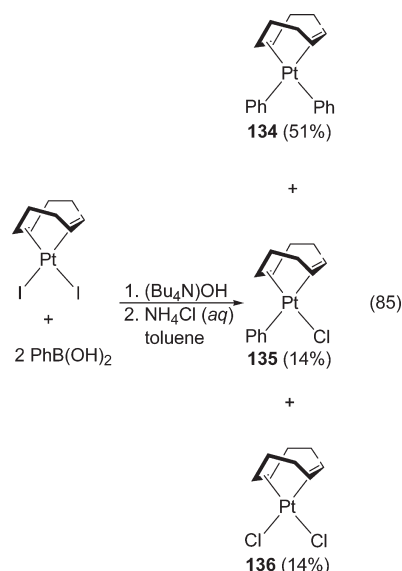
3.15. Gold

Initial reports of the transmetalation of organoboron compounds to gold(I) were made by the laboratories of Fackler and Schmidbaur. In the investigation by Fackler and co-workers,²⁴⁵ the exploration of the solubility of gold(I) complexes ligated by the water-soluble TPA (1,3,5-triaza-7-phosphaadamantane) ligand and its cationic, *N*-methylated analogue ((MeTPA)I) gave an unexpected result. Whereas $[(\text{MeTPA})_3\text{Au}]\text{I}_3$ reacted with NaPF_6 in a simple anion exchange reaction (to yield $[(\text{MeTPA})_3\text{Au}](\text{PF}_6)_3$), the same reaction with NaBPh_4 yielded the transmetalated product **145**; a similar transmetalation occurred with $[(\text{TPA})_3\text{Au}]\text{Cl}$ and NaBPh_4 to form **146** (Scheme 79). Both phenylgold(I) products were crystallographically characterized and, not surprisingly, were linear and two-coordinate (which is the most commonly observed coordination geometry for organogold(I) complexes). Interestingly, the reaction of

Scheme 72

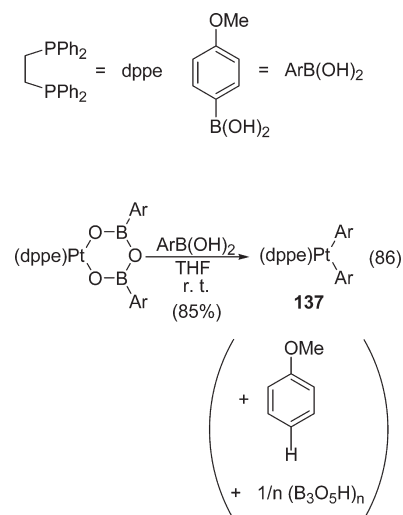


Scheme 73



naphthalene and pyrene to synthesize **164–168** in excellent isolated yields (79–90%) (Scheme 84).²⁵⁰ Auration protocols

Scheme 74



were repeated for SIPr-ligated gold(I) bromide and acetate precursors with similar effects, producing the diaurated naphthalenes **169** and **170** in 63% and 91% yields, respectively (Scheme 85). Once isolated, the products were interrogated for photophysical characteristics, and it was ascertained emission originated from triplet photoexcited states just as in their mono-nuclear analogues.

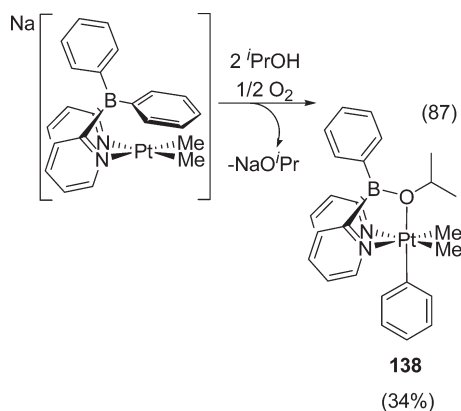
In two separate studies, a gold(I) chloride was used as an electrophile in the reaction with arylboronic acids. Hashmi and co-workers synthesized a series of aryl-, heteroaryl-, and alkenylgold(I) complexes, **171–177**, to study their reactivity with electrophiles, including Michael acceptors, electrophilic halogen sources (e.g., *N*-bromosuccinimide), and acids.²⁵¹ The reaction conditions were similar to those developed by the Gray group except $(\text{PPh}_3)\text{AuCl}$ was used as a starting material (Scheme 86). Isolated yields were no lower than 82% for each case. While the products failed to react with Michael acceptors, they did react with electrophilic halogen sources and trifluoroacetic acid. In a second study, Fackler and co-workers also used $[(\text{PPh}_3)\text{AuCl}]$ in an arylation reaction with a boronic acid (Scheme 87); the product **178** (isolated in 90% yield) was the subject of a crystallographic study.²⁵²

In all of the transmetalation syntheses discussed above, either a tetraarylboration or a neutral organoboron compound plus added base was necessary to effect B–C bond cleavage. However, Nolan and co-workers used a previously unknown gold compound (**179**) containing an *internal* base (hydroxide) in a reaction with $\text{PhB}(\text{OH})_2$ (Scheme 88).²⁵³ Isolated in 91% yield, **180** could also be synthesized using $\text{K}[\text{PhBF}_3]$.

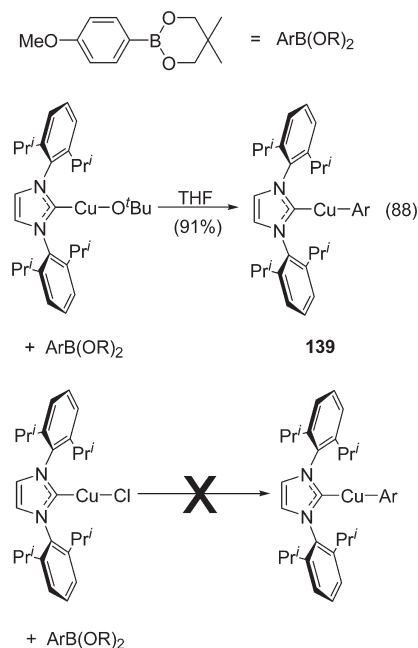
3.16. Zinc

Zinc is unusual among d-block metals in that transmetalation via organoboron compounds is more commonly observed by abstraction of alkyl ligands from the coordination sphere of Zn than by abstraction of O-bonded ligands; however, examples of transmetalation reactions of O-bonded complexes of Zn are known. For example, a dinuclear complex in which Zn was ligated by terminal methyl ligands and bridging boroxide ligands reacted with dimesitylborinic acid (Mes_2BOH) at an elevated temperature to yield dimesitylzinc **181** and mesitylboroxine²⁵⁴ (Scheme 89). The authors proposed the methyl ligands are

Scheme 75



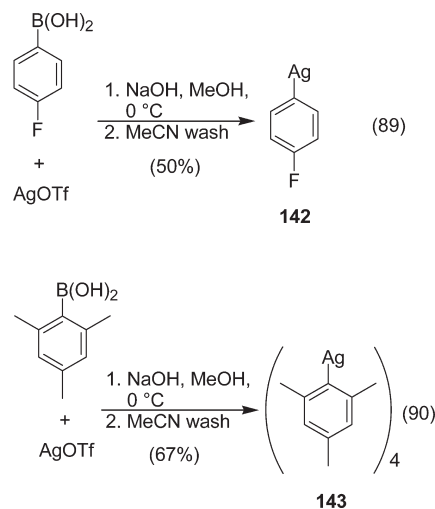
Scheme 76



extruded as methane, probably via borinic acid-induced protonolysis. However, the transmetalation does follow the pattern set by other d-block metals in that a metal–oxygen bond (that is, the zinc–boroxide bond) is broken to form the organometallic product. Significantly, this was the first investigation in which a linear, two-coordinate diarylzinc complex without stabilizing inter- or intramolecular interactions was crystallographically characterized.

Bochmann and co-workers were able to utilize the alkyl abstraction ability of B(C₆F₅)₃ to form alkylzinc cations or diarylzinc complexes **182** from ZnR₂ (R = Me, Et) in a solvent-dependent reaction (Scheme 90).²⁵⁵ The use of toluene for the formation of **182** (in 77% yield) was found to be crucial, as the same reaction done in Et₂O or in a toluene/Et₂O mixture gave the ionic compounds [RZn(OEt₂)₃][RB(C₆F₅)₃] (R = Me, Et). In these ionic compounds, B(C₆F₅)₃ abstracts an R group from Zn to form the borate anion. Other boranes, including BR₃ and BR₂(C₆F₅), were detected in solution.

Scheme 77



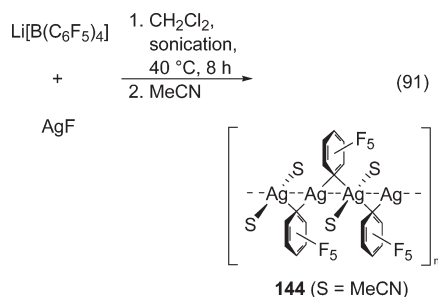
Roesky and co-workers investigated the synthesis of monomeric, three-coordinate organozinc by utilizing a sterically hindered β -diketoinmate ligand, 2-((2,6-diisopropylphenyl)-amino)-4-((2,6-diisopropylphenyl)imino)pent-2-ene ((dipp)-NacNac).²⁵⁶ Starting with a three-coordinate complex, ((dipp)-NacNac)ZnCl, NaBPh₄ was used as a phenylating reagent to synthesize the desired product **183** in 63% yield (Scheme 91).

As potential catalysts for the ring-opening polymerization of epoxides and lactones, Bochmann and co-workers were interested in Cp-ligated alkylzinc(II) complexes in which the Cp ligand was modified with a pendant group that could act as a hemilabile ligand to Zn.²⁵⁷ As one of their strategies to activate the alkylzinc complex, B(C₆F₅)₃ was added as an alkyl-abstracting agent. As another example of the sensitivity of transmetalation reactions to the coordination sphere of the metal complex, B(C₆F₅)₃ abstracted an ethyl group from [(Cp^{mes})ZnEt] to produce [(Cp^{mes})ZnC₆F₅] (**184**) in 41% yield (Scheme 92); EtB(C₆F₅)₃ was detected by NMR spectroscopy as the main byproduct. In contrast, the TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) adduct [(Cp^{mes})ZnEt(TMEDA)] reacted with B(C₆F₅)₃ to form the alkyl abstraction product [(Cp^{mes})Zn(TMEDA)][EtB(C₆F₅)₃] (**185**) in an NMR-scale reaction.

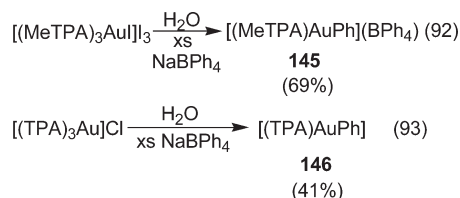
Electrospray mass spectrometry was the method of choice for Driess and co-workers in the detection of cationic, polynuclear “Zn_nO_m” aggregates generated in solution as models of ZnO catalysts.²⁵⁸ Alkoxide- and silyloxy-bridged [(ZnMe)₄(μ-OR)₄] tetranuclear aggregates were used as small-molecule precursors to cationic complexes via B(C₆F₅)₃-induced abstraction of a methyl ligand. In the case of R = SiMe₃, methyl abstraction formed a dinuclear aggregate (**186**) in 22% yield, the product of a C₆F₅ transfer from an intermediate borate, [MeB(C₆F₅)₃][−] (Scheme 93). The product was structurally authenticated by X-ray crystallography.

Using silanediol-based ligands, Krempner and co-workers synthesized disilyloxy-scaffolded aggregates, each with a well-defined trinuclear Zn₃O₄ core.²⁵⁹ To ascertain the reactivity of some of the aggregates, B(C₆F₅)₃ was used and found to not only abstract methyl groups from the terminal ZnMe groups, but replace them with C₆F₅ groups to form **187** and **188** in 67% and 61% yields, respectively (Scheme 94).

Scheme 78



Scheme 79



In another methyl abstraction reaction with $\text{B}(\text{C}_6\text{F}_5)_3$, Vigalok and co-workers studied the reactivity of some calixarene-ligated dinuclear alkylzinc complexes.²⁶⁰ In the case of the contact ion pair **189**, formed by treating a bis(methylzinc) precursor with $\text{B}(\text{C}_6\text{F}_5)_3$, the ion pair was unstable at room temperature and slowly (over the course of 6 h) collapsed to the aryl transfer product **190** (Scheme 95). Not surprisingly, the calixarene-shielded methyl ligand (the lower one) was not abstracted with $\text{B}(\text{C}_6\text{F}_5)_3$.

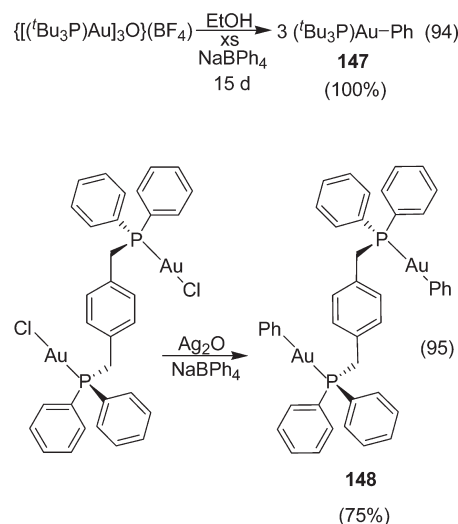
Similar to the investigation of Roesky,²⁵⁶ Parkin and co-workers utilized a bulky β -diketiminato ligand and (additionally) an anilidoimine ligand to enforce three-coordinate binding modes for Zn.²⁶¹ At slightly elevated temperatures (60 – 80°C), the three-coordinate complexes LZnR ($\text{R} = \text{Me}$ or Et) reacted with the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ in an alkyl abstraction reaction, the isolated products **191** and **192** of which were structurally ascertained to be the three-coordinate transmetalated complexes $\text{LZn}(\text{C}_6\text{F}_5)_3$ (Scheme 96).

Pericás and co-workers investigated by DFT the reaction of MeZnEt with phenyldimethylboroxine (Scheme 97).²⁶² Calculations suggested that the highest activation barrier to formation of **193** was relatively low, only 16.2 kcal/mol . Furthermore, calculations suggested the reaction is not initiated by electrophilic attack of Zn upon the phenyl group of the boroxine, but rather coordination of an O atom of the boroxine by Zn, ethyl group transfer to and quaternization of the Lewis acidic B atom, and finally phenyl group transfer to the Zn atom (Scheme 98). In relatively good agreement with calculations for the phenyldimethylboroxine (which predict the transmetalation to form **194** is exothermic by 1.9 kcal/mol), calorimetric measurements for the reaction of triarylboroxine with ZnEt_2 are exothermic (per aryl group transmetalation) by the following values at a 60°C reaction temperature: $\text{Ar} = \text{Ph}$, -5.1 kcal/mol ; $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$, -4.2 kcal/mol ; $\text{Ar} = 4\text{-CF}_3\text{-C}_6\text{H}_4$, -3.9 kcal/mol ; $\text{Ar} = 4\text{-Cl-C}_6\text{H}_4$, -2.9 kcal/mol .

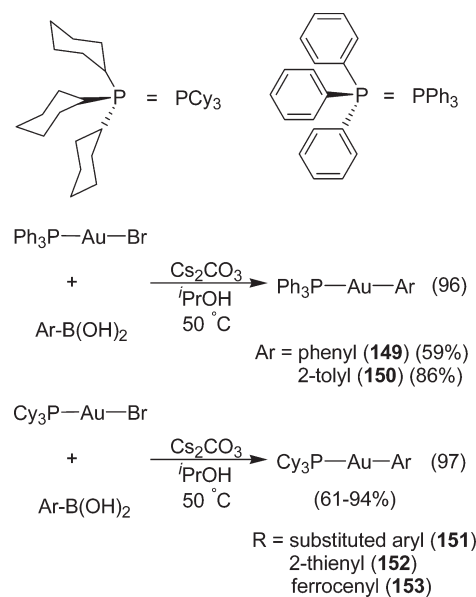
3.17. Cadmium

One example of the arylation of a cadmium-containing precursor has been reported in the literature by Parkin and co-workers.²⁶¹

Scheme 80



Scheme 81

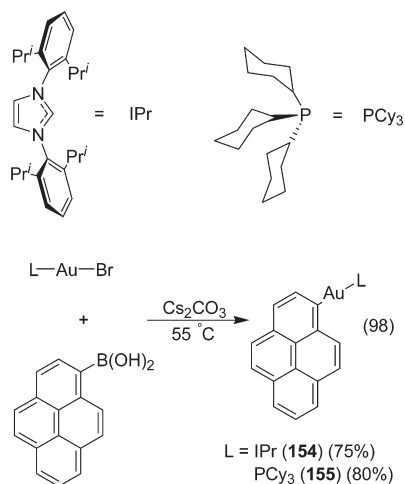


With the intent to demonstrate the utility of bulky β -diketiminato and anilidoimine ligands for the enforcement of uncommon metal coordination geometries, a β -diketiminato-ligated alkylcadmium complex served as a transmetalation precursor with $\text{B}(\text{C}_6\text{F}_5)_3$. The arylated product **195**, isolated in 16% yield, was structurally characterized as per the goals of the investigation (Scheme 99).

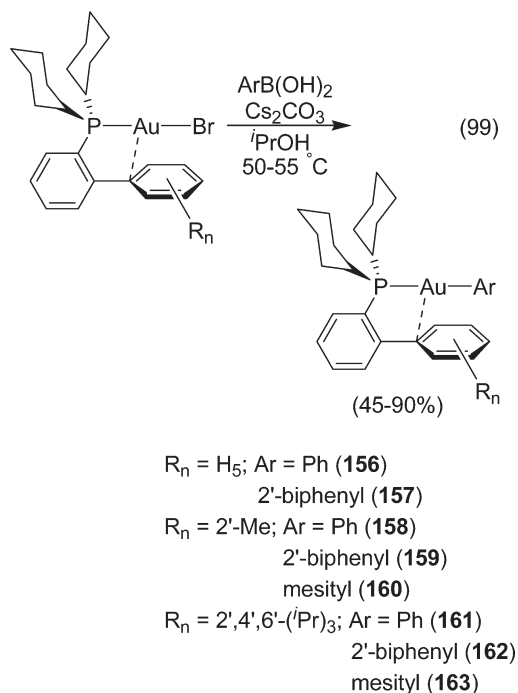
3.18. Mercury

Mono- and diarylmercurial syntheses via organoboron transmetalation protocols prior to 1984 have been thoroughly discussed;^{72,73} therefore, synthetic developments from 1984 will be covered in this section. However, mechanistic data reported before 1984 will be included. The phenylation of organomercury species via NaBPh_4 for analytical detection of mercury is noted to underscore the utility of organoboron compounds in organomercury chemistry, but will not be discussed further.^{263–271}

Scheme 82



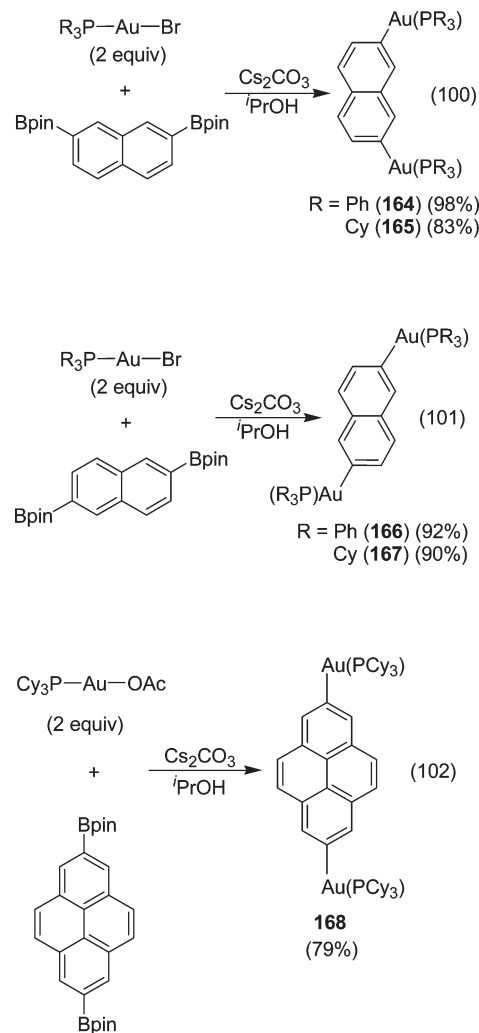
Scheme 83



An early report by Kuivila and Miller studied the kinetics of reaction 120 (Scheme 100), the product of which was diphenylmercury.²⁷² The reaction was found to be first-order in both reactants. Furthermore, it was pH-independent in the range 4–8, but above pH 10, the rate of reaction was proportional to the pH. PhHg⁺ and PhB(OH)₃[−] were suggested as species likely to be formed in solution and to react rapidly once formed.

Another early mechanistic investigation²⁷³ (an exception is made here as a transmetalation with an alkylboronic acid is discussed) measured the ¹⁰B/¹¹B kinetic isotope effect (KIE) for reaction 121 (Scheme 101). Theoretically, a ¹⁰B/¹¹B KIE would have a maximum value of *k*_{B10}/*k*_{B11} = 1.05–1.06. In this case,

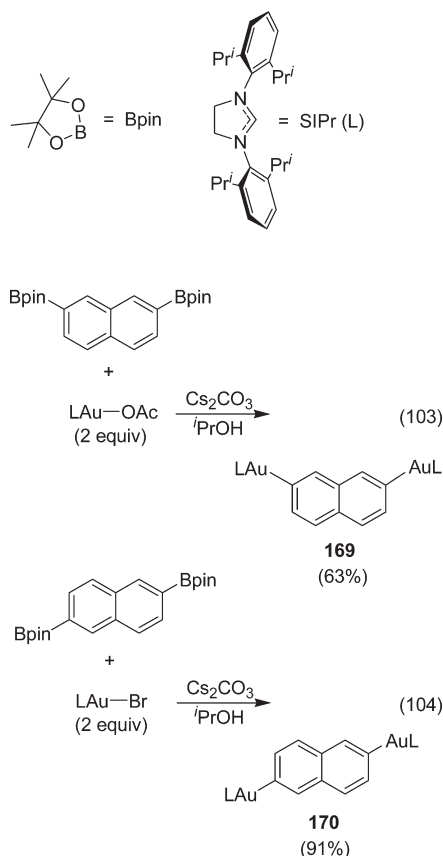
Scheme 84



KIE values of 1.033 ± 0.005 for the *exo*-substituted boronic acid and 1.027 ± 0.005 for the *endo*-substituted boronic acid were measured. Separately, the authors also measured a *k*_{B10}/*k*_{B11} of 1.021 ± 0.009 for the reaction of PhHg(NO₃) and PhB(OH)₂ (to form Ph₂Hg). As the authors concluded *k*_{B10}/*k*_{B11} was of the “expected value” for a KIE, they suggested that B–C bond cleavage was involved in the rate-determining step, perhaps in a concerted process. In fact, for the PhHg(NO₃) reaction, an activated complex, **197**, in which B–C bond cleavage and Hg–C bond formation were occurring, was envisioned (Figure 3).

In a series of halogenation reactions that generated alkenyl chlorides, bromides, or iodides, the utility of alkenylmercurials was demonstrated by Brown and co-workers.²⁷⁴ The alkenylmercuric chlorides **198** (which were formed in quantitative yields) were first synthesized and isolated by the reaction of 2-alkenyl-1,3,2-benzodioxoboroles with mercuric acetate in THF, followed by treatment with a saturated aqueous NaCl solution (Scheme 102). In addition, the same procedure was successfully applied to (*E*)-1-octenylborane and (*E*)-1-octenylboronic acid in THF or pyridine; however, the methyl or propylene glycol esters of (*E*)-1-octenylboronic acid yielded product that was difficult to purify. The purity of the

Scheme 85



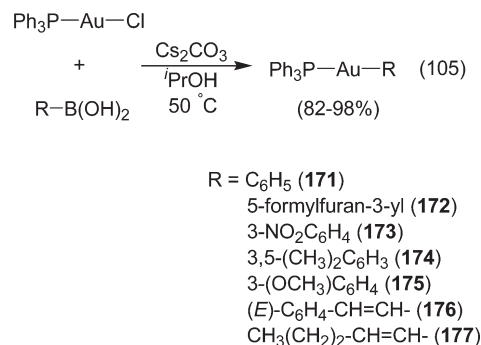
alkenylmercuric chlorides was ascertained via ^1H NMR spectroscopy and melting point determination.

Exploiting the ease of synthesis of diorganomercurials from organoboranes, Knochel and co-workers used these diorganomercurials as precursors to organozinc reagents of utility to the 1,2-alkylation and 1,2-alkenylation of aldehydes.²⁷⁵ In one previously unreported synthesis, the treatment of $\text{Hg}(\text{OAc})_2$ with an alkenylboropinacolate ester, followed by reducing conditions, gave the dialkenylmercurial **199** in 61% isolated yield (Scheme 103).

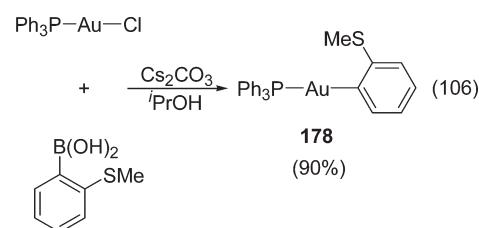
Gabbai and Melaimi were able to exploit the fidelity of transmetalation reactions between organoboron compounds and mercuric halides in the synthesis of a highly efficient F^- sensor.²⁷⁶ The organoborate chosen was a dimesitylnaphthalenediylborate, in which the naphthalenediyl forms two B–C bonds. Treatment of the borate with $\text{C}_6\text{F}_5\text{HgCl}$ yields the diarylmercurial **200**, in which the Hg–B separation is only 3.300(9) Å (Scheme 104). In a subsequent report from the same laboratory, an aryl group functionalized with a dimethylamino group was utilized to synthesize **201** (Scheme 105).²⁷⁷ This dimethylamino group was alkylated, giving a cationic analogue of **201**.

Henderson and co-workers, interested in building heterometallic sulfide-bridged complexes, chose the dinuclear, sulfido-bridged complex $[(\text{PPh}_3)_4\text{Pt}_2(\mu\text{-S})_2]$ as a metalloligand for this purpose.²⁷⁸ For this dinuclear Pt complex, the $\text{Pt}_2(\mu\text{-S})_2$ core is a puckered four-membered ring which acts as a chelating ligand through both sulfur atoms. In one reaction, $[(\text{PPh}_3)_4\text{Pt}_2(\mu\text{-S})_2]$

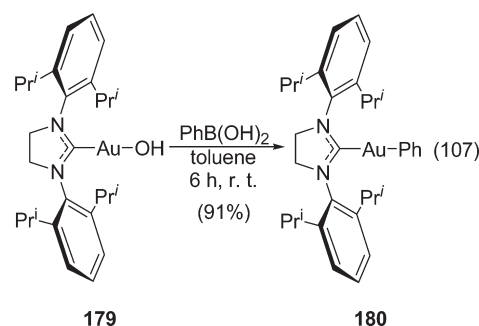
Scheme 86



Scheme 87



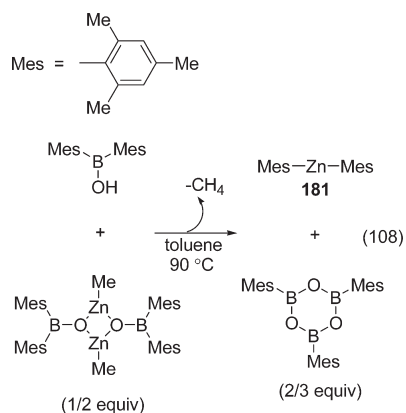
Scheme 88



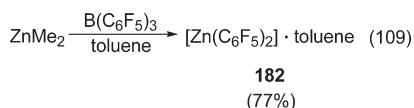
was treated with 1 equiv of $\text{Hg}(\text{OAc})_2$ and an excess of NaBPh_4 . The solid that was isolated was shown by ESI-MS to be a mixture of the transmetalation products $\{[(\text{PPh}_3)_4\text{Pt}_2(\mu\text{-S})_2]\text{HgPh}\}^+$ (**202**) and $\{[(\text{PPh}_3)_4\text{Pt}_2(\mu\text{-S})_2]\text{Hg}\}^{2+}$ (**203**) (presumably isolated as their BPh_4^- salts, Scheme 106).

In a recent report by Partyka and Gray,²⁷⁹ homoleptic diarylmercurials **204** were easily prepared by treating $\text{Hg}(\text{OAc})_2$ with various arylboronic acids in the presence of a base (Cs_2CO_3) in 2-propanol (Scheme 107). Heteroaryl- and ferrocenylboronic acids also successfully transmetalated under identical conditions. While the transmetalation does proceed in the absence of a base, multiple products were produced in its absence. Intriguingly, in an attempt to synthesize heteroleptic diarylmercurials, $\text{PhHg}(\text{OAc})$ was treated with 1 equiv of ArB(OH)_2 ($\text{Ar} \neq \text{Ph}$) at room temperature in 2-propanol in the presence of a base, but the majority products were the corresponding homoleptic diarylmercurials. In the case of MesB(OH)_2 plus $\text{PhHg}(\text{OAc})$, the ratio (by ^1H NMR spectroscopy) of Mes_2Hg to MesHgPh was approximately 8:1 after 12 h.

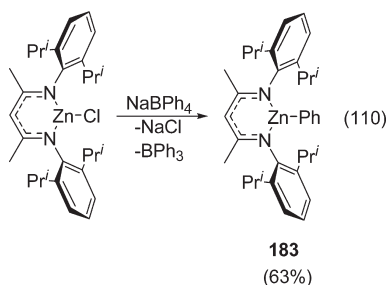
Scheme 89



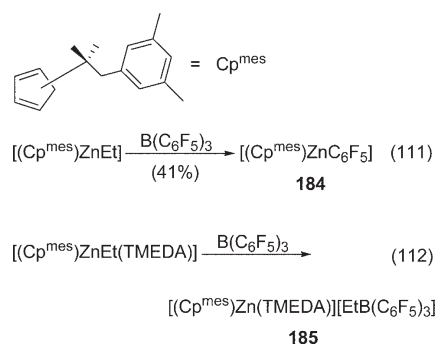
Scheme 90



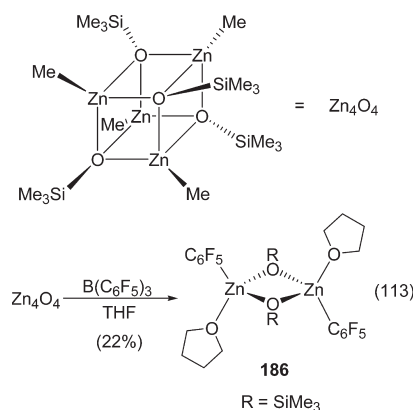
Scheme 91



Scheme 92



Scheme 93



4. ARRESTED TRANSMETALATION

As defined in the Introduction, a transmetalation reaction has not occurred unless a B–C bond is cleaved. However, as mentioned in the previous section, some ligands that are capable of transmetalation first bind to the metal to form a stable coordination complex (A), but at a temperature high enough to overcome the activation barrier to transmetalation, the activated complex B is reached (presumably forming a σ Rh–C bond in the example shown as a B–C bond is breaking), the B–C bond is cleaved, and M–C bond formation occurs to form C (see Figure 4 for a graphical representation). Under conditions in which the activated complex cannot be reached (e.g., the temperature is too low), the stable transmetalation precursor complex persists, and thus, transmetalation has been arrested. In general, the three ligands for which this scenario can occur are boroxides (*O*-bonded, deprotonated organoboronic or organoboronic acid derivatives), *O*-bonded hydroxyborates (ligands of general type HOBAr_3^-), and tetraorganylborates (*C*-bonded, where most frequently all four organic groups are aryl groups). In the case of tetraorganylborates, the π -face of the arene ring serves as the ligand with hapticity η^x , where $x = 1, 2, 3, 4, 5$, or 6 .^{280–285} Typically, neither tetraorganylborates nor hydroxyborates are strongly binding ligands, being

readily displaced by ligands that in and of themselves are not strongly binding. For example, in one mechanistic study of the Suzuki–Miyaura cross-coupling reaction, Crociani and co-workers detected an arylborate-ligated Pd complex (205) as an intermediate that was stable enough to isolate.²⁸⁶ The *O*-arylborate ligand was completely displaced from the Pd coordination sphere by a Cl^- ligand (delivered as an aqueous NaCl solution) in a biphasic ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$) reaction to form 206 (Scheme 108).

A $[\text{HOB(C}_6\text{F}_5)_3]^-$ -ligated Pt complex provides another example.²⁸⁷ After preparing 207, Muir and co-workers demonstrated ligand displacement by CO, PPh_3 , and even ethylene (Scheme 109). Arguing by analogy, the authors suggested that, since $[(^t\text{Bu-bpy})\text{PtMe(X)}]$ ($\text{X} = ^-\text{O}_2\text{CCF}_3$ or ^-OTf), the trifluoroacetate- and triflate-ligated analogues of 207, do not react with ethylene gas, $[\text{HOB(C}_6\text{F}_5)_3]^-$ is an even poorer ligand to Pt than the ligands X.

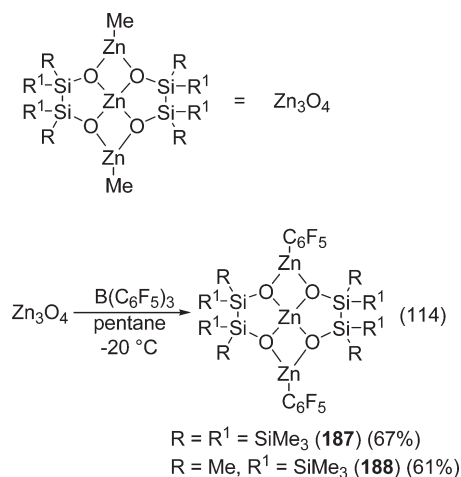
Borate ligands, η^x -bonded to a metal (especially when $x < 6$), can be readily displaced. An example is provided by comparing reactions 31 and 32 from Scheme 25; the η^2 -benzyl-ligated complex 31, stable in pentane, undergoes ligand substitution with THF. It should be noted that η^x -borate-ligated metal complexes have been previously addressed by Strauss.²⁸⁸

The following sections will focus on arrested transmetalation reactions in which a stable coordination complex, A, can be isolated, but transmetalation can ensue at elevated temperatures to form an organometallic complex, C.

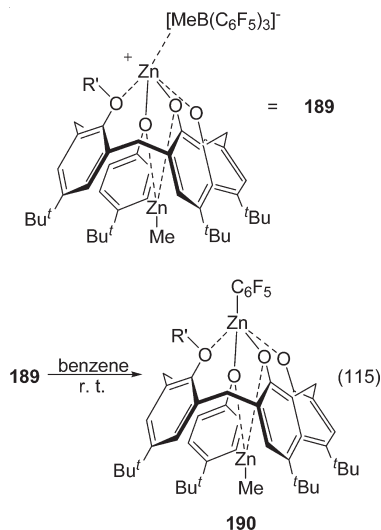
4.1. Oxygen-Bonded Organoboron Ligands

A Pt^{II} system studied by Osakada and co-workers, discussed above, yielded one of the earliest examples of a metal complex in

Scheme 94



Scheme 95

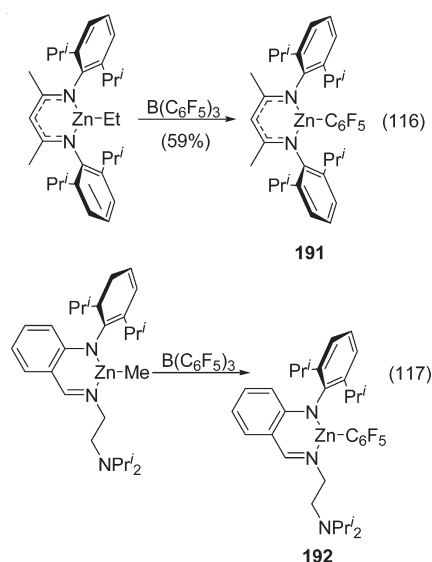


which a boroxide-ligated transmetalation intermediate could be isolated.^{228,229} At short reaction times (4–6 h) at room temperature, the boroxide-ligated complexes **211** and **212** could be isolated as shown in Scheme 110. Only after extended periods of stirring (>24 h) were the transmetalated products isolated in high conversion.

Although transmetalation was demonstrated in a dppe-chelated Pt system by Osakada and Pantcheva,²³⁵ the precursors for the transmetalation reactions (boroxide-chelated Pt complexes **213–215**) were stable compounds. These Pt complexes could be isolated in 69–86% yields and were not transmetalated provided additional arylboronic acid was not added and extended stirring times in the presence of arylboronic acid were not used (Scheme 111). Only when additional arylboronic acid was added to **213–215** and the reaction stirred for several more hours were the transmetalated products observed in high conversion (Scheme 74, vide supra).

In a seminal study discussed previously, Hartwig and co-workers were able to observe transmetalations from organoboron compounds to Rh^I at elevated temperatures (Scheme 34, vide

Scheme 96



supra).¹⁹⁵ However, at room temperature, the reactions were arrested at the boroxide complexes **216–219**, the products of an acid–base reaction (Scheme 112). Products **216–219** were isolated in 45–76% yields and were fully characterized; all were stable at room temperature (the *o*-anisyl derivative however was not isolable due to low stability). Product **52**, the borinic acid derivative of **216–219**, was isolable in 82% yield and stable at room temperature. As mentioned above, β -aryl elimination was observed for **216–219** at 70–80 °C to form the arylated derivatives **47–50**.

In the investigation of Vigalok and co-workers, **220**, the $[(\text{HOB}(\text{C}_6\text{F}_5)_3)]$ -ligated analogue of **189**, was considerably more robust (thermally) than **189**.²⁶⁰ In fact, the same aryl transfer product **190** could be synthesized from **220**, but only after **220** was heated in benzene (Scheme 113).

An induction period was observed which preceded aryl transfer, but once aryl transfer began to proceed, it did so rapidly. The authors invoked autocatalysis as an explanation, hypothesizing that, as arylation slowly occurred and released $\text{HOB}(\text{C}_6\text{F}_5)_2$, this strong Lewis acid coordinated to the O atoms of still-unreacted **220**, accelerating the transmetalation by disrupting Zn–O bonding. As corroborating evidence, the authors noted the ~ 12 -fold acceleration of the arylation at 63 °C by addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to a solution of **220**; this normally ~ 240 min reaction was complete in less than 20 min.

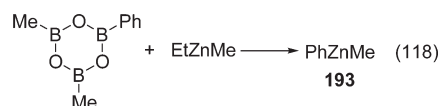
Other investigators have proposed O-bonded organoboron ligands as intermediates in catalytic transformations.²⁸⁹

4.2. Tetraarylborates as Ligands

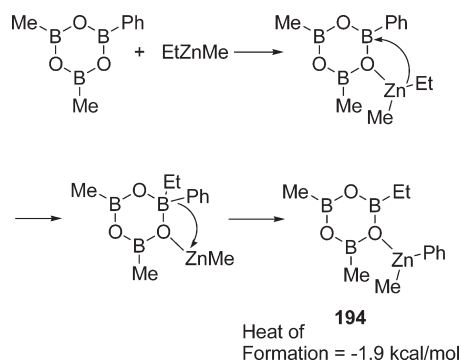
Some examples of η^x -borate-ligated complexes have already been discussed above in the context of B–C bond cleavage. For example, **41** (Scheme 31) is a thermally stable complex at room temperature that must be heated to 70 °C for transmetalation to occur to form **42**.^{191,192}

In an effort to activate dialkyliron(II) complexes to olefin polymerization, Bouwkamp and co-workers used the alkyl-abstrating agent $\text{B}(\text{C}_6\text{F}_5)_3$ as an activator.²⁹⁰ In one reaction series, the contact ion pair **222** (formed by alkyl abstraction via $\text{B}(\text{C}_6\text{F}_5)_3$) was stable in toluene-*d*₈ solution at room temperature

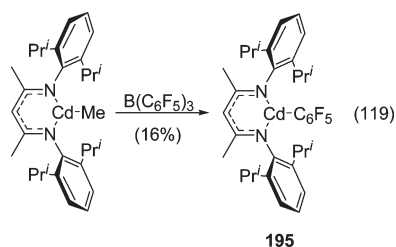
Scheme 97



Scheme 98



Scheme 99



and below, but at slightly elevated temperature (50 °C), the ion pair decomposed to form the aryl transfer product **223** (Scheme 114).

Other examples of formation of η^x -tetraarylborate-ligated metal complexes have speculatively invoked them as putative intermediates in metal-catalyzed coupling reactions or in decomposition reactions.^{291–294}

5. CATALYTIC REACTIONS INVOLVING TRANSMETALATIONS

5.1. Reactions That Propose Organometallic Catalytic Intermediates

Organoboronic acids have been utilized in over 40 different types of reactions, and within a reaction class, one or several different metals may be effective catalysts or mediators. Table 2 summarizes the different reaction types and the metals that catalyze or mediate each reaction.

5.2. Mechanistic Investigations of Proposed Intermediates

A transmetalation reaction from an organoboron compound to a metal complex has been proposed for each of the metal-catalyzed reactions mentioned in Table 2. However, only for about one-fourth of these reactions has spectroscopic or kinetic evidence been presented which corroborates the involvement of a transmetalation somewhere in the catalytic cycle. In addition,

Scheme 100

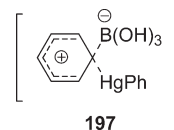
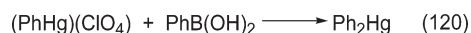
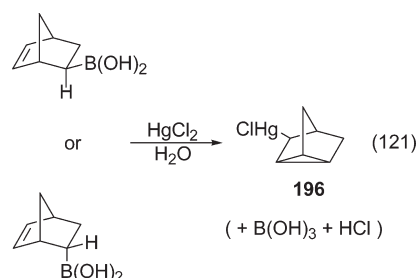


Figure 3. Activated complex suggested for electrophilic mercuration of arylboronic acids. Adapted with permission from ref 272. Copyright 1962 American Chemical Society.

Scheme 101

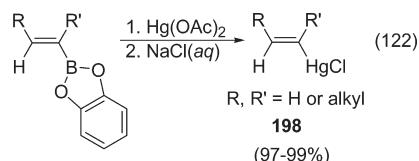


some groups have supplemented their experimental data with theoretical investigations. These data are presented here (in the general catalytic cycles below, an asterisk indicates the starting point in the cycle and transmetalation intermediates are boxed).

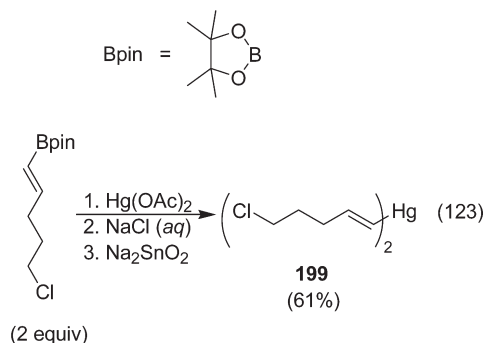
5.2.1. Arylation of Aldehydes. Impressive in breadth of catalytic diversity, the arylation of aldehydes by organoboron compounds has been reported to be catalyzed or mediated by nine different d-block metals. For several of these metals, a speculative catalytic cycle (or mechanism) has been posited.^{317–320,323,331,334–336,347,354} A general catalytic cycle is shown in Figure 5. Mechanistic data in support of the transmetalation step of this cycle have been gathered by Dahmen and Lormann.³⁵⁸ In an investigation of the utility of triarylborane–ammonia as a stoichiometric zinc arylation reagent for the arylation of aldehydes, kinetic data for the phenylation of ZnEt_2 were obtained for triphenylborane–ammonia and compared to those for triphenylborane and a diphenylborinate (2-aminoethoxy ester). Over short time intervals (<40 min), the rate of phenylation of ZnEt_2 was much faster for both BPh_3 and the diphenylborinate (BPh_3 transmetalated the fastest). However, by 60 min all three reagents had exchanged ~50% of their phenyl groups. Perhaps counterintuitively, the slower transmetalation with the triphenylborane–ammonia complex was desirable, with resultant phenylzinc concentrations much lower than with other boranes, leading to the highest ee for the phenylation of *p*-chlorobenzaldehyde (Scheme 115). Calculations by Pericás and co-workers²⁶² (Scheme 97, vide supra) are consistent with transmetalation of dialkylzinc by a phenylboron species (dimethylphenylboroxine).

A combined experimental and theoretical investigation of the arylation of aldehydes catalyzed by mono- and biscarbene complexes of $\text{Rh}_2(\text{OAc})_4$ was presented by Gois and co-workers.³⁵³ Although Rh-catalyzed arylation of aldehydes via

Scheme 102



Scheme 103

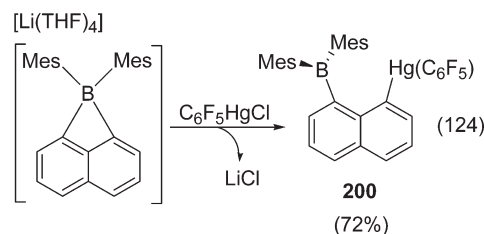


arylbaboronic acids was successfully demonstrated, attempts to obtain an isolable phenylrhodium complex as evidence of a transmetalation intermediate were fruitless. However, a boronic acid was necessary for arylation of aldehydes, since the same reactions with arylboronate esters yielded almost no product. The group turned to DFT calculations to reconcile these data, the results of which provided an excellent validation of the synergy of experimental data and calculations. With respect to transmetalation, the calculations evinced a series of putative steps, none of which included formation of a phenylrhodium intermediate via $\text{Rh}-\text{C}$ bond formation! The $\text{Rh}_2(\text{OAc})_4$ unit merely serves as a scaffold by which arylboronic acid and aldehyde are brought into and held in close proximity and perhaps activated by hydrogen bonding to effect aldehyde arylation.

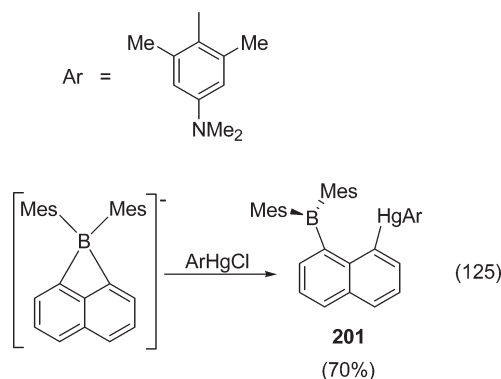
5.2.2. Carbon–Nitrogen Coupling (Chan–Evans–Lam Coupling). Catalytic $\text{C}-\text{N}$ coupling has been studied by myriads of investigators, but comparatively few have speculated on a mechanistic cycle.^{442,443,445,451,458,462,476,484,492,493,495} A general catalytic cycle that roughly agrees with the majority of investigators is shown in Figure 6. Indirect evidence in support of this cycle has been provided by Lam and co-workers.⁴⁴³ First, it was determined that a radical trap had no effect on reaction yields. In addition, it was suggested the transmetalation is the second step after $\text{Cu}-\text{N}$ bond formation, as $\text{C}-\text{N}$ coupling yields with *p*-tolylboronic acid were the same regardless of whether this arylboronic acid was added before the heterocycle– NH source or added directly to the preformed Cu –heterocycle complex.

The most detailed study on Cu -catalyzed $\text{C}-\text{N}$ coupling was provided by Tromp and co-workers,⁴⁹⁵ who used a combination of time-resolved spectroscopies to investigate the reaction in Scheme 116. The group elucidated some key points regarding transmetalation in this catalytic cycle. For example, without imidazole present, addition of $\text{PhB}(\text{OH})_2$ to the Cu catalyst forms biphenyl (the homocoupling product). Moreover, for $\text{C}-$

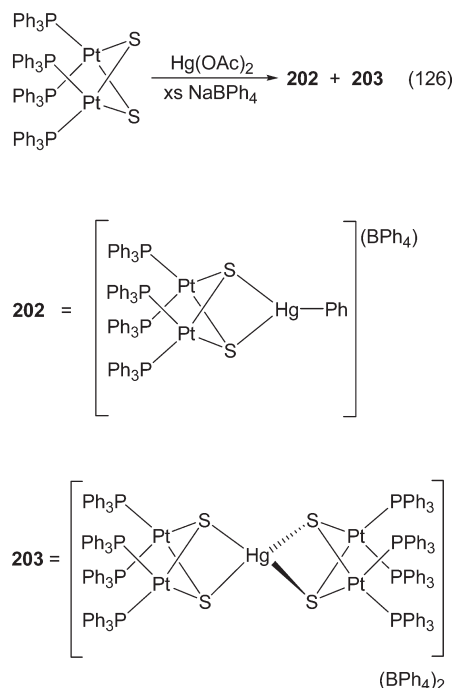
Scheme 104



Scheme 105



Scheme 106



N coupling to occur, imidazole must be added first (to form the Cu –imidazolate complex), followed by addition of $\text{PhB}(\text{OH})_2$. The group suggested that the Cu^{II} –imidazolate complex disproportionates to a Cu^{III} complex and Cu^{I} complex (Scheme 117). The Cu^{III} complex is transmetalated, followed

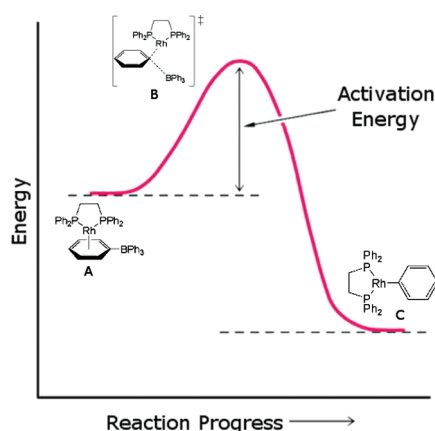
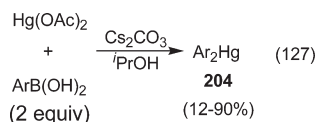


Figure 4. Reaction profile for an arrested transmetalation. Complex **A** is isolable and stable to B–C bond cleavage until sufficient thermal energy is added, at which point B–C bond cleavage and formal transmetalation occur to form **C**.

Scheme 107

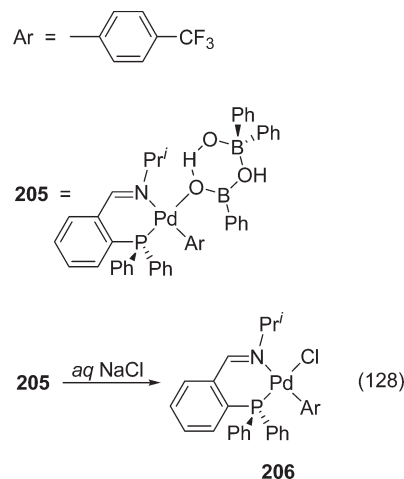


by reductive elimination of phenylimidazole to generate the same Cu^{I} complex. In addition, it was determined that, for coupling to occur, O_2 is not necessary, but H_2O is. Since the cycle requires Cu^{II} for the disproportionation step, the authors suggested (using ^{11}B NMR spectroscopic evidence to support their assertion) that, in addition to its usual role as a transmetalation reagent, $\text{PhB}(\text{OH})_2$ together with H_2O oxidizes the generated Cu^{I} back to Cu^{II} (as $[(\text{TMEDA})\text{Cu}(\text{OH})]_2\text{Cl}_2$) to close the cycle.

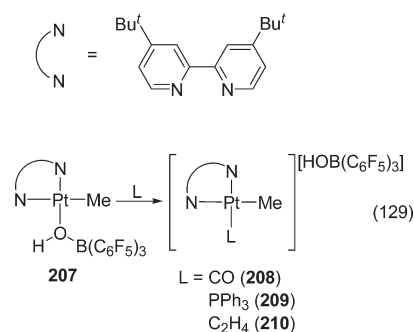
5.2.3. Carbon–Oxygen Coupling. A catalytic cycle for C–O coupling has been posited by a few investigators,^{462,496,506} all of whom agree on a fundamental sequence of steps, including transmetalation to copper, reductive elimination of Ar–OR , and reoxidation of Cu^{I} . However, the most detailed study (which incorporates these steps) was performed by Stahl and co-workers⁵⁰⁶ and is shown in abridged form in Figure 7. Transmetalation to Cu^{II} , the first step in the cycle, was kinetically ascertained to be the rate-limiting step. Note that one of the key differences in the cycle put forth by Stahl is that the arylcopper(II) is proposed to be oxidized (by CuX_2) to an arylcopper(III) intermediate which reductively eliminates Ar–OR . The role of oxygen is proposed to oxidize Cu^{I} back to the Cu^{II} resting state (the necessity of a stoichiometric oxidant was noted by previous investigators).

5.2.4. Carboxylation of Arylboronate Esters. The carboxylation of arylboronate esters has been studied less intensely than other catalytic coupling reactions,^{237,530,532} but a full catalytic cycle has been proposed by Hou (for Cu)²³⁷ and by Iwasawa (for Rh).⁵³² Both are similar in that a transmetalation step forms an arylmetal species, followed by insertion of CO_2 into the M–C bond. A general catalytic cycle is shown in Figure 8. The cycles only differ in the method by which regeneration of the metal precursor to transmetalation occurs

Scheme 108



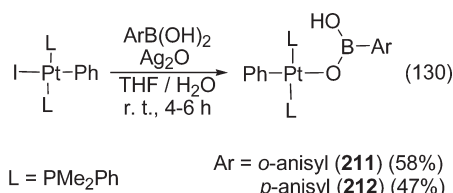
Scheme 109



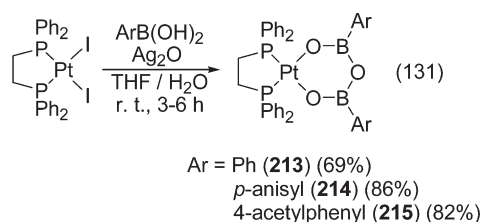
to close the catalytic cycle. In one catalytic cycle for Cu proposed by Hou,²³⁷ O^tBu displaces carboxylate from the coordination sphere of Cu , while for Rh , reaction of the Rh–carboxylate with organoboronate regenerates the arylrhodium intermediate. Evidence for the formation of an arylcopper intermediate via transmetalation has been provided by Hou.²³⁷ The reaction of $[(\text{IPr})\text{Cu}(\text{O}^t\text{Bu})]$ and *p*-anisylboronic acid produces $[(\text{IPr})\text{Cu}(\text{p-anisyl})]$ (**139**) (Scheme 76, vide supra) in nearly quantitative yield. It was further established that isolated **139**, when treated with CO_2 , generates the η^1 -carboxylate-ligated Cu complex **225** in nearly quantitative yield. Treatment of **225** with KO^tBu regenerates $[(\text{IPr})\text{Cu}(\text{O}^t\text{Bu})]$ and forms a precipitate that quantitatively hydrolyzes to 4-methoxybenzoic acid (Scheme 118); all of these data suggest **139** is an intermediate in the catalytic cycle.

These experimental findings were supported by DFT calculations at the B3LYP/6-311G* level.⁵³¹ Marder and co-workers executed calculations for the reactions in Scheme 119. The calculations suggested a number of interesting nuances to this reaction. First, electrophilic attack of the phenylboronate on the MeO^- ligand gives an energetically stabilized Cu–phenylborate complex, **226** ($\Delta G = -3.7$ kcal/mol for the formation of **226**). The phenylborate ligand, now activated to phenyl transfer, phenylates the Cu through a four-centered transition state ($\Delta G^\ddagger = 6.6$ kcal/mol relative to $\text{LCu–OMe} + \text{phenylboronate}$) reminiscent of the electrophilic mercuration transition state

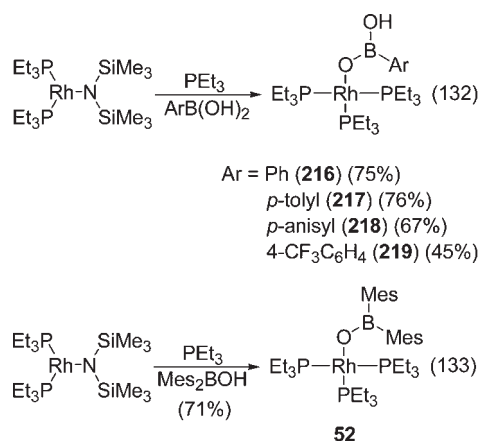
Scheme 110



Scheme 111



Scheme 112

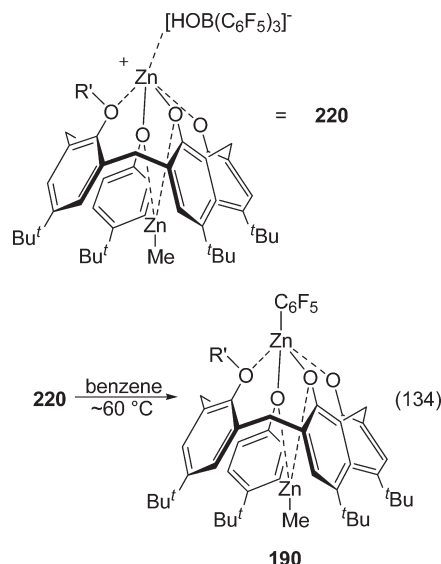


proposed by Kuivila²⁷² and Matteson²⁷³ (Figure 3, vide supra). The products **227** and the boronate ester of this transmetalation are considerably stabilized ($\Delta G = -16.4$ kcal/mol) relative to the isolated reactants (Scheme 120).

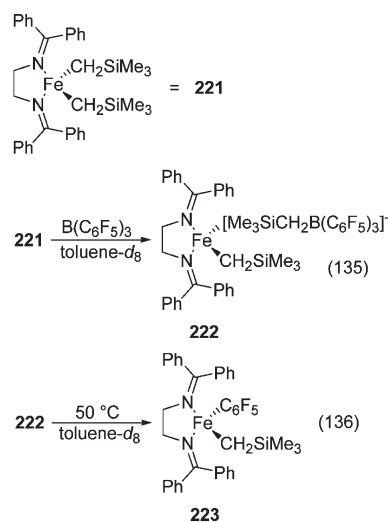
5.2.5. 1,4-Conjugate Addition to Electron-Deficient Alkenes. The metal-catalyzed 1,4-conjugate addition of organoboron compounds to electron-deficient alkenes and alkynes has arguably been the second most well studied catalytic coupling reaction of organoboron compounds to date (behind the Suzuki–Miyaura cross-coupling), and as such, several groups have posited a catalytic cycle for this transformation.^{537,539,541,545–548,554,555,559,564,566,567,569,573,574,579,581,585,597–600,605,606,610}

A general catalytic cycle is provided in Figure 9. A relatively abundant set of data have been gathered in direct and indirect support of the transmetalation step of this catalytic cycle. In a seminal investigation by Hayashi and co-workers, the Rh-catalyzed reaction of 2-cyclohexenone and PhB(OH)_2 was studied to ascertain the identity of the intermediates.⁵⁷³ In comparing the use of $[\text{Rh}(\text{acac})(S\text{-binap})]$ versus that of the dinuclear complex $[\text{Rh}(\text{OH})(S\text{-binap})]_2$ as the catalyst, the $[\text{Rh}(\text{OH})(S\text{-binap})]_2$ -

Scheme 113



Scheme 114



catalyzed reaction was considerably faster. The remarkable difference in catalytic potency was traced to the transmetalation step, which proceeded at 25 °C for $[\text{Rh}(\text{OH})(S\text{-binap})]_2$, whereas 80 °C was required for the reaction with $[\text{Rh}(\text{acac})(S\text{-binap})]$ to proceed at a “reasonable rate” (Scheme 121). However, it should be noted the Rh catalyst need not always be a Rh–OH-based catalyst for superior rates of reaction. Lalic and Corey, in an investigation of the $[\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}]_2$ -catalyzed enantioselective conjugate addition of isoprenyl trifluoroborates to various enones, determined that the active catalyst, generated by addition of Et_3N to the reaction mixture, was almost undoubtedly *not* a Rh–OH-based catalyst.⁶⁰⁹

Generally, the oxa- π -allyl-ligated Rh intermediate is hydrolyzed to close the catalytic cycle and regenerate the commonly invoked Rh–OH species as the transmetalation precursor. However, an intriguing variation was presented by Hayashi and

Table 2. Metal-Catalyzed or -Mediated Reactions That Involve Organoboron Compounds^{a–c}

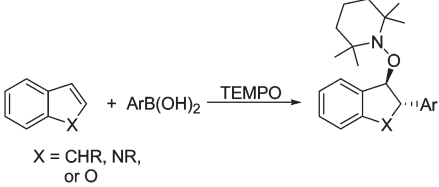
Type of Reaction	General Representation	Metal(s)
Acylation of Organoboron Compounds	$\begin{pmatrix} \text{RCOCl} \\ \text{or} \\ \text{RC(O)OR'} \end{pmatrix} + \text{ArB(OH)}_2 \longrightarrow \text{R}-\text{C}(=\text{O})-\text{Ar}$	Pd, ^{293, 295–306} Rh, ^{307, 308} Ru ³⁰⁹
Allene Synthesis by Arylation of Propargyl Electrophiles	$\text{RO}-\text{C}\equiv\text{C}-\text{R}^2 + \text{ArB(OH)}_2 \longrightarrow \text{R}^1-\text{C}=\text{C}(\text{Ar})-\text{R}^2$ <p>R = H, alkyl, OCO₂R' or P(O)(OEt)₂</p>	Pd ^{310–313}
Aminoxyarylation of Cyclic Olefins	 <p>X = CHR, NR, or O</p>	Pd ^{314, 315}
Arylation of Aldehydes	$\text{R}-\text{C}(=\text{O})-\text{H} + \text{ArB(OH)}_2 \longrightarrow \text{R}-\text{C}(\text{Ar})(\text{OH})-\text{H}$	Cu, ³¹⁶ Fe, ³¹⁷ Ir, ³¹⁸ Ni, ^{319–322} Pd, ^{323–332} Pt, ³³³ Rh, ^{318, 334–353} Ru, ³⁵⁴ Zn ^{355–370}
Arylation of Aldimines	$\text{R}-\text{C}(\text{NR}')=\text{H} + \text{ArB(OH)}_2 \xrightarrow{\text{H}^+} \text{R}-\text{C}(\text{Ar})(\text{NHR}')-\text{H}$	Pd, ^{371–373} Rh, ^{374–385} Zn ³⁸⁶
Arylation of Allylic Electrophiles ^d	$\text{R}-\text{CH}=\text{CH}-\text{CH}_2\text{X} + \text{ArB(OH)}_2 \longrightarrow \text{R}-\text{CH}=\text{CH}-\text{CH}_2\text{Ar}$ <p>or</p> $\text{R}-\text{CH}=\text{CH}-\text{CH}_2\text{X} + \text{ArB(OH)}_2 \longrightarrow \text{R}-\text{CH}(\text{Ar})-\text{CH}=\text{CH}_2$ <p>X = Cl, OH, OAc, OCO₂R''</p>	Cu, ^{238, 387, 388} Ni, ^{389–392} Pd, ^{393–407} Rh ^{408–411}
Arylation of Ketimines	$\text{R}-\text{C}(\text{NTs})=\text{R}' + \text{Ar}_4\text{B}^- \xrightarrow{\text{H}^+} \text{R}-\text{C}(\text{Ar})(\text{NHTs})-\text{R}'$	Rh ⁴¹²
Arylation of Ketones	$\text{R}-\text{C}(=\text{O})-\text{R}' + \text{ArB(OH)}_2 \xrightarrow{\text{H}^+} \text{R}-\text{C}(\text{Ar})(\text{OH})-\text{R}'$	Ir, ³¹⁸ Ni, ³²¹ Rh, ^{318, 413–415} Zn ^{416, 417}
Arylation of Nitriles	$\text{RCN} + \text{ArB(OH)}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{R}-\text{C}(=\text{O})-\text{Ar}$	Pd, ^{418–422} Rh ⁴²³
Azidation of Arylboronic Acids	$\text{ArB(OH)}_2 + \text{N}_3^- \longrightarrow \text{Ar}-\text{N}_3$	Cu ^{424, 425}

Table 2. Continued

Type of Reaction	General Representation	Metal(s)
Carbon-Fluorine Coupling	$\text{ArB(OH)}_2 + \text{"F"}^+ \text{ source} \longrightarrow \text{Ar-F}$	Ag, ²⁴³ Pd ²¹⁴
Carbon-Lead Coupling	$\text{Pb(OAc)}_4 + \text{ArB(OH)}_2 \longrightarrow \text{ArPb(OAc)}_3$	Hg ⁴²⁶⁻⁴³⁵
Carbon-Nitrogen (Chan-Evans-Lam) Coupling	$\text{RR'NH} + \text{ArB(OH)}_2 \longrightarrow \text{RR'N-Ar}$	Cu ⁴³⁶⁻⁴⁹⁵
Carbon-Oxygen Coupling	$\text{ROH} + \text{ArB(OH)}_2 \xrightarrow{[\text{O}]} \text{RO-Ar}$	Cu ^{436, 457, 458, 462, 496-507}
Carbon-Selenium Coupling	$\text{RSe-SeR} + \text{ArB(OH)}_2 \longrightarrow \text{RSe-Ar}$ or $\text{PhSe-Br} + \text{ArB(OH)}_2 \longrightarrow \text{PhSe-Ar}$	Cu, ⁵⁰⁸⁻⁵¹² Fe ^{509, 510, 513}
Carbon-Sulfur Coupling	$\text{RS-SR} + \text{ArB(OH)}_2 \longrightarrow \text{RS-Ar}$ or 	Cu ^{508, 509, 514-516}
Carbon-Tellurium Coupling	$\text{RTe-TeR} + \text{ArB(OH)}_2 \longrightarrow \text{RTe-Ar}$	Cu, ⁵⁰⁸⁻⁵¹⁰ Fe ⁵¹³
Carbonylative Coupling	$\text{RX} + \text{CO} + \text{ArB(OH)}_2 \longrightarrow \text{R-C(=O)-Ar}$ X = halide or other leaving group	Cu ⁵¹⁷ , Pd, ⁵¹⁸⁻⁵²⁷ Pt, ⁵²⁸ Rh ⁵²⁹
Carboxylation of Organoboron Compounds	$\text{ArB(OR)}_2 \xrightarrow[2. \text{H}^+]{1. \text{CO}_2} \text{Ar-CO}_2\text{H}$	Cu, ^{237, 530, 531} Pd, ⁵¹⁸ Rh, ⁵³² Zn ⁵³³
1,4-Conjugate Addition to Electron-Deficient Alkenes	$\text{Z} \text{---} \text{CH=CH}_2 + \text{ArB(OH)}_2 \longrightarrow \text{Z} \text{---} \text{CH}_2\text{---CH(Ar)}_2$ Z = EWG (e.g., CHO)	Cu, ⁵³⁴⁻⁵³⁷ Ir, ⁵³⁸ Pd, ^{139, 372, 539-557} Pt, ^{333, 549} Rh, ^{147, 335, 337, 558-609} Ru, ⁶¹⁰ Zn ⁶¹¹
1,6-Conjugate Addition to Electron Deficient Dienes		Ir ⁵⁹⁹ , Rh ^{597, 612, 613}
Cyanation of Arylboronic Acids ^e	$\text{ArB(OH)}_2 + \text{RS-CN} \longrightarrow \text{Ar-CN}$	(Pd + Cu) ⁶¹⁴
Decarbonylative Arylation		Ru ⁶¹⁵

Table 2. Continued

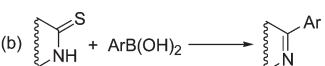
Type of Reaction	General Representation	Metal(s)
Decarboxylative Arylation	$\text{R-CO}_2\text{H} + \text{ArB(OH)}_2 \xrightarrow{\text{CO}_2} \text{R-Ar}$	Pd, ^{616, 617}
Desulfinitative Coupling of Thioorganics with Organoboronic Acids ^e	<p>(a) $\text{RSR}' + \text{ArB(OH)}_2 \longrightarrow \text{R-Ar}$ R = acyl, alkyl, aryl</p> <p>(b) </p>	(Pd + Cu) ^{515, 618-630}
Desulfonylative Arylation ^f	$\text{RSO}_2\text{Cl} + \text{ArB(OH)}_2 \xrightarrow{\text{SO}_2} \text{R-Ar}$	Pd ^{631, 632}
Diarylation of Alkynes	$\text{R}\equiv\text{R}' + 2 \text{ArB(OH)}_2 \xrightarrow{[\text{O}]} \text{R} \begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{R}' \end{array}$ <p>R' = H or alkyl/aryl</p>	Pd ⁶³³⁻⁶³⁶
Heck-Type Coupling (aka Oxidative Heck Coupling)	$\text{R-CH=CH}_2 + \text{ArB(OH)}_2 \xrightarrow{[\text{O}]} \text{R-CH=CH-Ar}$	Pd, ⁶³⁷⁻⁶⁵³ Rh, ⁶⁵⁴⁻⁶⁵⁷ Ru ^{189, 658}
Homocoupling of Organoboron Compounds	$2\text{ArB(OH)}_2 \xrightarrow{[\text{O}]} \text{Ar-Ar}$	(Ag + Cr), ⁶⁵⁹ Au, ⁶⁶⁰⁻⁶⁶⁴ Cu, ⁶⁶⁵⁻⁶⁶⁹ Mn, ⁶⁷⁰ Pd, ⁶⁷¹⁻⁶⁹³ Pt, ⁶⁷² Rh ⁶⁹⁴
Hydroarylation of (Unactivated) Alkenes	$\text{R-CH=CH}_2 + \text{ArB(OH)}_2 \longrightarrow \text{R-CH}_2\text{-CH}_2\text{-Ar}$	Ni, ⁶⁹⁵ Pd, ^{696, 697} Rh ^{654, 698-701}
Hydroarylation of Alkynes	$\text{R}\equiv\text{R}' + \text{ArB(OH)}_2 \longrightarrow \text{R-CH=CH-Ar}$ <p>R' = H or alkyl/aryl</p>	Co, ⁷⁰² Cu, ⁷⁰³ Ni, ⁷⁰⁴ Pd, ⁷⁰⁵⁻⁷⁰⁸ Rh ⁷⁰⁹⁻⁷¹⁶
Hydroarylation of Allenes	$\text{R}_2\text{C=C=CH}_2 + \text{ArB(OH)}_2 \longrightarrow \text{R}_2\text{C(Ar)-CH=CH}_2$	Ni, ⁷¹⁷ Pd, ⁷¹⁸⁻⁷²⁴ Pt, ⁷²³ Rh ⁷²⁵
Hydroarylation of Diazenes	$\text{R-N=N-R}' + \text{ArB(OH)}_2 \xrightarrow{\text{H}^+} \text{R-NH-N(Ar)-R}'$	Cu, ⁷²⁶⁻⁷²⁸ Pd ⁷²⁹
Oxidative Arylation of Aldehydes	$\text{Ar-CHO} + \text{ArB(OH)}_2 \xrightarrow[\text{or H}^+ \text{ acceptor}]{[\text{O}]} \text{Ar-CO-Ar}'$	Ir, ³¹⁸ Pd, ⁷³⁰ Pt, ⁷³¹ Rh ^{318, 732-736}
Oxidative Arylation of C-H Bonds (Excluding Heck) ^g	$\text{RC-H} + \text{ArB(OH)}_2 \xrightarrow[\text{or H}^+ \text{ acceptor}]{[\text{O}]} \text{RC-Ar}$	Cu, ⁷³⁷⁻⁷³⁹ Fe, ⁷⁴⁰ Pd, ⁷⁴¹⁻⁷⁴⁴ Rh, ⁷⁴⁵⁻⁷⁴⁷ Ru ⁷⁴⁸⁻⁷⁵⁴
Oxidative Arylation of Electron-Deficient Diazo Compounds	$\text{R-CH=N}_2 + \text{ArB(OH)}_2 \xrightarrow{[\text{O}]} \text{R-CH(Ar)-N}_2$ <p>Z = EWG (e.g., CO₂Me)</p>	Pd ^{755, 756}

Table 2. Continued

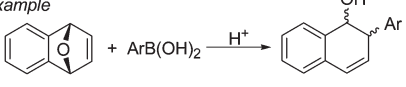
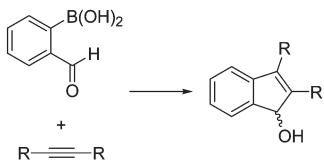
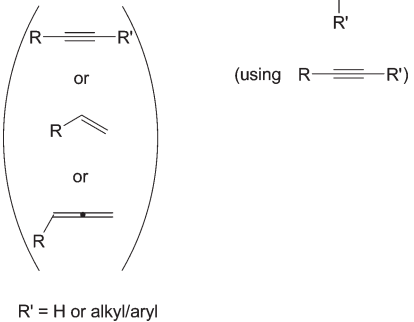
Type of Reaction	General Representation	Metal(s)
Oxidative Esterification of Aldehydes	$\text{Ar}-\text{CHO} + \text{Ar}'\text{B}(\text{OH})_2 \xrightarrow{[\text{O}]} \text{Ar}-\text{C}(\text{O})-\text{O}-\text{Ar}'$	Fe, ⁷⁵⁷ Pd ⁷⁵⁸
Polymerization Reactions	Various	Ni, ^{759, 760} Pd ^{759, 761, 762}
Ring-Opening Nucleophilic Addition ^h	<p>Example</p> 	Pd, ⁷⁶³ Rh ⁷⁶⁴⁻⁷⁶⁷
Sonogashira-Type Coupling	$\text{RC}\equiv\text{CX} + \text{ArB}(\text{OH})_2 \longrightarrow \text{RC}\equiv\text{C}-\text{Ar}$ X = H, I ⁺ Ph, B(O ⁱ Pr) ₃ , B(O ⁱ Pr) ₂ F, BF ₃ , B-OMe-BBN	Cu, ⁷⁶⁸ Pd ⁷⁶⁹⁻⁷⁷⁶
Sulfonylation of Arenes	$\text{ArB}(\text{OH})_2 + \left(\begin{array}{c} \text{R}'-\text{S}(=\text{O})_2\text{ONa} \\ \text{or} \\ \text{R}'-\text{S}(=\text{O})_2\text{Cl} \end{array} \right) \longrightarrow \text{R}-\text{S}(=\text{O})_2-\text{Ar}$	Cu, ⁷⁷⁷⁻⁷⁸⁰ Pd ⁷⁸¹
Suzuki-Miyaura Cross-Coupling	$\text{RX} + \text{ArB}(\text{OH})_2 \longrightarrow \text{R}-\text{Ar}$	Au, ^{664, 782, 783} Cu, ^{517, 784-789} Fe, ⁷⁹⁰ Ir, ⁷⁹¹ Mn, ⁷⁹² Ni, ⁷⁹³⁻⁸⁴¹ Pd, ^{138, 144, 156, 157, 286, 405, 526, 682, 800, 807, 811, 817, 842-1091} Pt, ^{1033, 1092-1094} Rh, ^{410, 423, 1095-1097} Ru ^{1098, 1099}
Tandem Cyclization	<p>Example</p> 	Ir, ^{1100, 1101} Pd, ¹¹⁰²⁻¹¹¹⁶ Rh ^{159, 1117-1134}
Three Component Coupling	$\text{ArB}(\text{OH})_2 + \text{"electrophile" (e.g., Ar'X)} \longrightarrow \text{R}-\text{C}(\text{Ar})(\text{Ar}')-\text{R}'$ 	Au, ¹¹³⁵ Ni, ^{717, 1136-1138} Pd, ¹¹³⁹⁻¹¹⁴⁵ Rh ^{1146, 1147}
Type of Reaction	General Representation	Metal(s)
Trifluoromethylation of Arylboronic Acids	$\text{ArB}(\text{OH})_2 + \text{CF}_3\text{SiMe}_3 \xrightarrow{[\text{O}]} \text{Ar}-\text{CF}_3$	Cu ¹¹⁴⁸

Table 2. Continued

^a At least one citation per reaction type posits or provides evidence for a transmetalation step as part of the catalytic cycle. ^b ArB(OH)_2 is used as a representative organoboron compound for each reaction (with the exception of arylation of ketimines and carboxylation). ^c Theoretical investigations are included as references. ^d Arylation of allylic electrophiles is considered as a coupling reaction separate from Suzuki–Miyaura cross-coupling because the α -to- γ chirality transfer is observed in the former coupling reaction but not the latter. ^e The combination of metals (Pd + Cu) is more accurate than Pd alone, as Cu must be present to serve as a stoichiometric cofactor. ^f Considered as distinct from desulfative coupling since no Cu cofactor is necessary and SO_2 extrusion is not observed for Cu-mediated desulfative coupling reactions. ^g As a well-known, “named” reaction that traditionally has only included olefin C–H bonds, Heck-type coupling reactions are considered separately from other oxidative C–H bond breaking/C–C bond forming reactions. ^h Reactions which feature β -X (X = C, N, O) elimination as a ring-opening elementary step are considered in this reaction class as separate from olefin hydroarylation reactions (which typically do not feature a ring-opening β -X elimination step).

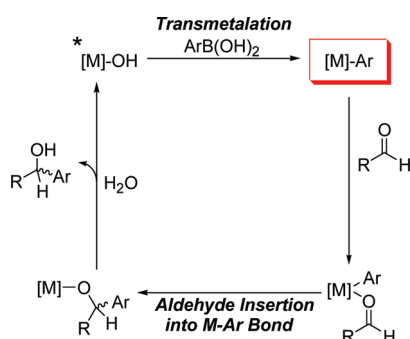


Figure 5. General catalytic cycle for the arylation of aldehydes.

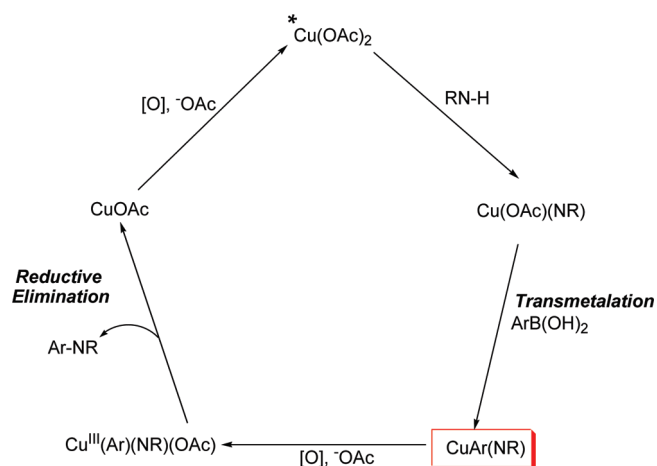
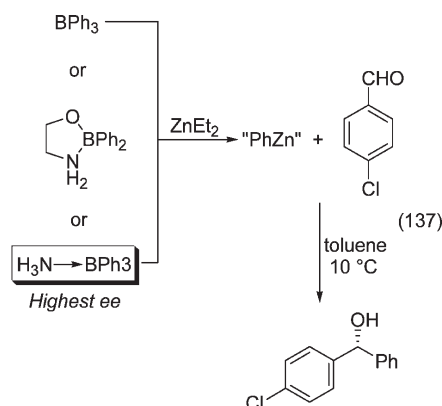


Figure 6. General catalytic cycle for C–N (Chan–Evans–Lam) coupling. Adapted with permission from ref 476. Copyright 2006.

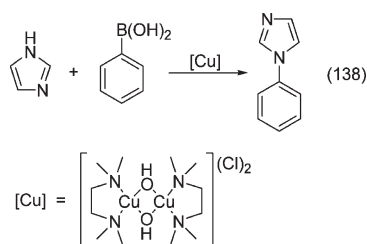
co-workers, who circumvented the Rh–OH completely.⁵⁸¹ Their approach was to directly transmetalate the intermediate oxa- π -allyl-ligated Rh species with 9-PhBBN to regenerate the insertion-competent phenylrhodium complex **229**, which was corroborated by ^{31}P NMR spectroscopy (Scheme 122).

A key question in the Rh-catalyzed 1,4-conjugate addition has been that of the rate-determining step in the catalytic cycle. This was addressed by Hayashi and co-workers, who studied the kinetics of the $[\text{Rh}(\text{OH})(\text{R-bina})]_2$ -catalyzed reaction of PhB(OH)_2 with methyl vinyl ketone (MVK; Scheme 123).⁶⁰⁰ Interestingly, the reaction was first-order in PhB(OH)_2 concentration, and half-order in $[\text{Rh}(\text{OH})(\text{R-bina})]_2$. These data were interpreted to suggest the dimeric Rh complex

Scheme 115



Scheme 116



had to fragment into “monomers” **230** before it could become catalytically active (Scheme 124). Once formed, **230** could be transmetalated to form **231**, with a measured rate constant of $0.5 \text{ M}^{-1} \text{ s}^{-1}$.

Hayashi extended this concept to a trinuclear Rh complex, $[\text{Rh}_3(\mu_3\text{-O})(\mu_3\text{-OH})\text{L}_3]$ (**232**), where L is a chelating phosphine-appended diene.⁶⁰⁵ By ^{31}P NMR spectroscopy, it was determined **232** reacts with PhB(OH)_2 in the presence of phosphine to yield a mixture of diastereomeric, transmetalated products, **233**–**236** (Scheme 125). The stereochemistries of **233/234** (7:1 observed ratio) and **235/236** (>15:1 observed ratio) were determined by an analysis of the coupling constants. Kinetic data gathered for the Rh trimer catalyzed reaction of PhB(OH)_2 with MVK were indicative of a first-order dependence on the PhB(OH)_2 concentration and a ~ 0.4 -order dependence on **232**, suggesting the necessity (as with the Rh dimer in Scheme 124) of the trimer to fragment into reactive monomers before transmetalation could occur. The authors

Scheme 117

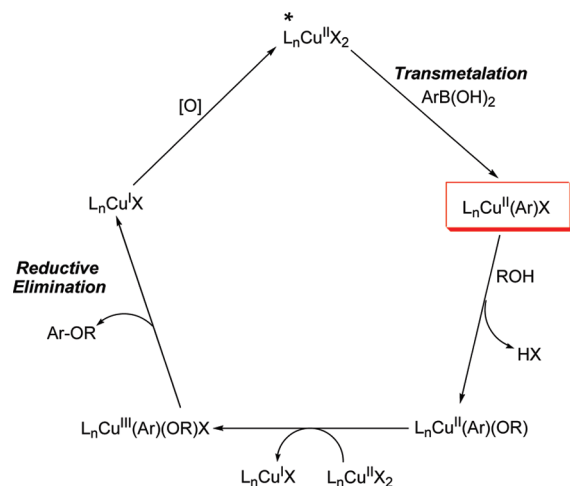
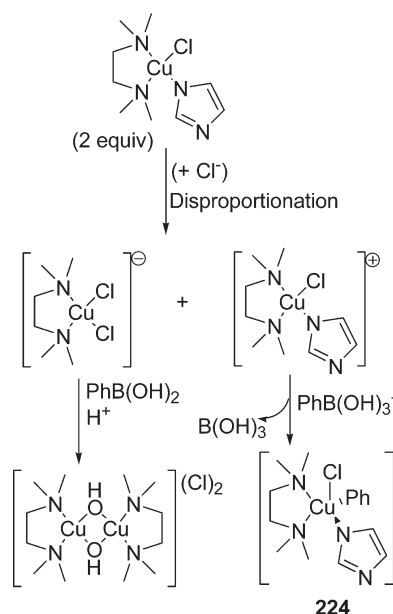


Figure 7. General catalytic cycle for C–O coupling ([O] = general oxidant). Adapted with permission from ref 506. Copyright 2009 American Chemical Society.

suggested the rate-determining step is the transmetalation step (followed by a fast insertion of the olefin into the Rh—aryl bond); the work of Genet has some qualitative agreement with these results.⁵⁹⁸ Genet's group compared the rates of reaction of PhB(OH)_2 and PhBF_3K with that of ethyl oct-2-enoate (catalyzed by $[\text{Rh}(\text{cod})_2](\text{PF}_6)$) and concluded that, in the reaction with PhBF_3K , the transmetalation step seems to be rate-determining.

In an investigation of the 1,4-conjugate addition of organoboron and organosilicon compounds to acyclic and cyclic enones and specifically the reaction of a cationic Pd catalyst and PhB(OH)₂, Miyaura and co-workers detected a transmetalation intermediate, **237**, via ¹H and ³¹P NMR spectroscopies (Scheme 126).⁵⁴¹ Furthermore, although a yield of pure, isolated

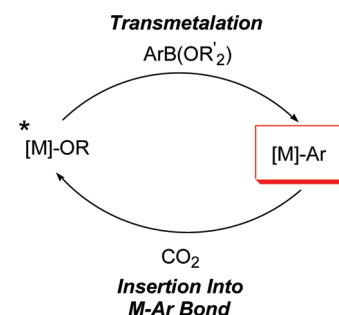
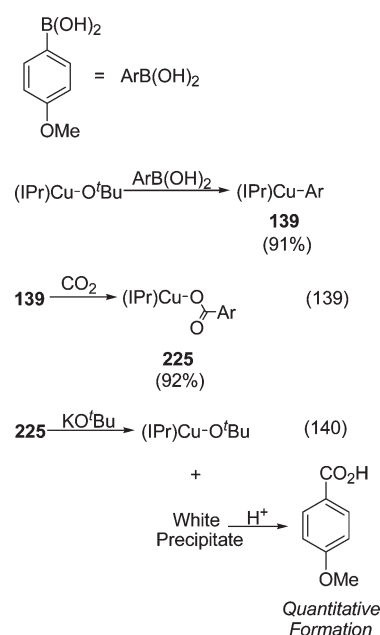
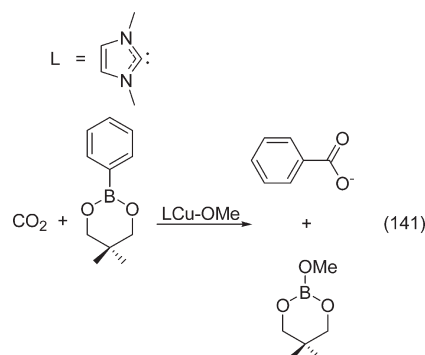


Figure 8. General catalytic cycle for catalytic carboxylation of arylboronate esters (M = Cu, Rh). Adapted with permission from refs 237 and 532. Copyright 2008 and 2006 American Chemical Society.

Scheme 118



Scheme 119



arylpalladium was not reported, the identity of **237** was structurally authenticated via X-ray crystallography. Using a cyclopalladated catalyst for 1,4-conjugate addition reactions, Bedford and co-workers detected by ^{31}P NMR spectroscopy a transmetalation

Scheme 120

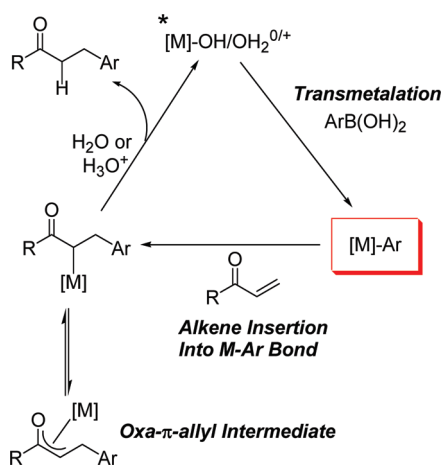
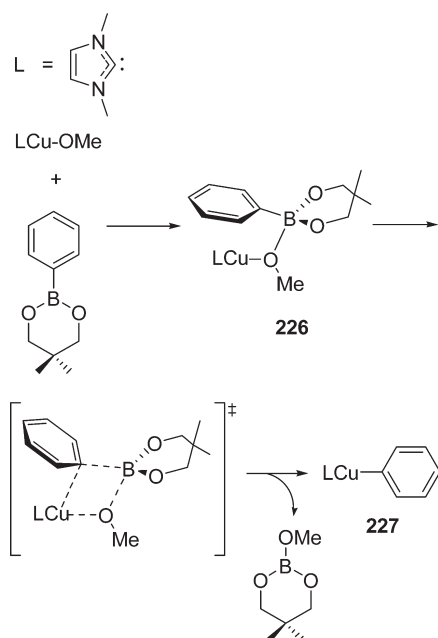
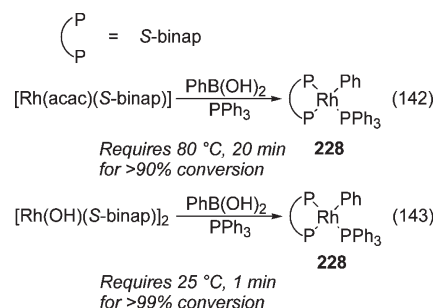


Figure 9. General catalytic cycle for the 1,4-conjugate addition. Note that 0/+ refers to neutral or cationic catalyst.

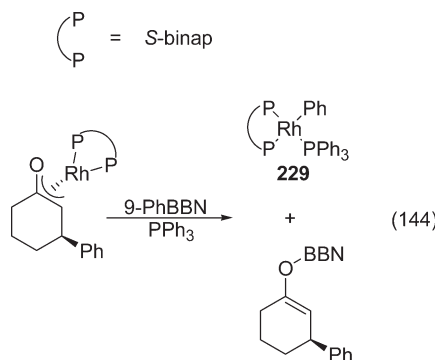
intermediate, **238**, in a reaction with *p*-anisylboronic acid (Scheme 127).

5.2.6. Desulfative Coupling of Thioorganics with Boronic Acids. Liebeskind and Musaev recently performed a theoretical investigation on the transmetalation and reductive elimination steps of the Pd-catalyzed, Cu-mediated desulfative coupling of thioorganics and boronic acids.¹¹⁴⁹ Starting their calculations from the postoxidative addition intermediate $\text{L}_n\text{PdMe(SH)}$ ($\text{L} = \text{PH}_3$, PMe_3 , or PPh_3 ; $n = 1$ or 2), calculations for the transmetalation step (with MeB(OH)_2) were performed starting from **239** and **240**, the adducts of $\text{L}_n\text{PdMe(SH)}$ with the cofactor Cu(HCOO) (Figure 10). The transmetalation pathways were calculated for three R groups (H, Me, and Ph) considering “Pd-side attack” or “Cu-side attack” of MeB(OH)_2 . The calculated transition states and transmetalated intermediates

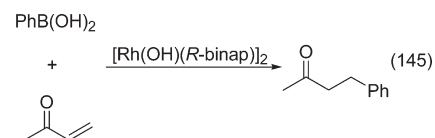
Scheme 121



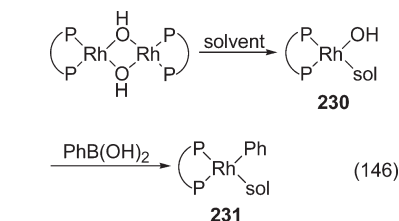
Scheme 122



Scheme 123

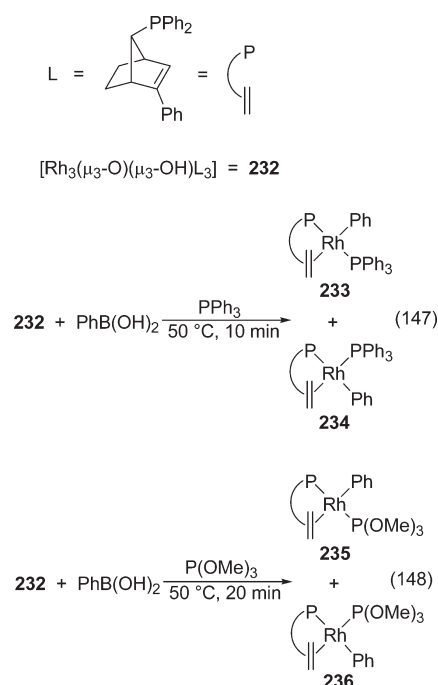


Scheme 124

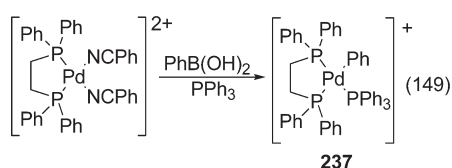


for reaction with **239** and **240** are shown in Schemes 128 and 129, respectively. Some trends in the calculated transmetalation data included (1) for four-coordinate complexes **239**, the free energy of activation for Cu-side attack of MeB(OH)_2 was much lower than for Pd-side attack (ΔG^\ddagger for R = H, Me, and Ph was 34.9, 36.2, and 36.4 kcal/mol, respectively, for Cu-side attack (reaction 151, Scheme 128) versus 47.7, 50.6, and 53.7 kcal/mol, respectively, for Pd-side attack (reaction 152, Scheme 128)), (2) for four-coordinate complexes **239**, ΔG for formation of

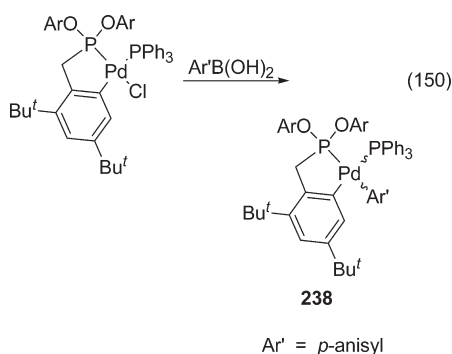
Scheme 125



Scheme 126



Scheme 127



products was endergonic (ΔG for $R = H$ and Me was 7.2 and 10.3 kcal/mol, respectively, for Cu-side attack (reaction 151) and 16.5 and 22.4 kcal/mol, respectively, for Pd-side attack (reaction 152)), and (3) for three-coordinate complexes **240**, ΔG^\ddagger was more nearly equal for either Cu- or Pd-side attack (ΔG^\ddagger for $R = H, Me$, and Ph was 36.3, 34.6, and 36.0 kcal/mol, respectively, for Cu-side attack (reaction 153, Scheme 129) versus 36.2, 37.6, and 43.5 kcal/mol, respectively, for Pd-side attack (reaction 154,

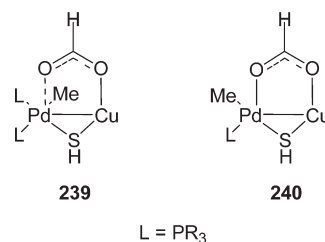
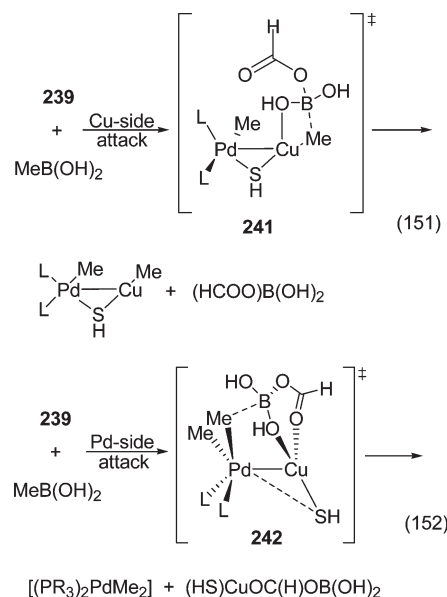


Figure 10. Model complexes for theoretical determination of transmetalation intermediates in desulfative coupling via $MeB(OH)_2$. Adapted with permission from ref 1149. Copyright 2009 American Chemical Society.

Scheme 128



Scheme 129)). The calculations suggested that the rate-determining step is transmetalation only for the Cu-side attack of $MeB(OH)_2$ on $LPdMe(SH)$ (reaction 153).

5.2.7. Homocoupling of Organoboronic Acids/Organoboronates. The oxidative homocoupling of organoboron compounds (also known as self-coupling) for several different metals has been well-studied, and the hypothesized mechanistic cycles include recognition of a transmetalation step, reductive elimination, and the need for a stoichiometric oxidant.^{660,662,663,665,667,669,671,673,675,676,678,683,684,686,691–693} A general catalytic cycle for Pd is shown in Figure 11.

In an early study of the homocoupling mechanism, Moreno-Mañas and co-workers gathered NMR data on the reaction of $Pd(OAc)_2$ and various $ArB(OH)_2$ compounds, the product of which was anticipated to be $[ArPd(OAc)]$.⁶⁷³ Phenol formation was confirmed, suggesting the possibility of peroxide generation as a byproduct. Relevantly, peroxide was detected as a homocoupling byproduct (via horseradish peroxidase assay) by Finn and co-workers⁶⁸⁴ (the relevance of peroxide in homocoupling is evinced by the experiments of Jutand and co-workers, *vide infra*). A subsequent study by Moreno-Mañas and co-workers used ESI-MS to discern species present in solution.⁶⁷⁶ While no evidence

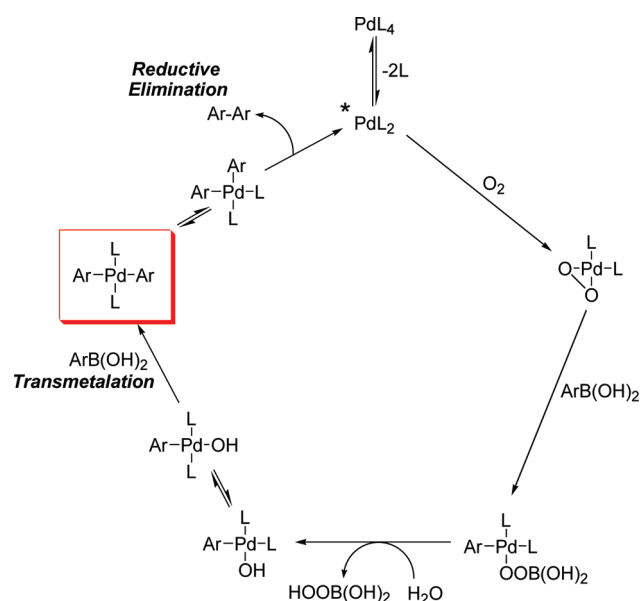
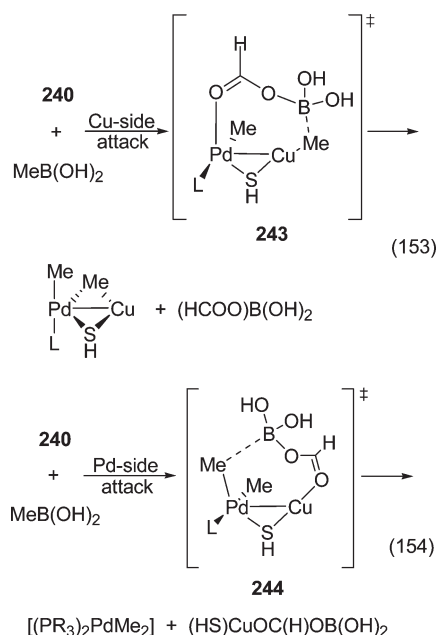


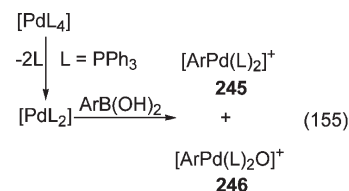
Figure 11. General catalytic cycle for the homocoupling of arylboronic acids. Adapted with permission from ref 692. Copyright 2008 American Chemical Society.

Scheme 129

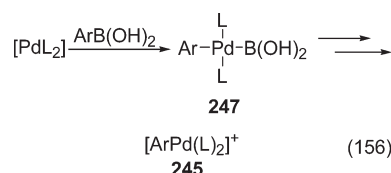


for a diarylated Pd intermediate was obtained at any concentration of Pd, the species detected in solution varied with the concentration of $[\text{Pd}(\text{PPh}_3)_4]$ that was used. Two arylated species (including one assigned as having an "O" ligand) were consistently observed, as shown in Scheme 130. The authors asserted that **247**, which was formed from the product of an oxidative addition reaction of $\text{ArB}(\text{OH})_2$ with PdL_2 , was the precursor to **245** (Scheme 131). In agreement with these results, DFT calculations (at the B3LYP/SDD/6-31+G(d,p) level plus the PCM water solvation model) by Khinast and co-workers suggest the oxidative addition of Pd^0 (the calculations use one

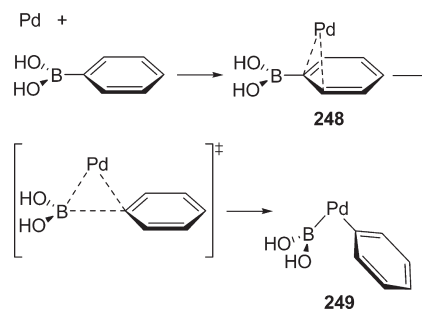
Scheme 130



Scheme 131



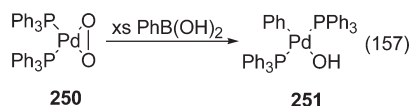
Scheme 132



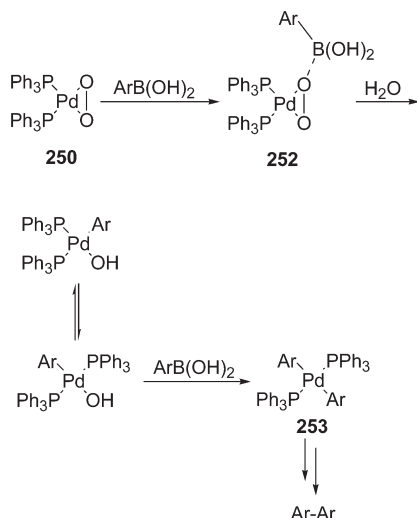
atom of Pd) into the C–B bond is a composite of two steps, the formation of a Pd–arene π -complex, **248** (calculated binding energies between -103.3 and -115.5 kJ/mol for a variety of arylboronic acids), followed by insertion into the C–B bond to form **249** (Scheme 132).⁶⁹¹ The authors stated that no energy minimum could be found in which Pd initially binds to B. The calculated free energies of activation for the insertion of Pd^0 into the C–B bond range from 51.4 to 60.1 kJ/mol, and the calculated free energies of the overall oxidative addition reaction in Scheme 132 to form **249** range from -70.4 to -84.3 kJ/mol.

In a well-executed set of experiments, Jutand and co-workers investigated the homocoupling of arylboronic acids in air and concluded the true catalyst is a Pd^{II} -peroxide complex, $[\text{Pd}(\text{PPh}_3)(\eta^2\text{-O}_2)]$ (**250**).⁶⁸⁶ With an excess of phenylboronic acid (other arylboronic acids reacted similarly), **250** reacted rapidly to form *trans*- $[\text{PdPh}(\text{OH})(\text{PPh}_3)_2]$ (**251**), as determined by ^1H and ^{31}P NMR spectroscopies and ESI-MS (Scheme 133). However, when using substoichiometric amounts of arylboronic acid, another species was observed by ^{31}P NMR spectroscopy. On the basis of these data and kinetics measurements, which revealed a first-order dependence on **250** and a second-order dependence on the arylboronic acid, the authors proposed that the first equivalent of arylboronic acid reacted with **250** to form an intermediate **252**, which hydrolyzed and reacted with a second equivalent of arylboronic acid to form an intermediate $[\text{PdL}_2\text{Ar}_2]$ species, **253**. In its *cis*-stereochemistry, **253** reductively eliminates the homocoupled product (Scheme 134). The formation

Scheme 133



Scheme 134



of intermediates **252** was corroborated by DFT calculations as part of the same investigation, which predicted a solution energy of formation (LANL2DZ basis set) of 1.713, −2.545, and −17.895 kJ/mol for Ar = *p*-anisyl, phenyl, and *p*-cyanophenyl, respectively. A subsequent investigation by the same group corroborated the series of steps shown in Scheme 134.⁶⁹²

Corma and co-workers investigated the use of gold supported on nanocrystalline CeO₂ as a catalyst for the oxidative homocoupling of arylboronic acids.⁶⁶² The authors believed that surface Ce—OH species participated in the catalytic reaction and, convincingly, demonstrated that surface hydroxide species (detected by Raman spectroscopy *after* the addition of water to the Au/CeO₂) disappeared after addition of PhB(OH)₂ (the gold was necessary as in its absence no homocoupled product formed). It was proposed that the surface hydroxide species activate the boronic acid to phenyl transfer to Au³⁺, which can reductively eliminate biphenyl. The Au³⁺ thus generated is then reoxidized by Ce⁴⁺ to close the catalytic cycle.

Indirect evidence for transmetalation to Au in poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized Au nanoparticles was provided by Sakurai and co-workers.^{660,663} Oxygen was found to be necessary for homocoupling of arylboronic acids to occur, and formation of phenols was commonly observed as a byproduct. The authors believed that peroxide formation was implied by the formation of phenol byproducts, and as such, the surface of the Au nanoparticles could be oxidized to form surface Au—superoxides that could undergo transmetalation reactions with arylboronic acids. Though speculative, the authors noted that the suppressed homocoupling of *o*-tolylboronic acid and the enhanced reactivity of the smaller Au nanoparticles were consistent with transmetalation to the Au surface at some point in the catalytic cycle. Other indirect evidence for transmetalation was collected by Yoshida

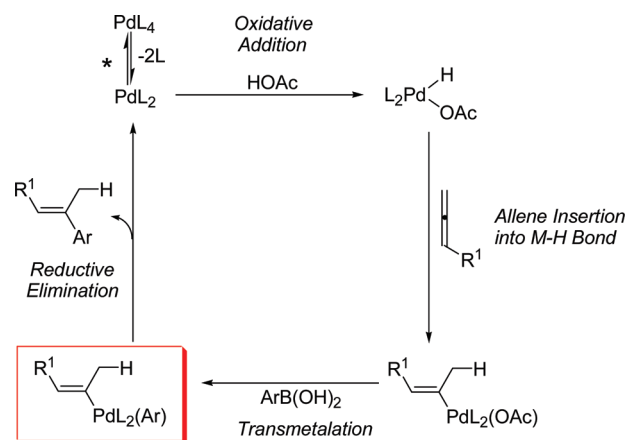
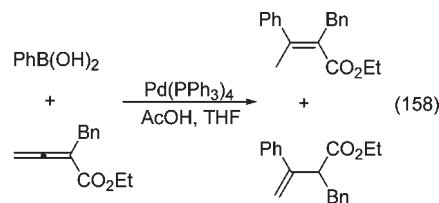


Figure 12. General catalytic cycle for Pd-catalyzed hydroarylation of allenes in the presence of acetic acid. Adapted with permission from ref 720. Copyright 2005.

Scheme 135



and co-workers, who suggested a double transmetalation mechanism instead of an oxygen-mediated radical pathway on the basis of the lack of influence that galvinoxyl (a radical scavenger) had on the rate and yield of reaction.⁶⁸³

5.2.8. Hydroarylation of Allenes. Mechanistic speculation for the hydroarylation of allenes has been provided for Ni, Pd, and Pt.^{717,719,720,723,724} On the basis of the data available for Pd (*vide infra*), a general catalytic cycle is presented in Figure 12. One mechanistic study has provided evidence of the formation of an arylpalladium intermediate via transmetalation.⁷²⁰ Using ESI-MS, the reaction in Scheme 135 was investigated. Evidence was found for the initial formation of a cationic Pd^{II} species, [(AcO)Pd(PPh₃)₂]⁺, which attacks allene to form the vinylpalladium intermediate **254** (detected by ESI-MS). This intermediate is proposed to react with PhB(OH)₂ (perhaps by electrophilic attack of the Pd species on the phenyl group) in a transmetalation reaction to form the phenylpalladium species **255**. Once formed, **255** formally loses H[−] (one electron plus one H[•]) to form **256**, which is detected by ESI-MS (similar results were obtained using *p*-anisylboronic acid) (Scheme 136).

5.2.9. Oxidative Arylation of C—H Bonds. Though not as well-investigated as some of the other catalytic coupling reactions of Table 2, several groups have speculated on a catalytic cycle for oxidative arylation with arylboronic acids via C—H bond cleavage.^{739–741,743,748–751} A general catalytic cycle is shown in Figure 13. Some indirect experimental evidence (relevant to transmetalation) in support of the mechanism has been gathered. For example, in the Ru-catalyzed oxidative arylation, a sacrificial hydride acceptor is proposed to react with an intermediate Ru—H (**257**) species to form a Ru—OR species (**258**). The Ru—OR intermediate reacts with an arylboron compound to form an

Scheme 136

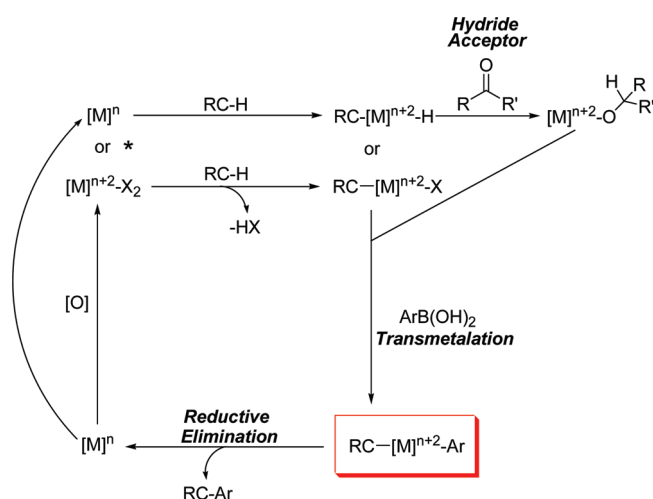
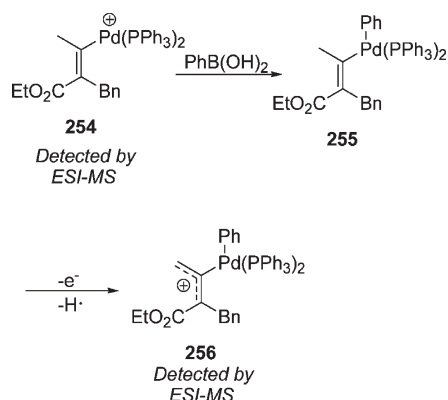


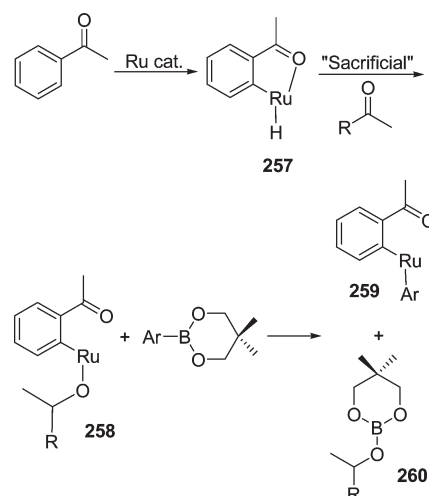
Figure 13. General catalytic cycle for oxidative arylation. The general cycle combines attributes of Ru-catalyzed (upper/outer route) and Pd-catalyzed (inner route) reactions. [O] is a general oxidant.

arylruthenium intermediate (259) plus a boronate ester (260) (Scheme 137). If this mechanism were operative, one would anticipate 260 could be detected. In fact, 260 has been detected by ¹H and ¹¹B NMR spectroscopies and GC/MS spectrometry in two separate investigations of Ru-catalyzed oxidative arylation.^{748,750}

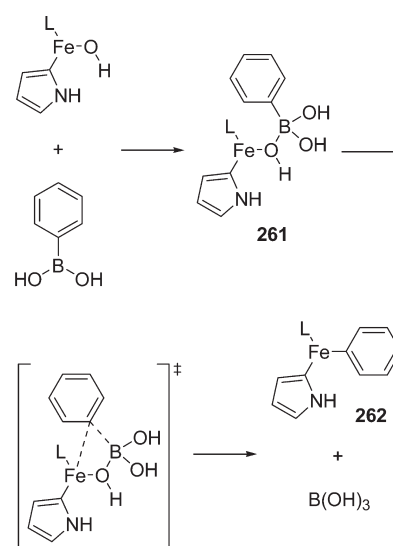
A theoretical investigation of the mechanism of the Fe-catalyzed oxidative arylation of pyrroles and pyridines was executed by Yu and co-workers.⁷⁴⁰ Calculations (at the B3LYP-(PCM)/6-311+G(d,p) level) suggest the O atom of LFe=O inserts into a C–H bond of a pyrrole to form LFe–OH, which reacts with PhB(OH)₂ to form an intermediate (local minimum) O-ligated Fe–borate complex (261) which subsequently transfers its phenyl group to Fe to form 262 with concomitant loss of B(OH)₃ (Scheme 138). Overall, the calculations are consistent with the general catalytic cycle proposed above provided one treats the terminal oxo ligand as “X”. Starting from the isolated “reactants” (LFe–OH and PhB(OH)₂), the activation energies for transmetalation are 144.2 and 113.9 kJ/mol for the quartet and sextet states, respectively.

5.2.10. Oxidative Heck Coupling. Several groups have suggested a catalytic cycle for the oxidative Heck coupling reaction with organoboron compounds that includes a

Scheme 137



Scheme 138



transmetalation step.^{637,638,642,646,648,650,652,655,656} Most of the suggested catalytic cycles for the oxidative Heck-type coupling of olefins and organoboronic acids have the sequence of steps as shown in Figure 14. In fact, Brown and co-workers even stated that “the predominant pathway in ruthenium catalysis parallels that already established for palladium catalysis”.⁶⁵⁸ With the exception of the cycle posited by Uemura and Cho⁶³⁷ in which an organopalladium(II) intermediate is formed by oxidative addition of an organoboronic acid to Pd⁰, other authors agree the formation of an organometallic species by transmetalation of an organoboronic acid to M–X (to form M–R) is the first step in the oxidative Heck-type coupling. In a few cases, spectroscopic evidence has been gathered to support the existence of a transmetalation step in the catalytic cycle.

In one report by Jung and co-workers,⁶⁴⁸ the dimeric Pd complex 263 was prepared and investigated for catalytic activity in the oxidative Heck coupling reaction (reaction 159, Scheme 139).

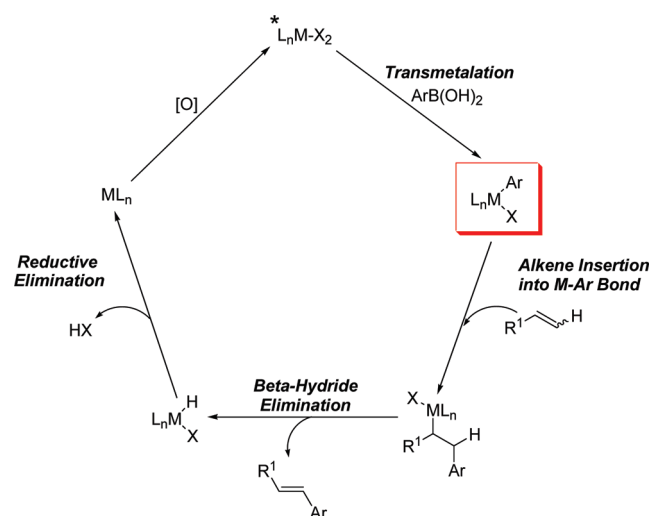
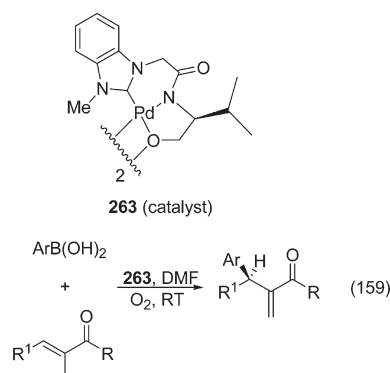


Figure 14. General catalytic cycle for the oxidative Heck coupling.

Scheme 139

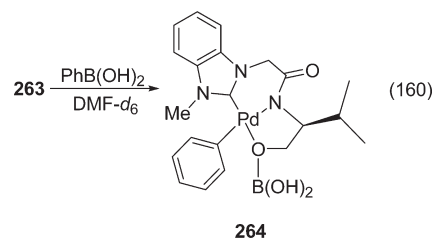


As a dimer, **263** could not catalyze reaction 159 in Scheme 139. However, the dimer was easily broken into a catalytically active monomer by several reagents, including PhB(OH)_2 . The phenylated monomer **264** was formed in 82% conversion and detected by ^1H NMR (Scheme 140).

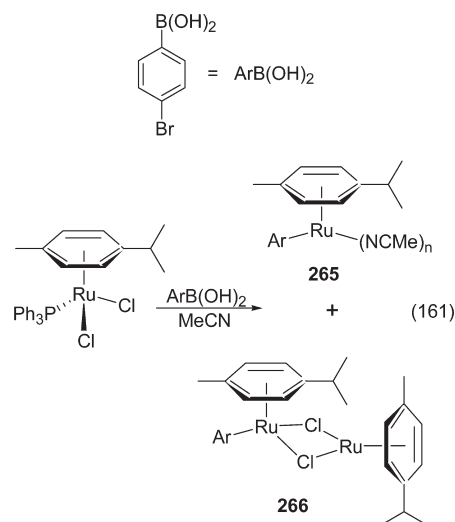
The Ru-catalyzed oxidative Heck reaction was previously discussed (Scheme 29, *vide supra*) and a phenylruthenium species isolated by reaction with PhB(OH)_2 . Additionally, intermediates in the transmetalation of 4-bromophenylboronic acid with $(p\text{-cymene})(\text{PPh}_3)\text{RuCl}_2$ were detected by ESI-MS and identified as an acetonitrile-solvated arylruthenium, **265**, and a chloride-bridged dinuclear ruthenium complex, **266** (Scheme 141). Interestingly, when the initial reaction products **265** and **266** were treated with an electron-deficient olefin substrate before being subjected to mass spectrometry, intermediates **267** and **268** (Heck-type coupling products) were detected (Scheme 142). In a follow-up report by the same set of investigators,⁶⁵⁸ the set of substrates for this transmetalation reaction was expanded to include 2,6-difluorophenylboronic acid (Scheme 143), the product **269** of which was characterized by ^{19}F NMR spectroscopy.

5.2.11. Suzuki–Miyaura Cross–Coupling. The Suzuki–Miyaura cross-coupling reaction, a C–C bond forming reaction which utilizes organoboron compounds as the nucleophilic

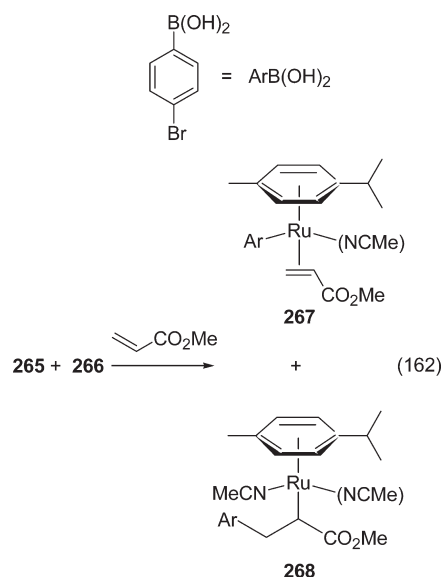
Scheme 140



Scheme 141



Scheme 142



coupling partner, is without a doubt the most thoroughly studied metal-catalyzed coupling reaction of organoboron compounds. As such, a myriad of authors have speculated on the mechanistic

Scheme 143

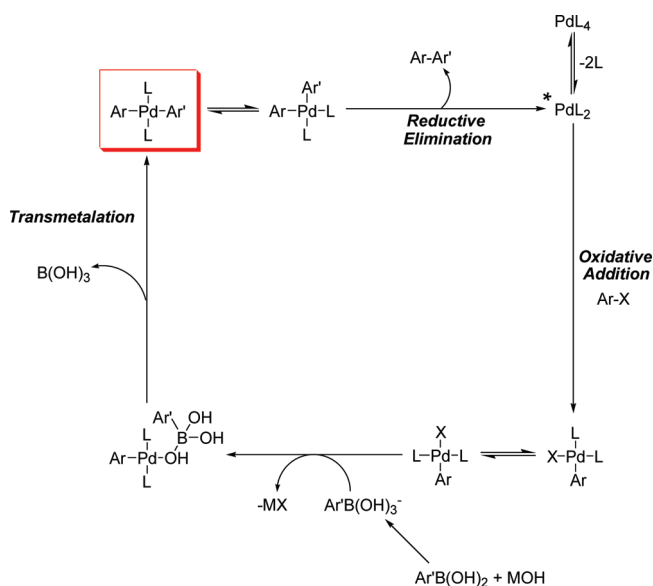
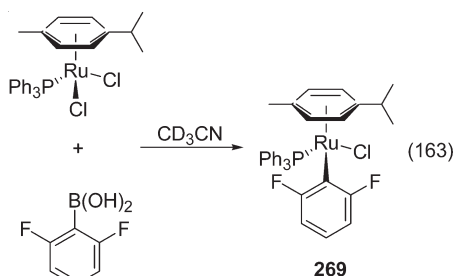


Figure 15. General catalytic cycle for the Suzuki–Miyaura cross-coupling reaction.

details of the putative catalytic cycle (catalyzed by complexes of Cu ,^{784,787–789} Ni ,^{793,797,798,806,826,828–830,833,835,840} Pd ,^{157,286, 811,844,845,853,857,861,866,868,878,885,889,893,894,900,918,923,927,928,933, 935,936,938,942,946,947,949–951,954,955,961,965,966,969,970,974,976,978,981–983,1021,1032,1069,1085} Pt ,^{1033,1092} Rh ,^{423,1097} and Ru ¹⁰⁹⁹). A general catalytic cycle is shown in Figure 15. A plethora of experimental and theoretical data gathered from a variety of spectroscopic and spectrometric techniques have refined our understanding of the transmetalation step of this catalytic cycle. To begin with, most authors agree that a base is necessary to quaternize the boron and activate it to transmetalation, making the organic group more nucleophilic (vide infra for theoretical data). In qualitative agreement with this, Fu and co-workers, in an alkyl–alkyl cross-coupling report, detected (by ^{11}B NMR spectroscopy) the quaternized adduct of $^t\text{O}^t\text{Bu}$ with R-9-BBN and noted that, in the absence of a base, no cross-coupled product was formed;¹⁰⁵ a similar result was obtained by Matos and Soderquist.⁹⁹ A theoretical study has even been focused on the “role of the base” in Suzuki–Miyaura cross-couplings, concluding the catalytic cycle begins with the reaction of base and organoboronic acid.⁹⁴⁹ As important as the base is, the identity of the organoboronic acid also matters, as the Mulliken charge of C_1 (*ipso*) of $\text{ArB}(\text{OH})_2$ was calculated to be 0.07 and -0.11 for $\text{Ar} = \text{Ph}$ and C_6F_5 , respectively, whereas that of $\text{ArB}(\text{OH})_3^-$ was

calculated to be -0.92 and -0.21 for $\text{Ar} = \text{Ph}$ and C_6F_5 , respectively.⁹⁵¹ This comparison underscores the relatively small influence quaternization of boron has on the nucleophilicity of a highly electron deficient aryl group. In addition, calculations suggest not all quaternized borate ions transmetalate with equal efficiency. In a recent study by Lloyd-Jones and co-workers, calculations suggested the transmetalation step of the Suzuki–Miyaura coupling of PhBr with the set of borates $\text{PhBX}_{3-n}\text{Y}_n^-$ ($\text{X} = \text{F}$; $\text{Y} = \text{OH}$) proceeded with increasing ease (decreasing activation barrier) from PhBF_3^- to $\text{PhB}(\text{OH})_3^-$.¹⁶³

Aliprantis and Canary utilized ESI-MS to detect intermediates in the $\text{Pd}(\text{PPh}_3)_4$ -catalyzed coupling of bromopyridines and arylboronic acids.⁸⁶⁶ Though intermediates of the type $[\text{ArPd}(\text{PPh}_3)_2(\text{OH})]$ or $[\text{ArPd}(\text{PPh}_3)_2(\text{OCH}_3)]$ (as precursors to transmetalation) were not observed, the authors noted that transmetalated intermediates of the type $[(\text{pyrH})\text{ArPd}(\text{PPh}_3)_2]^+$ were consistently observed, especially with the more hindered arylboronic acids. However, ESI-MS has detected transmetalated arylpalladium species and the presumed Pd-OH -containing transmetalation precursors in an ionic liquid based cross-coupling system.¹⁰⁰⁹ ESI-MS was also used by Roglans and co-workers to detect a transmetalated intermediate in the Pd -catalyzed cross-coupling of PhBF_3K and an arenediazonium coupling partner¹⁰⁸⁵ and by Stefani and co-workers to detect a transmetalated intermediate in the Pd -catalyzed cross-coupling of ArBF_3K and an aryltelluride coupling partner.⁹⁶³

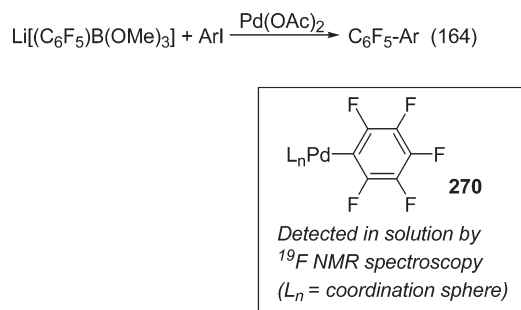
To discern the reactive surface intermediates in a variety of Pd -catalyzed coupling reactions, including the Suzuki–Miyaura cross-coupling reaction, Choudary and co-workers utilized EXAFS and XPS on an LDH-Pd^0 catalyst ($\text{LDH} = \text{layered double hydroxide}$) to monitor the coupling of aryl halides and arylboronic acids.¹⁰³² In particular, when starting with LDH-ArPdCl ($\text{Ar} = \text{Ph}$ or *p*-anisyl) treated with KF , surface transients of the type $(\text{Ar})(\text{Ph})\text{Pd-B}(\text{OH})_2$ were detected. These tricoordinate intermediates had a peak assignable to a Pd-B bond. The transient intermediates, on heating, yielded biphenyl or 4-methoxybiphenyl for $\text{Ar} = \text{Ph}$ and *p*-anisyl, respectively.

Solution analytical techniques such as NMR spectroscopy have repeatedly distinguished themselves as indispensable for the detection of Suzuki–Miyaura cross-coupling intermediates. In one example, Frohn and co-workers have utilized ^{19}F NMR to detect an arylpalladium species, **270** ($\text{Ar} = \text{C}_6\text{F}_5$), as an intermediate in a cross-coupling reaction (Scheme 144).

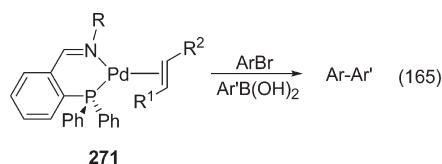
In a very detailed study of the cross-coupling of aryl bromides and arylboronic acids, Crociani and co-workers spectroscopically monitored reactions of the type shown in Scheme 145.²⁸⁶ Interestingly, though ^{31}P NMR spectroscopy indicated oxidative addition of Ar-Br is the slowest step of the cycle starting from **271**, transmetalation was shown to be faster than reductive elimination (the slowest step in the cycle appears to be system dependent, as kinetic data collected by Smith and co-workers on a Pd -catalyzed Suzuki–Miyaura cross-coupling system suggested the transmetalation step is the slowest step when using aryl iodides⁸⁶⁸ while Kishi and co-workers found oxidative addition was not rate determining in a system using vinyl iodides¹⁰⁶³). A borate-ligated intermediate (**205**, Scheme 108, vide supra) was isolated from the reaction milieu, presumably the precursor to aryl group transfer. In one case, a Pd-OH species (also presumably a precursor to transmetalation) was detected by ESI-MS.

An intriguing cross-coupling system has been reported by Wendt and Olsson.⁹⁸³ It has been previously shown that the

Scheme 144



Scheme 145

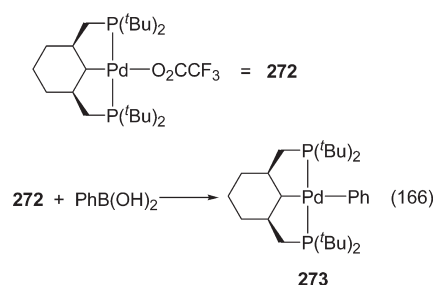


catalytic activity of palladacycles comes from the Pd nanoparticles formed from decomposition of the palladacycle. However, in the cross-coupling catalyzed by **272**, a mercury poisoning test suggested that no Pd⁰ was present and therefore nanoparticles were not forming. As corroborating evidence for transmetalation, ³¹P NMR spectroscopy indicated **272** and PhB(OH)₂ reacted to form **273** (Scheme 146). Since the latter reacted with aryl bromides to yield biphenyls, these combined data provided strong evidence for the intermediacy of **273** in a molecularly catalyzed cross-coupling cycle. High thermal stability and nearly identical catalytic results for a similar, adamantyl-based analogue of **272** in a nearly concurrent study led Frech and co-workers to almost the same conclusion.⁹⁸²

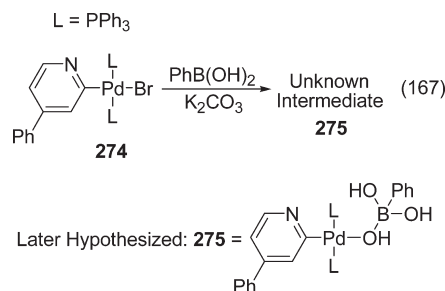
In another report showcasing the usefulness of ³¹P NMR spectroscopy for detecting reaction intermediates in cross-coupling reactions, Cid and co-workers used experimental and theoretical methods to discern reaction intermediates for the Pd-catalyzed cross-coupling of PhB(OH)₂ with bromopyridine.⁹⁸¹ An initially unknown intermediate, **275**, was detected (Scheme 147). Supplementing their data with calculations, **275** was ultimately assigned as the O-phenylborate-ligated complex shown in Scheme 147. Calculations on the reaction of the PH₃ analogue of **274** with PhB(OH)₃[−] suggested the transmetalation step is exergonic (ΔG = −14.9 kcal/mol in the gas phase but −8.5 kcal/mol when including solvation). A similar calculation of the reaction of the phenylated analogue of **274** with PhB(OH)₃[−] yielded similar values (ΔG = −11.3 kcal/mol in the gas phase but −6.5 kcal/mol when including solvation). Starting from isolated reactants, the highest activation barrier is 7.8 kcal/mol for the first reaction and 11.3 kcal/mol for the second reaction. In both cases, calculations suggested that transmetalation in the Suzuki–Miyaura system is not an elementary step but rather a composite of multiple steps. Scheme 148 shows the initial transition-state structure for transmetalation from the borate-ligated complex **275**.

In a DFT study by Maseras and co-workers, the full cycle of the cross-coupling of vinyl bromide with vinylboronic acid catalyzed

Scheme 146



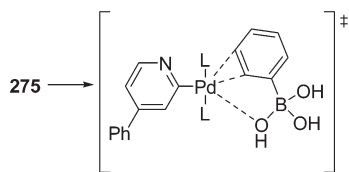
Scheme 147



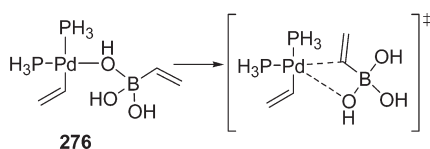
by Pd(PH₃)₂ was investigated.⁹⁶⁹ Calculations suggested that [−]OH first attacks the boronic acid, forming a borate ligand which then attacks Pd–Br to form Pd–vinylborate **276**. In all of the reaction pathways that were calculated, transmetalation occurs by vinyl group transfer from the vinylborate ligand of **276** to Pd; an example with the *cis*-variation is shown in Scheme 149. Regardless of the pathway (dissociative or associative), the calculations suggested that transmetalation by replacement of Br[−] with a vinyl ligand on Pd (with concomitant formation of B(OH)₃) is a highly exergonic step, with relative free energies ranging from −18.1 to −36.7 kcal/mol. This is in relative agreement with calculations by Maseras on an almost identical system, with a calculated energy difference of −17.4 kcal/mol between separated reactants and products.⁹⁴⁹

Also in 2006, the group of Maseras published another DFT study, this time specifically on the transmetalation step of the Suzuki–Miyaura cross-coupling of PhBr and PhB(OH)₂.⁹⁶¹ The catalyst used was Pd(PH₃)₂, and the base was [−]OH. Beginning the calculations from the oxidative addition product *trans*-[PhPd(PH₃)₂Br] (**277**), some general conclusions were drawn. The first was that the reaction of **277** with PhB(OH)₂ in the absence of a base is energetically unfeasible, endergonic by 32.3 kcal/mol with an energy barrier of nearly 49 kcal/mol (this agrees with theoretical studies of another Pd-catalyzed system in which the base-free activation energy to transmetalation was calculated to be 44.6 kcal/mol above the separated reactants⁹⁴⁹ and a Ni-catalyzed system in which base-free transmetalation via PhB(OH)₂ had an energy barrier of over 50 kcal/mol⁸⁴⁰). On the other hand, the reaction of **277** with PhB(OH)₃[−] was energetically favorable by −14.9 kcal/mol, and the highest energy barrier was only 10.8 kcal/mol above the isolated reactants. Interestingly, the most favorable path is one in which *trans*-[PhPd(PH₃)₂(OH)] reacts with PhB(OH)₂, a multistep pathway that is overall exergonic by −20.4 kcal/mol with a

Scheme 148



Scheme 149

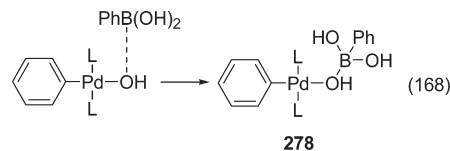


highest activation barrier of only 5.2 kcal/mol above the isolated reactants. The reaction is proposed to proceed through a series of steps similar to those found with other calculations, except that the PhB(OH)_3^- ligand on Pd forms by initial electrophilic attack of PhB(OH)_2 on the coordinated hydroxide ligand to form **278** (Scheme 150).

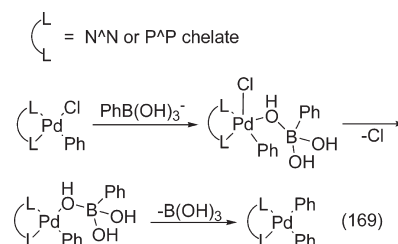
In an excellent theoretical study by Hong and co-workers, $\text{N}^{\wedge}\text{N}$ - and $\text{P}^{\wedge}\text{P}$ -chelated Pd was investigated in the coupling of PhCl with PhB(OH)_2 with ^-OH as the base.⁹⁷⁸ The route shown in Scheme 151 was calculated to be thermodynamically feasible. The calculated relative ΔG for the transmetalation step (the final step with extrusion of B(OH)_3) was -22.9 kcal/mol for the diimine-ligated Pd and -17.3 kcal/mol for the diphosphine-ligated Pd. Though calculated to proceed through a series of steps, the authors suggested the transmetalation proceeded through a three-centered transition state to give the activated complex **279** as shown in Scheme 152. Interestingly, the lowest energy of the transition state (17.0 kcal/mol) is seen for an electron-deficient diimine ligand. In addition and in agreement with previous studies of the Suzuki–Miyaura cross-coupling, in the absence of a base the activation energy for the transmetalation of Scheme 151 jumped to 34.4 kcal/mol and the overall reaction is endothermic. Other DFT calculations studying Pd-catalyzed systems yield broadly similar results, with activation barrier and relative energies that mostly depend on the coordination sphere of Pd and quaternization of B.^{950,966}

DFT studies of the Suzuki–Miyaura-type cross-coupling were not only restricted to Pd-catalyzed variants. A theoretical study of the full cycle of the Ni-catalyzed reaction of aryl esters with arylboronic acids was recently executed by Liu and co-workers.⁸⁴⁰ Starting from the oxidative addition product of $\text{Ni(PCy}_3)_2$ with PhOAc , that is, $\text{trans-[PhNi(PCy}_3)_2(\text{OAc})]$ (**280**), calculations on the transmetalation step elucidated trends roughly similar to those of Pd systems. First and foremost, the reactions had a prohibitively high barrier to transmetalation in the absence of a base (>50 kcal/mol). In addition, no reaction pathway could be extracted from the reaction of PhB(OH)_2 with **280** unless one phosphine dissociated from **280** (to form **281**). This parallels some of the dissociative mechanisms for Pd. Finally, the presence of a base lowered the activation barrier of the transmetalation, which was ascertained to be the rate-limiting step in the catalytic cycle, to ~ 31 kcal/mol. A four-centered transition state (shown in Scheme 153) bearing similarity to

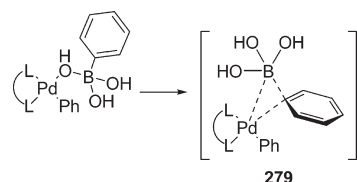
Scheme 150



Scheme 151



Scheme 152



those shown in Schemes 148 and 149 was proposed, ultimately collapsing to the transmetalated product **282**.

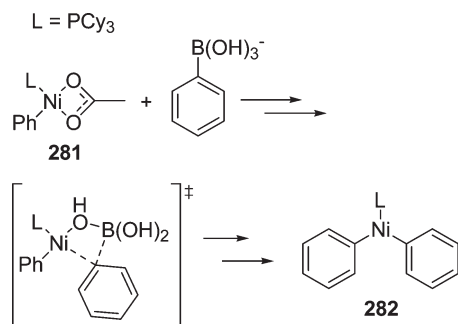
5.3. Applications in Organic Synthesis

Several of the reactions that are illustrated in Table 2 (all of which are believed to involve a transmetalation step) have been utilized in the synthesis of natural products (and other complex organic molecules) and pharmaceuticals. To further underscore the symbiosis through which stoichiometric transmetalation reactions and catalytic transformations (of Table 2) thrive, this section briefly discusses some examples of key metal-catalyzed steps leading to target organic molecules.

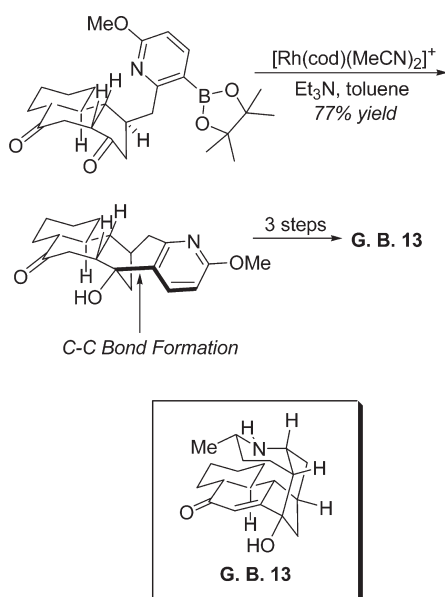
5.3.1. Rhodium-Catalyzed Arylation of a Ketone. Larson and Sarpong recently reported a total synthesis of the alkaloid G. B. 13.¹¹⁵⁰ Some of the most important considerations for a practitioner of applied transmetalation chemistry were key aspects of the investigation, for example, choice of metal catalyst and possible side reactions. Ultimately, a late-stage Rh^{I} -catalyzed arylation of a ketone was strategic to completion of the total synthesis (Scheme 154).

5.3.2. Copper-Mediated Carbon–Oxygen Coupling. With the objective of developing practical and concise routes to cycloisodityrosines, Takeya and co-workers used commercially available L-tyrosine derivatives and copper-mediated carbon–oxygen coupling to realize this goal.⁵⁰¹ Though protodeboronation was a significant side reaction, careful screening of the reaction conditions (and in particular meticulous screening of the amine base) ultimately proved fruitful, yielding two different L,L-cycloisodityrosines in moderate yield and minimizing the amount of protodeboronation side product (the most

Scheme 153



Scheme 154



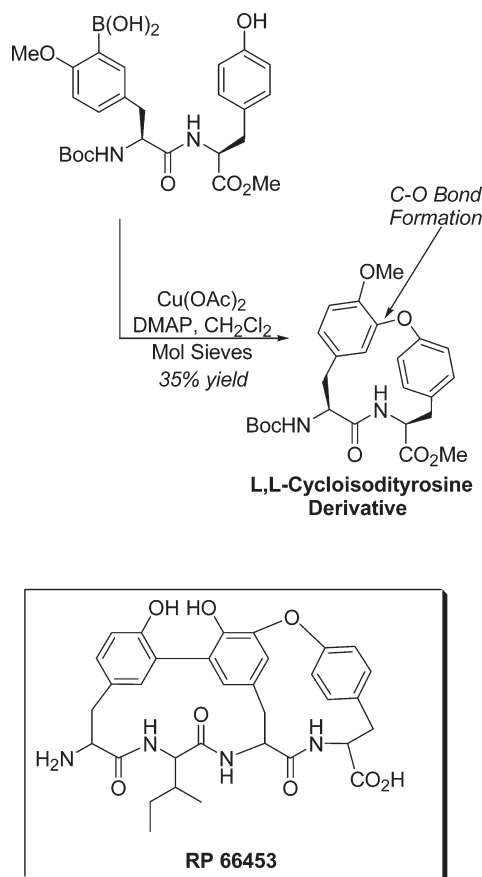
successful base was DMAP). It was noted that one of the cycloisodityrosines (shown as the product in Scheme 155) formed part of RP 66453 (a neurotensin receptor antagonist).

5.3.3. Rhodium-Catalyzed 1,4-Conjugate Addition to an Electron-Deficient Alkene. Hayashi and co-workers reported a methodological study of the Rh^I-catalyzed asymmetric 1,4-conjugate addition of organoboron compounds to various coumarins.⁵⁹⁴ In a showcase of the utility of the methodology, a synthesis of (*R*)-tolterodine (a urological drug) was included in the report (Scheme 156).

5.3.4. Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling. Carbon–carbon bond formation via the Suzuki–Miyaura cross-coupling reaction has been included as part of a review by Nicolaou.¹¹⁵¹ Two examples in which this methodology is featured prominently will be briefly discussed.

The synthesis of the cytotoxic natural product (–)-FR182877 by Evans and Starr¹¹⁵² featured the palladium-catalyzed Suzuki–Miyaura cross-coupling of a vinyl bromide and methylboroxine to form a trisubstituted olefin. A key step in the synthesis, the transformation was effected in 71% yield (Scheme 157). Elsewhere in the Suzuki–Miyaura cross-coupling literature, diastereoselective biaryl formation has been ubiquitous.^{1153,1154} One

Scheme 155



example was in the palladium-catalyzed, diastereoselective synthesis of ancistrotanzanine B, an antileishmanial alkaloid.¹¹⁵⁵ In the carbon–carbon bond forming step, diastereoselection was induced by using a chiral phosphine ligand (Scheme 158).

6. DECOMPOSITION REACTIONS THAT PRECLUDE DESIRED TRANSMETALATIONS

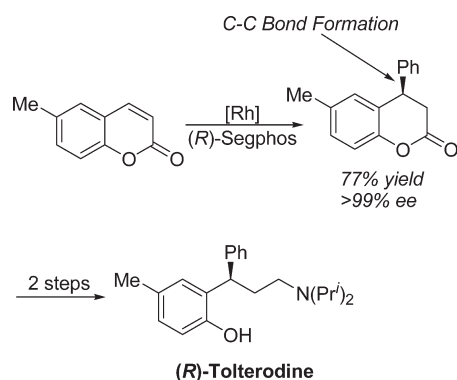
As has already been discussed, several catalytic transformations require organoboronic acids as stoichiometric transmetalating agents during the course of the catalytic cycle. However, in some cases, these transmetalation events are precluded from occurring due to decomposition reactions that occur either (a) before the transmetalation of the organic group occurs or (b) after the transmetalation occurs, but before the metal complex is able to transfer the organic group to the organic substrate of interest to “couple” the substrates (e.g., the reductive elimination step that forms biaryl in the Suzuki–Miyaura cross-coupling reaction).

6.1. Homocoupling of Arylboronic Acids (as a Side Reaction)

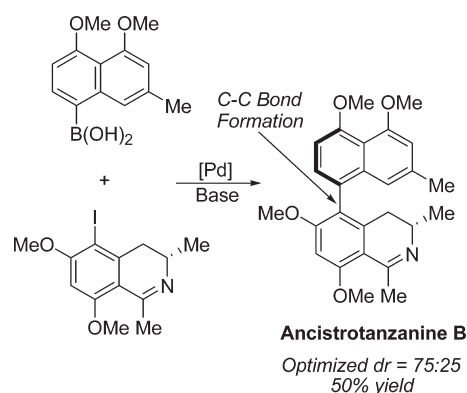
In catalytic coupling reactions discussed in this review, homocoupling of organoboron compounds is the second most common undesired side reaction (protodeboronation is the most common). Oxidative homocoupling occurs between two organoboron compounds in the presence of an oxidant to yield the C–C coupled product (Scheme 159).

As an undesired side reaction for catalytic coupling reactions with organoboron compounds, homocoupling byproducts have

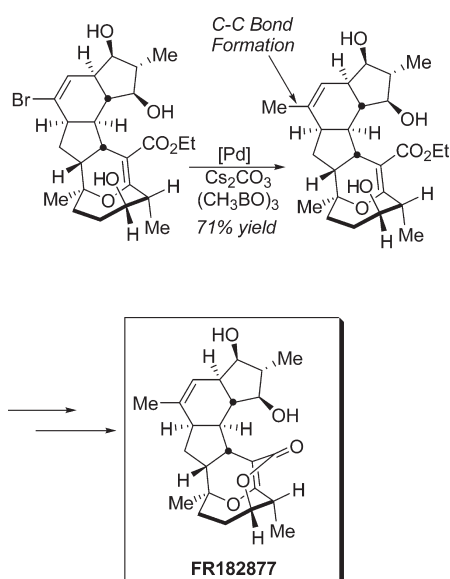
Scheme 156



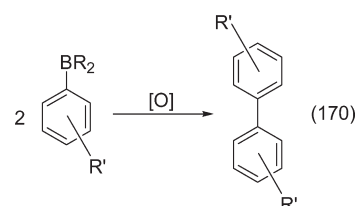
Scheme 158



Scheme 157



Scheme 159



been observed for (1) acylation of organoboron compounds,^{305,306} (2) arylation of allylic electrophiles,³⁹⁵ (3) arylation of benzylic electrophiles,^{990,991} (4) C–N coupling reactions,^{485,489} (5) 1,4-conjugate addition reactions,^{547,555} (6) desulfative homocoupling,⁶²³ (7) Heck-type coupling,^{637,642} (8) oxidative esterification of aldehydes,⁷⁵⁸ (9) sulfonylation of arenes,⁷⁷⁹ and (10) Suzuki–Miyaura-type coupling.^{144,639,942,963,993,997,1089,1156–1162} Some reports have indicated the amount of homocoupling byproducts formed decreases in the absence (or lowered amount) of oxygen^{942,1150,1156} or increases with increasing temperature.³⁰⁶ Surprisingly, an oxidative homocoupling byproduct (ascertained to be the *main* product) was even observed for a Suzuki–Miyaura cross-coupling under solventless conditions (ball milling in NaCl under air).¹⁰⁸⁹

6.2. Oxidation of Arylboronic Acids to Phenols

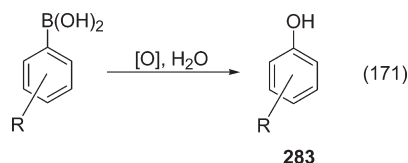
Another unproductive side reaction that occurs in some metal-catalyzed or -mediated transformations with arylboronic acids in the presence of an oxidant (such as oxygen) and water is the formation of phenols (Scheme 160). Obviously, formation of

phenol is tantamount to removal of arylboronic acid from the coupling cycle, ultimately precluding formation of product. In the laboratory, this means that a superstoichiometric amount of arylboronic acid must be used for full conversion to product. Some authors have cited the formation of phenols as a minor or competing side reaction. Evans and co-workers prepared a series of diaryl ethers from various phenols and arylboronic acids (Scheme 161).⁴⁹⁶ Consistently, however, more than 1 equiv of arylboronic acid relative to the phenol was required to maximize yield. In one reaction between 4-*tert*-butylphenol and PhB(OH)₂, GC/MS analysis of crude product mixtures indicated that phenol and diphenyl ether were two of the undesired side products, which were speculated to originate from the arylation of water (this was later confirmed).

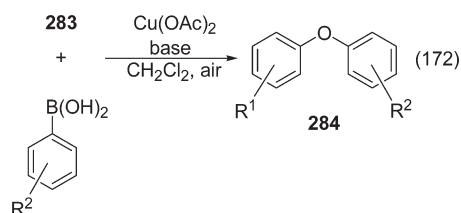
In the *N*-arylation of α -aminoesters studied by Lam and co-workers, *p*-tolylboronic acid was used as a stoichiometric arylating agent (Scheme 162).⁴⁵⁵ Yields ranged from 17% to 67%, but 2 equiv of *p*-tolylboronic acid was necessary. The authors cited the oxidation of the boronic acid to *p*-cresol as a competing side reaction. Moreover, in an insightful set of comparative experiments using ¹⁸O-labeling, the authors were able to demonstrate that, while an oxidant is necessary for phenol formation, the oxygen atom incorporated into the phenolic product is from water, confirming Evans's original hypothesis. Further confirming the source of oxygen as water, a separate investigation of the synthesis of symmetric diaryl ethers by Sagar and co-workers confirmed not only the necessity of water for product formation, but a yield enhancement proportional (up to 10 equiv of water) to the amount of water added (Scheme 163).¹¹⁶³

Batey and Huang investigated the Cu^{II}-catalyzed cross-coupling of organoboronic acids and sulfinate salts to form aryl and alkenyl sulfones **286** (Scheme 164).⁷⁷⁹ Though phenol was not a byproduct, biphenyl ethers (Ph–O–Ph) were formed in

Scheme 160



Scheme 161



significant quantities ($\geq 22\%$ yield) when $\text{Cu}(\text{OAc})_2$ was used in concentrations of 15 mol % or higher. The biphenyl ether was presumed to be the result of phenol formation and eventual reductive elimination of biphenyl ether (via phenoxide and phenyl ligands) from the coordination sphere of Cu^{III} . The authors used molecular sieves and an excess of arylboronic acid to minimize phenol formation and maximize product formation, respectively.

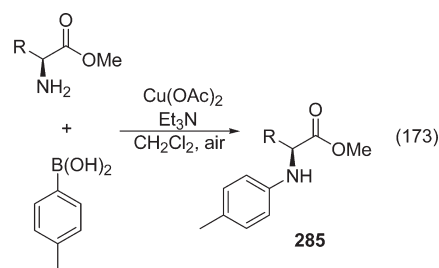
An iron-mediated oxidative arylation reaction of arylboronic acids and pyridine or pyrrole derivatives (Scheme 165) recently reported by Yu and co-workers required the presence of oxygen for the formation of products **287** and **288**.⁷⁴⁰ The ligands employed were from a series of 12-membered tetraazamacrocycles. As expected, the conditions (air and moisture present) led to formation of phenol as the main byproduct, which for one of the tetraazamacrocycles employed gave as much as 17% phenol as a byproduct. The optimization procedure was in part motivated by a desire to minimize phenol formation, which was accomplished with one of the tetraazamacrocycles.

Studer and Vogler demonstrated the Rh-catalyzed homocoupling of aryl- and alkenylboronic acids in good to excellent yield (Scheme 166).⁶⁹⁴ In this case, TEMPO was the preferred oxidant; these conditions lent themselves to formation of phenolic byproducts, which in fact was observed for the organoboronic acids which did not efficiently homocouple.

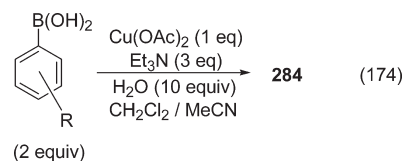
Sigman and co-workers reported the Pd-catalyzed hydroarylation of olefins by arylboronate esters in air (Scheme 167).⁶⁴⁹ One of the main questions the authors had during the course of this investigation was regarding the necessity of 3 equiv of arylboronate. Gas chromatographic monitoring of the reaction answered this question, as phenol was found to be the major byproduct (approximately 1.3 of the 3.0 equiv of arylboronate used formed phenol). The authors attributed this to the reaction of arylboronate with H_2O_2 formed from O_2 via catalytic turnover.

In their study of the AgOTf -mediated fluorination of arylboronic acids (Scheme 76, *vide supra*),²⁴³ Ritter and Furuya noted that the best solvent for the reaction was acetone, but molecular sieves needed to be added to suppress formation of phenol. In the presence of molecular sieves, the yield of phenol decreased to less than 2%. Formation of phenol was postulated to

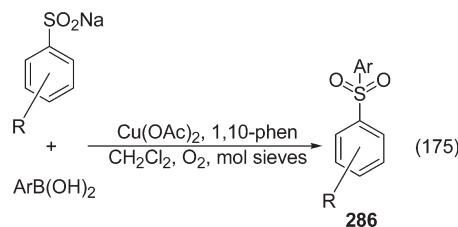
Scheme 162



Scheme 163



Scheme 164



be the result of reductive elimination of hydroxide and aryl ligands from the coordination sphere of the Ag^{II} intermediate.

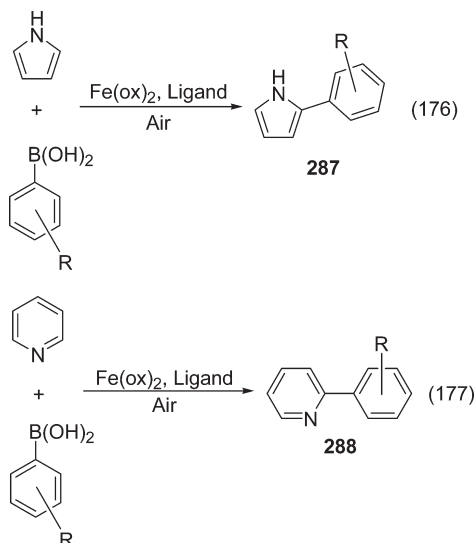
Other investigators have mentioned side reactions, including formation of phenols from arylboronic acids, as part of a reaction mechanism⁷⁵⁷ or as a reason for depressed yields in metal-catalyzed coupling reactions.^{459,1164}

6.3. Polymerization of Vinylboron Compounds

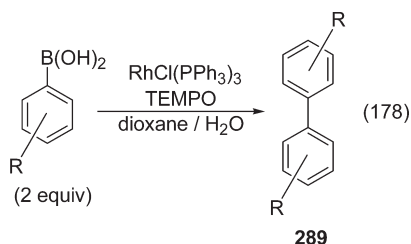
Vinylboronic acids are particularly problematic as transmetalating agents because of their tendency to decompose by polymerization. This is especially problematic in catalytic coupling reactions where a stoichiometric amount of the organoboron is required. The problem of polymerization of vinylboronic acid (also known as ethyleneboronic acid) was first noticed and discussed by Matteson.^{1165,1166} Matteson was able to prepare a 1:1 adduct of pyridine with 2,4,6-trivinylboroxine by distillation of butanol from a solution of the dibutyl ester of vinylboronic acid to azeotropically remove water, followed by addition of pyridine and distillation to azeotropically remove water and form the pyridine adduct **x** (Scheme 168). The identity of **x** was later structurally authenticated by X-ray crystallography as **291**.¹¹⁶⁷

O'Shea and Kerins took advantage of Matteson's work and used **291** (which they found to be a bench-stable solid) in the Pd-catalyzed cross-coupling reaction with various substituted aryl bromides and iodides to form substituted styrenes in 68–84% isolated yields (Scheme 169).¹¹⁶⁸ One of the approaches taken to circumvent polymerization is to use other organoboron compounds that are less prone to this route of decomposition. For

Scheme 165



Scheme 166



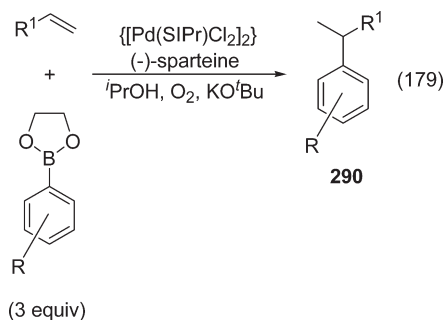
example, Molander and Rivero prepared potassium vinyltrifluoroborate **293** in one pot in 93% yield by the reaction of vinylmagnesium bromide with B(OMe)_3 , followed by fluorination via KHF_2 .¹¹⁶⁹ As a test case, the Suzuki–Miyaura cross-coupling reaction of **293** with 4-acetylphenyl triflate catalyzed by $\text{PdCl}_2(\text{dppf})$ in the presence of Et_3N proceeded in 95% yield (Scheme 170). In combination with other similar coupling conditions, (hetero)aryl halides, electron-rich or electron-deficient aryl triflates, and (*E*)-bromostyrene were vinylated in 60–95% yields.

Grubbs and Morrill also noted the problem of polymerization when trying to concentrate solutions of vinylboronic acid.¹¹⁷⁰ Their approach was to treat in situ generated vinylboronic acid with pinacol, thereby forming the boropinacolate ester **294**, a compound stable enough to be purified by silica gel column chromatography, in 60% yield (Scheme 171). The compound was further used in Ru-catalyzed olefin cross metathesis.

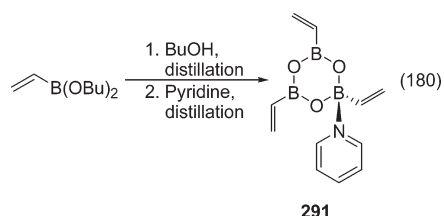
On the other hand, Whiting and co-workers found stability problems with **294** as a neat liquid when stored over the course of several months; a distinct thixotropy was also noted.¹¹⁷¹ Their solution to this was the pair of new arylboronates **295** and **296** (Figure 16), which were reported to pay dividends in the form of increased yields and ease of purification in Heck and Suzuki coupling reactions.

Whiting and co-workers later used vinylboronates **296** in Suzuki–Miyaura cross-coupling reactions and found that substituted aryl and alkenyl halides ($\text{X} = \text{Cl}$) coupled to form

Scheme 167



Scheme 168



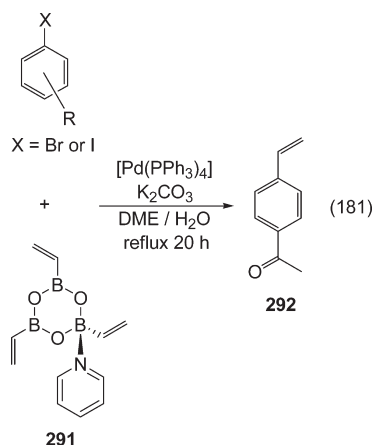
substituted styrenes and dienes in high yields.⁹⁵⁴ This indicated that the transmetalation step of the catalytic cycle occurred effectively.

6.4. Protodeboronation of Organoboron Compounds

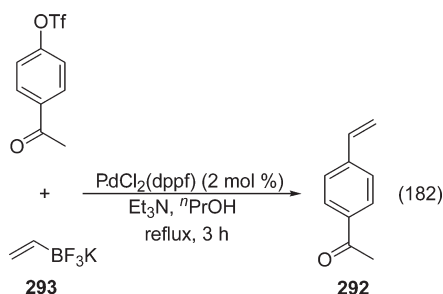
The displacement of an R group from an organoboron compound via substitution of a hydrogen atom for the $-\text{BR}_2$ or $-\text{B(OR)}_2$ functional group is most commonly called protodeboronation, but has also been called “protodeboration”,⁶⁹⁴ “deboronation”,¹¹⁷² “hydrodeboronation”,¹¹⁷³ “protonolysis”,¹¹⁷⁴ “protodeborylation”,⁷⁹⁷ “deboration”,¹⁰⁴⁰ and “hydrolytic deboronation”.⁸⁶³ In catalytic coupling reactions that utilize organoboron compounds, protodeboronation is the most frequently observed undesired side reaction. The overall transformation is depicted in Scheme 172 for reaction of ArB(OH)_2 with an acid, HA.

Several investigators have devoted a considerable amount of time and effort into identifying the factors that cause or prevent protodeboronation; a brief summary is presented. The rate of protodeboronation of (hetero)arylboronic acids usually (but not always) correlates with the acidity function H_0 for several different acids and depends on the substitution pattern of the boronic acid.^{1175–1179} Furthermore, protodeboronation probably proceeds by more than one mechanism in acidic solution.¹¹⁸⁰ In one investigation, even MeOH was acidic enough to cause protodeboronation of alkenyldicyclohexylboranes, but the more sterically hindered alkenyldisiamylboranes required a stronger acid.¹¹⁶⁸ Similarly, under acidic conditions boranes containing secondary alkyl groups appeared to protodeboronate less readily than those containing primary alkyl groups.¹¹⁸¹ For a series of fluorinated alkenyltrifluoroborates, Frohn and co-workers presented data showing that the rate of protodeboronation was proportional to the electron-richness of the alkenyltrifluoroborate and that, for $\text{C}_6\text{F}_5\text{BF}_3^-$ in 40% aqueous HF at 85–95 °C, the half-life to protodeboronation was about 1 h.¹¹⁶⁷ Perhaps unexpectedly however, in one series of experiments, it

Scheme 169



Scheme 170



was shown RBF_3^- (R = alkyl) was more resistant to protodeboronation by aqueous HF than ArBF_3^- (Ar = aryl). Some kinetic evidence suggests that, under acidic conditions, an arylborate ion is approximately a factor of 10^6 times more reactive in protodeboronation reactions than the corresponding arylboronic acid.¹¹⁸²

Base and certain metals were shown to catalyze protodeboronation;^{1183–1185} Frohn and co-workers also demonstrated base-catalyzed protodeboronation for fluorinated arylboronic acids but showed that the rate was inversely proportional to the number of fluorine atoms on the aryl ring and also depended on their location on the ring.¹¹⁸⁶

Several of the catalytic transformations discussed in this review have identified undesired protodeboronation as minor, competitive, or dominant modes of reactivity. The categories are (1) arylation of aldehydes,^{319,337} (2) arylation of benzylic electrophiles,^{985,990} (3) C–N coupling,^{455,459,465,485} (4) C–O coupling,^{501,503} (5) carbonylative coupling reactions,⁵²⁹ (6) 1,4-conjugate addition reactions to electron-deficient olefins,^{542,560,563,566,586} (7) desulfative coupling of thioorganics with arylboronic acids,⁶¹⁸ (8) Heck-type coupling,⁶³⁷ (9) homocoupling,^{669,674,691,694} (10) hydroarylation of alkynes,⁷⁰² (11) oxidative esterification of aldehydes,⁷⁵⁸ (12) Sonogashira-type coupling,⁷⁷¹ (13) Suzuki–Miyaura cross-coupling,^{503,797–799,809,846,850,863,865,885,914,916,936,943,976,1040,1045,1067,1153,1154,1166,1187–1190} and (14) tandem cyclization reactions,^{159,724,1119} including polymerization reactions and

Scheme 171

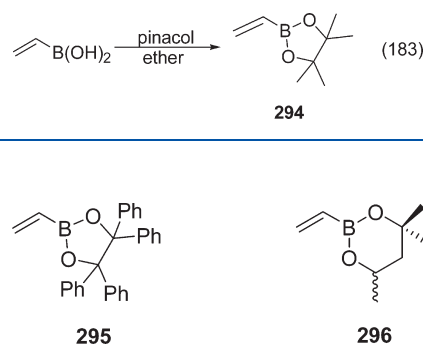
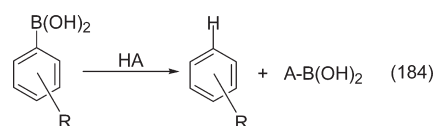


Figure 16. Vinylboronate esters developed to address polymerization of vinylboronic acid (and some of its derivatives).

Scheme 172



nanoparticle-catalyzed reactions. Although protodeboronation side reactions must be addressed on an individual basis, some of the most salient generalizations about this side reaction are (1) it is a common side reaction in Suzuki–Miyaura cross-coupling reactions between sterically demanding aryl coupling partners,^{846,850,863,885,943,1045,1067,1166,1182,1183} (2) avoidance of aqueous bases (for reactions that require a base) and/or scrupulously dry reaction conditions can help minimize the side reaction, and conversely, increasing the concentration of water can increase protodeboronation,^{459,563,691,976,1045,1067,1181} (3) it can show dependence on the base employed,^{1067,1181,1182} (4) in some systems it is solvent dependent,^{465,797,799,850,936} (5) it has been reported to be proportional to the reaction temperature,^{465,691} (6) it can show dependence on the substituents (not referring to the organic group) on the boron atom of the organoboron compound,^{846,863,916,1045,1067} (7) in Suzuki–Miyaura cross-coupling reactions, it can show dependence on the leaving group of the electrophile (coupling reactions with aryl chlorides are generally most difficult),⁹¹⁴ and (8) heteroarylboronic acids in which the heteroatom is α to the boron protodeboronate more readily.^{1171–1173,1191,1192} Other investigators have speculated on protodeboronation as a reason for depressed yields in certain catalytic coupling reactions or just as a possible factor to consider in their results.^{701,894}

7. CONCLUDING REMARKS

It is my hope that this review not only evinced the ubiquity of transmetalation as a synthetic route to organometallic complexes of the d-block metals, but also enhanced the reader's awareness of the almost codependent—if not symbiotic—relationship between stoichiometric transmetalation reactions and catalysis. Though not a defined “field” in and of itself, the transmetalation chemistry treated in this review can indubitably be further incorporated into the synthetic chemist's toolbox. However, as any experienced practitioner knows, over time one realizes there are gaps that need to be filled and improvements that can be

made within the current set of tools. As such, it is the author's opinion that some of the following questions address gaps or potential improvements in organoboron transmetalation chemistry with the d-block metals: (1) Can the relatively abundant and inexpensive d-block metals, such as copper and iron, show increased catalytic proficiency in coupling reactions more traditionally associated with the less abundant metals? For example, the Suzuki–Miyaura cross-coupling reaction is most strongly connected with palladium, but iron and copper have shown some potential to execute this same coupling reaction. (2) Will investigators further explore the organoboron-mediated transmetalation chemistry of cobalt and chromium in stoichiometric reactions and catalysis? Precisely one chromium-catalyzed homocoupling reaction and one cobalt-catalyzed alkyne hydroarylation reaction have been extracted from the set of organoboron transmetalation data, but there is only one example of stoichiometric organochromium synthesis from organoboron compounds and no examples of organocobalt syntheses from organoboron compounds. However, similar to copper in the catalyses discussed above, both chromium and cobalt have two easily accessible oxidation states (II and III for both metals) and can access (not easily) a third, less stable oxidation state (Co^{I} and Cr^{IV}). (3) Will transmetalation reactions using organoboronic acids be routinely demonstrated (if at all) for the early d-block metals? As mentioned above, transmetalation reactions with early d-block metals are typically observed using tetraarylborates (or tetraorganylborates).

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David V. Partyka received his undergraduate education from The College of New Jersey. As a graduate student at Harvard University under the supervision of Professor Richard H. Holm, he studied the biologically relevant inorganic chemistry of molybdenum, tungsten, and rhenium and received his Ph.D. in 2005. His postdoctoral work with Professor Thomas G. Gray of Case Western Reserve University was strongly focused on the synthesis of organogold complexes and their emission properties. In 2007, he founded Creative Chemistry LLC, a start-up company dedicated to the targeted preparation of air- and water-stable ligands and inorganic synthons of practical value to the practitioner of synthetic chemistry. In his free time,

Dr. Partyka enjoys cross-training workouts, reading classic literature and essays, watching and critiquing both great films and B-movies, savoring high-quality pizza and unfiltered beer, and, of course, reading the latest ACS publications.

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NOTE ADDED IN PROOF

A rhodium-catalyzed protocol for the cyanation of arylboronic acids has been developed, yielding a series of substituted benzotriazoles (Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 519). The authors invoke a transmetalation step in the catalytic cycle.

A rhodium-catalyzed protocol has been developed for the asymmetric addition of aryl and vinylboronic acids to *N*-benzyl-nicotinate salts, forming 6-substituted dihydropyridines (addition is α to the ring nitrogen atom at the 6-position). Arylation with phenylboronic acid has even been demonstrated when the 6-position of the pyridinium ring bears a methyl group (Nadeau, C.; Aly, S.; Belyk, K. *J. Am. Chem. Soc.* DOI: 10.1021/jall1540g).

A synthetic strategy that could lead to the catalytic carbonylation of olefins has been reported (Dauth, A.; Love, J. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 9219). The reactivity of a 2-rhodaaxetane complex with various organoboronic acid has been investigated as a potential key step in the carbonylation process. Spectroscopic data was collected which suggest the 2-rhodaaxetane complex reacts with organoboronic acids in a transmetalation reaction in which a new Rh—C bond is formed at the expense of the Rh—O bond (from the rhodaaxetane).