Reviews

Borylene Transfer from Transition Metal Borylene Complexes

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Transition metal borylene complexes ($L_nM{=}BR$) were predicted to be possible sources of the borylene fragment (:BR) in 1973, decades before the first complex had even been isolated. Over the past 15 years, routes to a small range of borylene complexes have been developed by a handful of research groups, including a family of active borylene donor complexes. Through these and other borylene donors, the borylene transfer to transition metal fragments has recently emerged as the most reliable and mild route to new transition metal borylene complexes, with the synthesis of a number of novel “second-generation” borylene complexes. Borylene transfer to alkynes was found to be a dependable route to the unusual “borirene” architecture, and more recently, the insertion of a borylene fragment into an unactivated alkenyl C−H bond has hinted at further borylene insertions into element−element bonds. This review covers borylene transfer reactions to both transition metal and main group substrates, from the first adventitious reports in the late 1990s up to the current state of intentional employment of the borylene transfer reaction in synthesis.

1. Introduction

“*...the quest for stable carbenoid complexes of transition metals seems worthwhile as they may provide useful sources of carbenoids in some reactions where the gaseous carbenoid species cannot be used successfully*” (P. L. Timms, *Accounts of Chemical Research*, 1973)

The borylene fragment “:B-X” has been a compelling subject of spectroscopic, theoretical, and synthetic chemical investigations since the 1950s, in particular the reactive diatomic BF molecule, due to its relation to the stable isoelectronic CO and N_2 molecules.[1] Attempts to generate and trap a useful quantity of this species were successful a little later, when the passage of gaseous BF_3 over solid boron at high temperatures by Timms et al. was reported to yield around 85% of the boron fluoride molecule (Figure 1), based on mass spectral evidence accounting for the amount of recovered product possessing fluorine−boron ratios greater than unity (including unreacted BF_3, B_2F_4, and B_3F_5) (Scheme 1).[2] Addition of an alkyne to the reaction mixture resulted in products with formulas consistent with a borylene−alkyne ratio of 1:1 and pointed to initial formation of cyclic three-membered borirene species followed by ring-opening and dimerization processes. In a 1973 account,[2b] Timms alluded also to the synthesis of a highly reactive product of the reaction of B_2F_4 and PF_3 with iron vapor, which he was unable to isolate. The suggested formula of the obtained product, $[Fe(PF_3)_4BF]$, was based on mass spectral, infrared, and ^{19}F NMR spectroscopic data and in hindsight seems plausible.

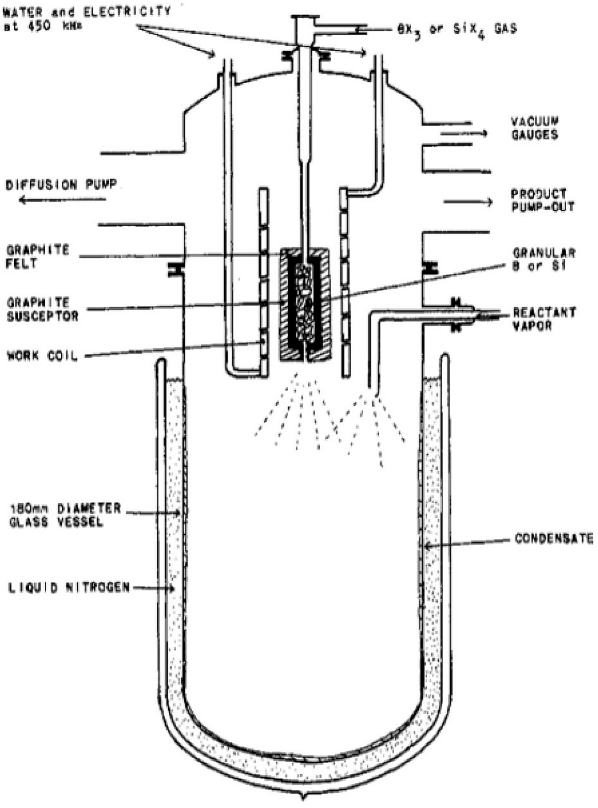

Figure 1. Schematic of the apparatus used by Timms to produce boron and silicon carbenoid species. Figure reprinted from P. L. Timms, *Accounts of Chemical Research*, 1973 (ref 2b).

However, Timms’ work lacked the characterization of a definitive product of expected “borylene” chemistry. In 1984

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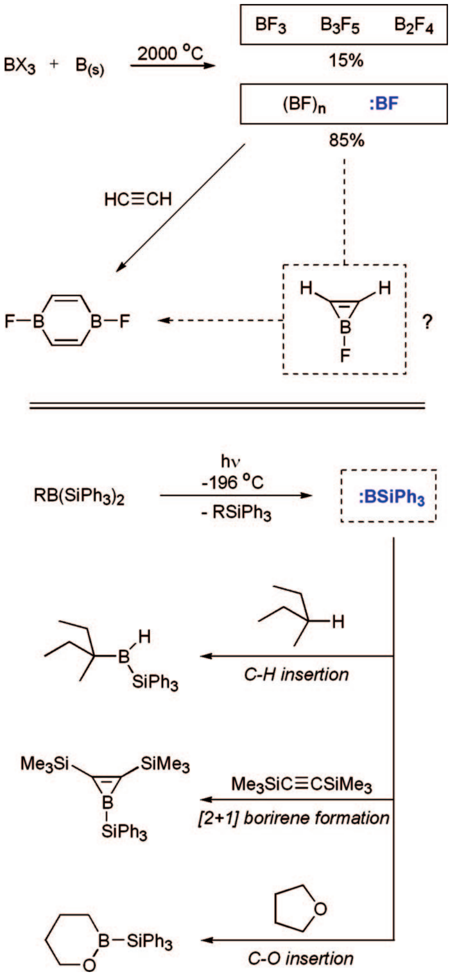
Scheme 1. Borylene Generation and Subsequent Reactions by the Groups of Timms (above) and West (below)



the group of West reported a number of well-characterized trapping products of their generated borylene "Ph_3SiB:", including products of borylene insertion into alkane C−H and ether C−O bonds, and of borirene formation with an alkyne, providing strong evidence for the borylene species (Scheme 1).[3]

While Timms' purported synthesis of an iron-borylene complex came relatively early,[2b] transition metal borylene complexes have developed far slower than their related carbene neighbors, with suitable synthetic routes being limited. As a result, only a handful of conveniently synthesized examples occur in the literature. The bridging dimanganese borylenes **I** were the first well-defined examples of borylene-type bonding,[4] while the first terminal borylene complexes, **II** and **III**, respectively, were synthesized by the group of Cowley[5] and in this laboratory in 1998 (Scheme 2).[6] The latter family of group 6 borylene complexes has since proved particularly adept in transferring the borylene unit to other transition metal substrates, giving a number of "second-generation" borylene complexes (vide infra). Later a family of cationic borylene complexes **IV** was discovered by Aldridge and co-workers. These currently are attracting much attention due to their facile reactivity.[7]

In addition to the aforementioned borylene transfer reactions, which are the focus of this review, borylene complexes show intriguing reactivity, as expected for low-coordinate boron species, with reactions including acid-induced B−N bond cleavage,[8] nucleophilic substitution[8−10] and addition,[7,11−13] metal-fragment addition[14−19] and extrusion,[18] dimerization,[20] cycloaddition,[21] and auxiliary ligand exchange.[22] The synthesis and some aspects of the reactivity of transition metal borylene compounds have been reviewed a number of times,[23] whereas the current review focuses on the transfer chemistry from transition metal borylenes beginning with the first report in 1995.[4] For simplicity we will consider "borylene transfer" to be a reaction, or series of reactions, in which both the original metal−boron bonds of a (terminal or bridging) borylene ligand are ruptured, and only such reactions will be covered herein.

2. Borylene Transfer to Main Group Substrates

Transfers from Dimanganese-Bridging Borylene Complexes. The first examples of complete cleavage of a borylene ligand from its transition metal support(s) feature, unsurprisingly, the archetypal bridging dimanganese borylene complexes developed in this laboratory.[4] Upon addition of trifluorostibine to $[\{(\eta^5\text{-}C_5H_4Me)(OC)_2Mn\}_2(\mu\text{-}BCl)]$ (**B1**), the known chlorostibinidine complex **1**[24] was observed along with chlorodifluoroborane (Scheme 3), while with elemental iodine the dinuclear

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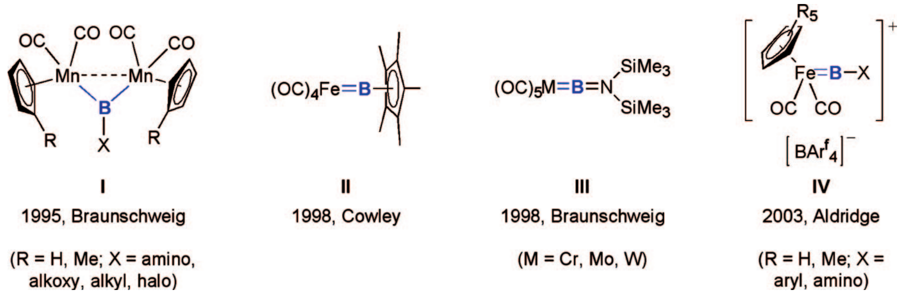
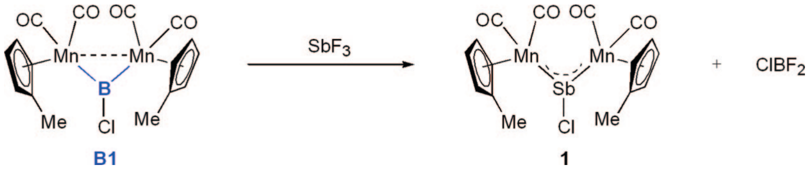
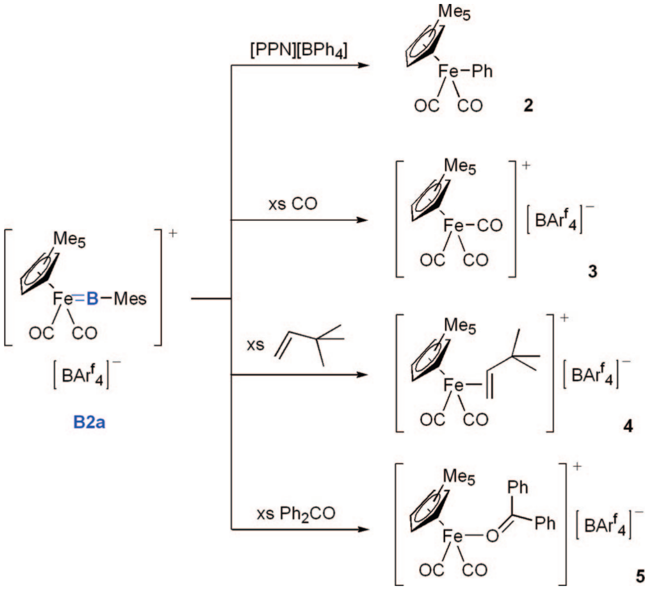
Scheme 2. Families of "First-Generation" Bridging (I) and Terminal (II–IV) Transition Metal Borylene Complexes ($Ar^f = 3,5-(CF_3)_2C_6H_3$)



Scheme 3. Transfer of a Borylene Fragment to Fluoride



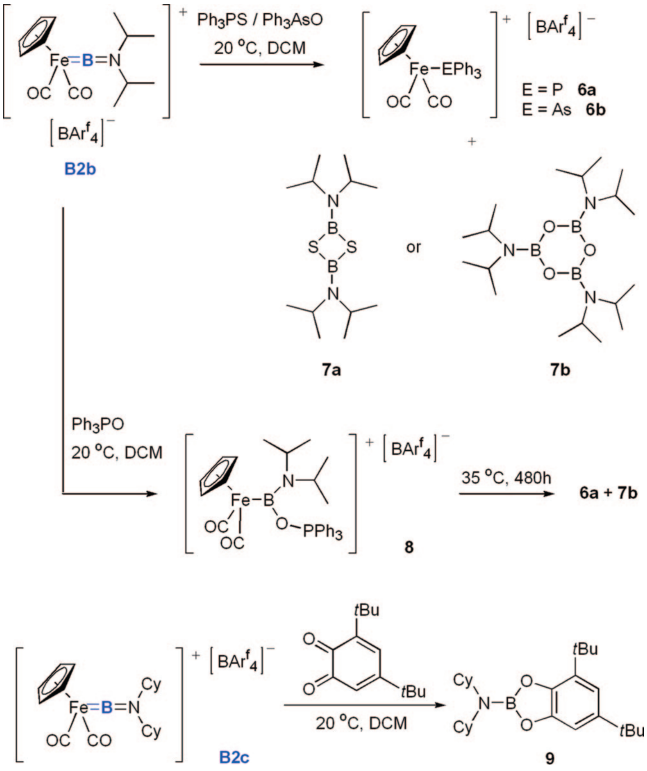
Scheme 4. Replacement of a Borylene Ligand with $C_6H_5^-$ and Common Donor Ligands



B1 framework was destroyed, providing MnI_2 as the only identifiable product.[23b] The decomposition of the Mn_2BX skeleton had been observed earlier. However these were the first examples in which the products of such a reaction could be definitively identified.

Transfers from Cationic Iron Terminal Borylene Complexes. Aldridge and co-workers discovered very early that the metal–boron bonds of their cationic borylene complexes **B2** underwent reactions with main group compounds.[25] Their first observation of a transfer reaction was one in which the iron atom of mesitylborylene complex **B2a** is attacked, formally, by a phenyl anion from [PPN][BPh_4] [PPN = $N(PPh_3)_2$], resulting in displacement of the borylene ligand. The isolated products were the phenyl complex **2** and BPh_3 (Scheme 4). A mechanism involving initial attack of Ph^- at the iron atom was favored over the alternative mechanism, featuring Ph^- attack at the boron atom followed by migration of the phenyl group to the iron. This work was extended with the discovery that the borylene ligand could be displaced by neutral two-electron donor ligands such as CO, 3,3-dimethyl-1-butene, and benzophenone to give the cationic iron complexes **2**–**5**. Noteworthy was that carbene-like reactivity, such as metathesis reactions or cycloaddition to the unsaturated substrates to give "C_2B" or "COB" ring systems, was not observed. In all of the above reactions the boron-containing product that was detected, on the basis of the spectral data, appeared to have resulted from borylene insertion into a C–H bond of the CH_2Cl_2 reaction solvent, namely, the dimer $[Mes(Cl_2CH)B(\mu\text{-}H)]_2$. This insertion mechanism was further supported by the isolation of $MesB(SMe)_2$ from the reaction of **B2a** with dimethyl disulfide.

Scheme 5. Reactions of Cationic Borylene Complexes B2b and B2c with O- and S-Donors



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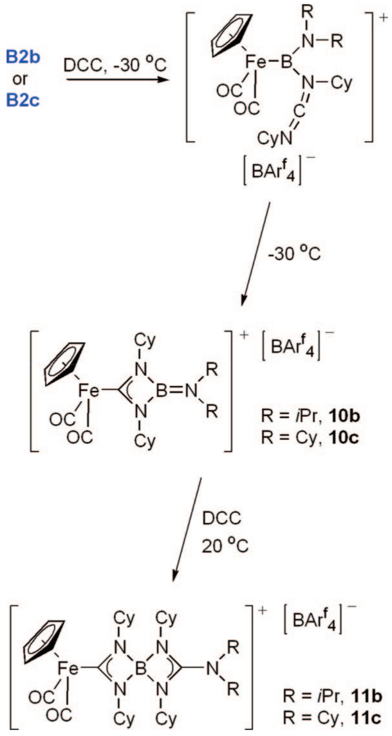
Scheme 6. Stepwise Insertion Reactions of Dicyclohexylcarbodiimide into M=B and B=N Bonds



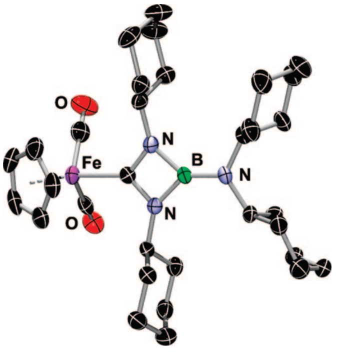


Figure 2. Molecular structure of **10c**. Thermal ellipsoids are set at the 50% probability level.

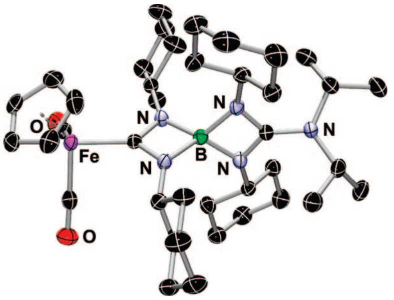


Figure 3. Molecular structure of **11b**. Thermal ellipsoids are set at the 50% probability level.

Soon after this initial study, Aldridge et al. reported the first interactions of external ligands with the boron atom of cationic borylene complexes (Scheme 5).[12,26] While in the earlier report the borylene ligand was cleanly displaced and reacted solely with the methylene chloride solvent, no reaction with methylene chloride was noted when Ph$_3$PS and Ph$_3$AsO were added to the cationic diisopropylaminoborylene complex **B2b**. However, the borylene fragment was lost from the metal, giving the iron-phosphine and iron-arsine complexes **6a** and **6b** and the cyclic chalcogenoboranes **7a** and **7b**. This net metathesis process established a link between the reactivity of the neighboring transition metal-borylene and -carbene families, just as free borylenes mimic free carbenes as reactive intermediates.[3] The analogous reaction with Ph$_3$PO at 20 °C instead yielded the simple triphenylphosphine oxide adduct (Ph$_3$PO$\rightarrow$B) **8**, which upon gentle heating (35 °C, 480 h) completed the metathesis, giving phosphine complex **6a** and boroxine **7b**. The isolation of complex **8** adds weight to a mechanism involving initial coordination of the P=X or As=X (X = O, S) moiety to the boron atom. From the iron-boryl-phosphonium canonical form of **8** it can be assumed that cycloreversion furnishes the metathesis products. A theoretical DFT investigation by Jemmis et al. in 2007 confirmed the initial attack of the nucleophilic chalcogen atom at boron, forming a relatively stable acyclic intermediate, whereupon the attached P or As accepts electron density from an iron d-orbital to form a four-membered transition state, which collapses with initial cleavage of the Fe–B bond.[27] In related studies, the reaction of **B2b** with H$_2$O in methylene chloride yielded B(OH)$_3$, [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$, and the corresponding secondary ammonium salt. In a later report,[13] it was found that 3,5-di-*tert*-butyl-*ortho*-benzoquinone strips the boron from the metal center of dicyclohexyl derivative **B2c** under mild conditions, forming the chelating amino(catechol)borane **9**.

More recently, Aldridge and co-workers reported the unexpected reaction of **B2b** and **B2c** with 2 equiv of dicyclohexylcarbodiimide (DCC) (Scheme 6).[28,29] Similar to the above reactions, the Fe=B linkage was completely cleaved, as well as, surprisingly, the usually robust B=N bond, providing **11b** (Figure 3) and **11c**. However, in contrast to the previous borylene transfer reactions, in which the boron atom was ejected from the complex, here it is held in place by two chelating dinitrogen "ligands" formed by the insertion of the DCC. The boron is bound to the two nitrogen atoms of a diaminocarbene-like (or amidinium-like) ligand, which is attached to the iron atom by the carbon atom, in addition to two nitrogen atoms of a guanidinium-like ligand, resulting in a tetrahedral, borate-like coordination of the boron atom, while the formal positive charges on the amidinium and guanidinium moieties provide the net positive charge on the complex.

Further reactions showed that the second insertion could be prevented by careful control of the temperature and addition rates, showing that the most facile insertion is that into the Fe=B bond, resulting in the diaminocarbene complexes **10b** and **10c** (Figure 2), the corresponding free carbene of which was prepared independently only one year earlier.[30] The second insertion was found to occur even at −20 °C, which is in accordance with previous reports of mild insertion of DCC into

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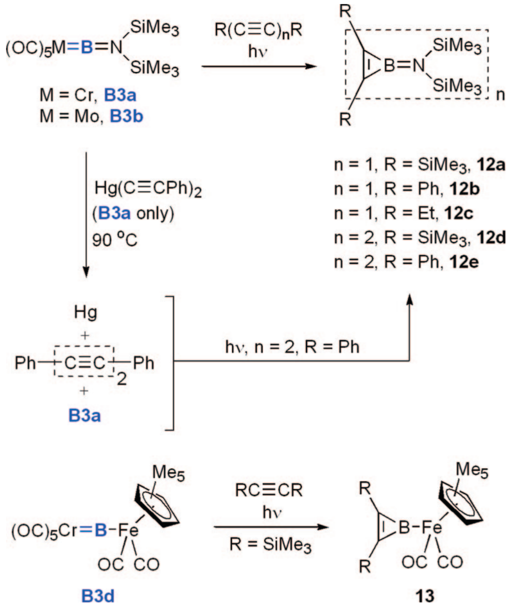
Scheme 7. Transfers of Amino- and Metalloborylene Fragments to Alkynes



B=N bonds of simple amino(dihalo)boranes.[31] Subsequent DFT calculations suggested that the reaction occurs with initial coordination of a nitrogen atom of DCC to the boron atom. From the intermediate thus formed, the slippage into the Fe=B and the B=N bonds is an exothermic process in both cases, much more so in the former. Thus the route is favored in which the strong B=N bond is retained in the product. No trace of the alternative (Fe−B) isomer was detected.

Transfers from Neutral Group 6 Terminal Borylene Complexes. Borylene transfer reactions from the other prominent family of terminal borylene complexes, the pentacarbonyl group 6 borylenes **B3**, developed in this laboratory, were until 2005 restricted to transfers to transition metal substrates (vide infra). This changed with the discovery of photochemical borylene transfer from **B3a** and **B3b** to a range of alkynes and diynes, providing borirenes **12a**−**c** and bis(borirene) **12d** (Scheme 7, Figure 4).[32] A few examples of the products of this reaction, the three-membered borirenes, had been synthesized previously, albeit via highly specific routes.[3,33] The most relevant of these is the reaction of a free, photochemically generated borylene with an alkyne at −196 °C by West and co-workers, formally analogous to the above reaction but involving a highly reactive intermediate species and proceeding in low yields.[3] The borylene transfer from the stable borylene complexes **B3** proceeds at room temperature in up to 88% yield and is thus a useful route to a range of borirenes with different R groups. An analogous borylene-alkyne transfer was observed later as the final step of the synthesis of bisborirene **12e** by the stoichiometric photochemical reaction of bis(alkynyl)mercurial [Hg(C≡CPh)$_2$] with borylene complex **B3a**.[34] The first step of this reaction was demercuration and coupling of the alkynyl groups, a process that in the absence of irradiation results in no net loss of the borylene fragment and was shown in substoichiometric reactions to be catalytic with regard to the metal complex. As expected, the reaction mixture from this experiment (containing **B3a**, diphenylbutadiyne, and metallic mercury) subsequently underwent borylene transfer when irradiated at room temperature, yielding diborirene **12e**.

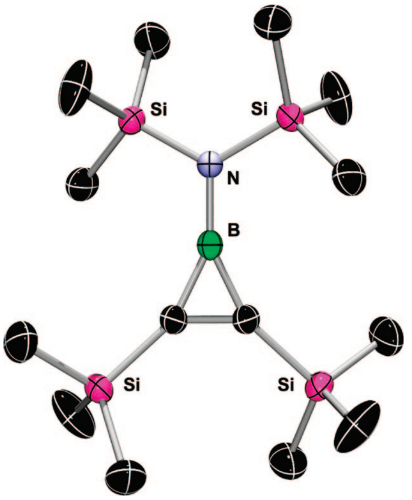


Figure 4. Molecular structure of **12a**. Thermal ellipsoids are set at the 50% probability level.

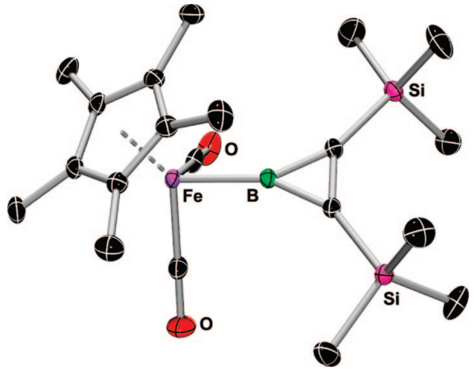


Figure 5. Molecular structure of **13**. Thermal ellipsoids are set at the 50% probability level.

The dimetallic borylene complex **B3d**[35] (Cr=B−Fe) provided an opportunity to test the limits of the photochemical borylene transfer reaction to alkynes, which, if successful in this case, would amount to the transfer of the "metalloborylene" fragment [:B−FeL$_n$]. The photolysis of **B3d** with bis(trimethylsilyl)ethyne occurred rapidly at room temperature, and the expected ferroborirene **13** was isolated and characterized (Scheme 7, Figure 5).[36] Through detailed theoretical calculations it was ascertained that the delocalization of the π-electrons from the backbone sp^2 carbon atoms was extensive and that the boron acts primarily as a σ-donor to the iron atom.

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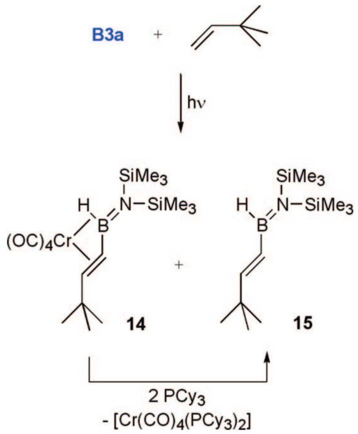
Scheme 8. Insertion of a Borylene Fragment into an Olefinic C−H Bond



In recent work, this laboratory has explored the photochemical reactions of borylene complexes of type **B3** with alkenes (Scheme 8).[37] While the [2+1] addition of a borylene fragment to an alkyne is expedited by the (2π-electron) aromatic stabilization of the resulting borirene compound, the product of the analogous reaction with an alkene would lack this stability, and thus we expected this line of research to be more complicated. Indeed, no saturated "bori*rane*" compounds were detected in the reaction of **B3a** with 3,3-dimethyl-1-butene; absent also were products corresponding to replacement of the borylene ligand with the alkene, as seen with Aldridge's cationic borylene complexes (vide supra). The products of this reaction, the free alkenylborane **15** and its chelating chromium-bound complex **14** (Figure 6), were isolated, both products of an insertion of the borylene fragment into a C−H bond of the alkene. Subsequently it was found that treatment of **14** with 2 equiv of tricyclohexylphosphine liberated **15**, forming [Cr(CO)$_4$(PCy$_3$)$_2$]. The selectivity for activation of only the *trans* vicinal C−H bond of the alkene, and the facility of the reaction even with an unactivated alkene, shows promise for the future use of this reaction in forming alkenylboranes of this type from alkenes.

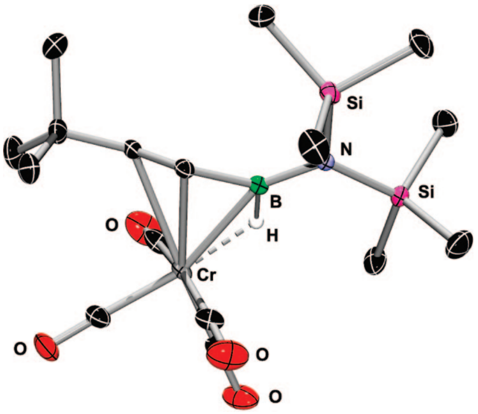


Figure 6. Molecular structure of **14**. Thermal ellipsoids are set at the 50% probability level.

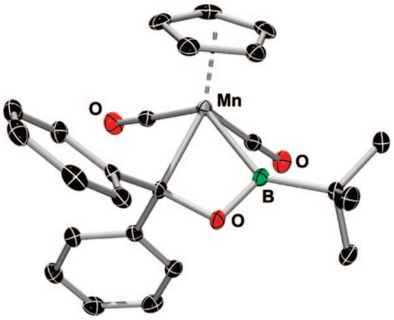
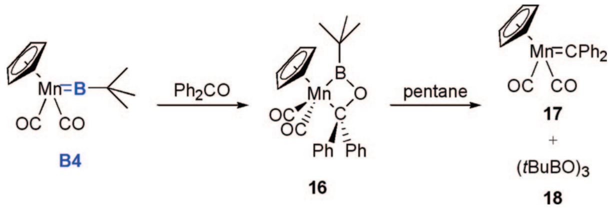


Figure 7. Molecular structure of **16**. Thermal ellipsoids are set at the 50% probability level.

Scheme 9. Stepwise Formal Metathesis of M=B and C=O Bonds



From Neutral, Terminal Manganese Borylene Complex [(η^5-C$_5$H$_5$)(OC)$_2$Mn(=B*t*Bu)]. Yet another difference between the reactivity of neutral and cationic borylene complexes was observed in the reaction of the terminal borylene **B4** with benzophenone.[21] In the case of the cationic borylene complex **B2a** (in methylene chloride solution), benzophenone merely displaced the borylene fragment, acting as a two-electron donor to the iron atom (**5**, vide supra). When benzophenone was added to terminal manganese borylene complex **B4** at −35 °C (in the absence of methylene chloride), the cyclic [2+2] addition product **16** precipitated (Scheme 9, Figure 7). Warming a solution of **16** to room temperature effected cycloreversion of the "OB*t*Bu" fragment, trimerizing to the boroxine **18**, leaving the diphenylcarbene complex **17**. This metathesis behavior, seen previously by Aldridge with abstraction of O or S from Ph$_3$PO, Ph$_3$PS, or Ph$_3$AsO, is a surprising result and an example of noninnocence of the carbonyl group of benzophenone.

3. Borylene Transfer to Transition Metal Substrates

The report of the synthesis of the pentacarbonyl group 6 terminal borylene complexes [(OC)$_5$M=B=N(SiMe$_3$)$_2$] (M = Cr, **B3a**; Mo, **B3b**; W, **B3c**) in 1998 reignited interest in metal−boron multiple bonding.[6] The facile synthesis of these complexes, namely, via salt elimination from dianionic metal carbonylates Na$_2$[M(CO)$_5$] (M = Cr, Mo, W) and an appropriate haloborane X$_2$BN(SiMe$_3$)$_2$ (X = Cl, Br), has rendered them attractive for a number of reasons, not least because they may be viewed as a source of the highly reactive borylene ":BR" moiety. While the so-called "salt elimination" protocol is successful in the synthesis of selected borylene complexes, its principal limitation is that this approach is restricted to a few specific combinations of transition metal dianions and dihaloboranes. This obstacle has spurred interest in finding alternate syntheses for compounds that are, at present, inaccessible by conventional methodologies. One synthetic approach to broaden the scope of available borylene complexes focuses on intermetallic borylene exchange, i.e., the transfer of a borylene moiety between two transition metal atoms. Indeed, intermetallic borylene exchange reactions first developed in this laboratory are increasingly becoming a valuable synthetic approach for M=B bond construction with alternative transition metals.

Transfer to Group 5, 6, and 7 Transition Metals. The facile synthesis of the above-mentioned terminal borylene complexes **B3** provided a turning point in the search for alternative synthetic

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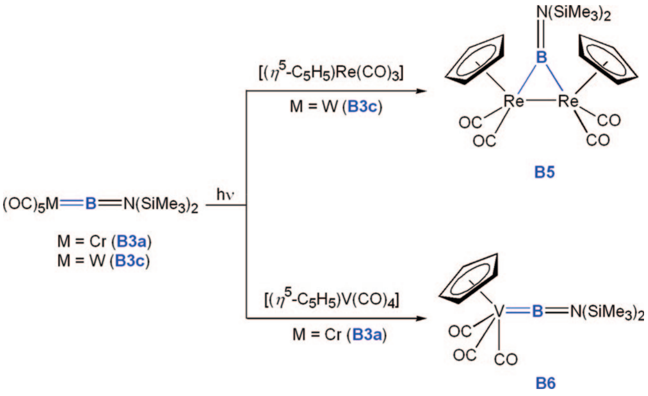
[37] Braunschweig, H.; Dewhurst, R. D.; Herbst, T.; Radacki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5978–5980.

Scheme 10. Photolytic Transfer of the “B=N(SiMe$_3$)$_2$” Fragment to V and Re Complexes



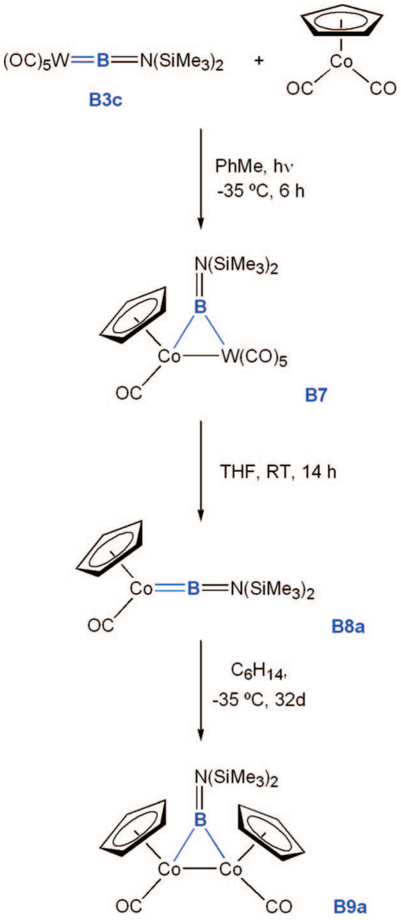
methodologies for borylene-containing transition metal complexes. It was found that photolytic irradiation of **B3c** in the presence of sources of the [Cr(CO)$_5$] fragment afforded an alternate route for the synthesis of **B3a**.[38] Initial investigations centered on the use of [Cr(CO)$_6$] as the source of the pentacarbonyl chromium moiety. However the formation of **B3a** was achieved only in 50% yield. Further investigation showed that use of the more soluble [(OC)$_5$Cr(NMe$_3$)] afforded **B3a** in quantitative yield (>95% by ^{11}B NMR spectral integration). Also, it was noted that replacement of the toluene solvent by THF resulted in decomposition of **B3c**, presumably by insertion of the borylene fragment into a THF C−O bond.

The photolytic activation of the “B=N(SiMe$_3$)$_2$” fragment of **B3c** was further utilized in its reaction with rhenium complexes (Scheme 10). While manganese complexes of the general formula [{LMn(CO)$_2$}$_2${μ-BNR$_2$}] (L = η^5-C$_5$H$_5$, η^5-C$_5$H$_4$Me; R = alkyl) can be prepared by more traditional synthetic approaches,[4,39] the corresponding rhenium complexes are not accessible using this approach. In contrast, photolytic irradiation of **B3c** with [(η^5-C$_5$H$_5$)Re(CO)$_3$] was found to yield [{(η^5-C$_5$H$_5$)Re(CO)$_2$}$_2${μ-BN(SiMe$_3$)$_2$}] (**B5**), in ca. 20% yield. The presence of the borylene-bridged dirhenium complex was indicated by the appearance of a downfield shifted resonance in its ^{11}B NMR spectrum relative to the signal ascribed to that of the parent tungsten borylene complex **B3c** (**B5**, δ_B: 100 ppm; **B3c**, δ_B: 87 ppm).

In a related approach, photolytic irradiation of [(OC)$_5$Cr=B=N(SiMe$_3$)$_2$] (**B3a**) in the presence of [(η^5-C$_5$H$_5$)V(CO)$_4$] afforded [(η^5-C$_5$H$_5$)(OC)$_3$V=B=N(SiMe$_3$)$_2$] (**B6**), the first half-sandwich compound with a terminal borylene ligand and the first example of a group 5 complex with an electron-precise boron−metal multiple bond (Scheme 10).[40] The formation of **B6** was demonstrated by an upfield shift in the ^{11}B NMR spectrum (**B6**, δ_B: 98 ppm; **B3a**, δ_B: 92 ppm). The molecular structure of **B6** confirmed the expected linear arrangement of the “V=B=N” moiety with the bond distances being within the range of those anticipated for a terminal borylene complex (V−B 1.959 Å; B−N 1.378 Å).

Transfer to Group 9 Transition Metals. In contrast to the scattered reports of intermetallic borylene transfer to group 5, 6, and 7 transition metals, there have been markedly more reports of the use of group 9 metal complexes as suitable substrates for borylene functionalization. Investigations of the reaction of **B3c** with [(η^5-C$_5$H$_5$)Co(CO)$_2$] demonstrated transfer of the borylene ligand from W to Co in a stepwise fashion (Scheme 11).[19] Photolytic irradiation of equimolar quantities of **B3c** and [(η^5-C$_5$H$_5$)Co(CO)$_2$] initially afforded the unusual heterometallic bridging borylene complex [(η^5-C$_5$H$_5$)(OC)Co{μ-BN(SiMe$_3$)$_2$}W(CO)$_5$] (**B7**), whose ^{11}B NMR spectrum shows the expected downfield-shifted resonance (**B7**, δ_B: 103 ppm; **B3c**, δ_B: 87 ppm). Structural characterization of the **B7** complex revealed an unusually long W−B bond [2.434(3) Å] in comparison to that observed for the parent terminal tungsten borylene complex **B3c** [2.151(7) Å], which is in agreement with an increase in the coordination number of the boron atom. By comparison, the Co−B bond distance [1.913(3) Å] is found within the expected range for complexes of this type.

Scheme 11. Stepwise Introduction of an Aminoborylene Moiety to [(η^5-C$_5$H$_5$)Co(CO)$_2$]



Complete transfer of the aminoborylene fragment from W to the Co atom was readily achieved by simple dissolution of **B7** in THF, to afford the first example of a terminal Co complex, [(η^5-C$_5$H$_5$)(OC)Co=B=N(SiMe$_3$)$_2$] (**B8a**).[19] Again, the terminal borylene complex **B8a** showed a characteristic shift in its ^{11}B NMR spectrum at δ_B 79 ppm. The unstable nature of the monometallic **B8a**, however, was demonstrated by its slow degradation to form the dimetallic complex [{(η^5-C$_5$H$_5$)(OC)Co}$_2${μ-BN(SiMe$_3$)$_2$}] (**B9a**) (Figure 8) through scavenging of a second [(η^5-C$_5$H$_5$)Co(CO)] fragment. The molecular structure of this dicobalt complex confirmed the bridging nature of the aminoborylene fragment, with its ^{11}B NMR shift of δ_B 106 ppm. The isolation of **B9a** in moderate yield (29%) was consistent with the nonstoichiometric formation of this new bridged species.

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(38) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H. G.; Neumann, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2298–2300.

(39) (a) Braunschweig, H.; Ganter, B. *J. Organomet. Chem.* **1997**, *545*, 163–167. (b) Braunschweig, H.; Koster, M. *J. Organomet. Chem.* **1999**, *588*, 231–234.

(40) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 205–208.

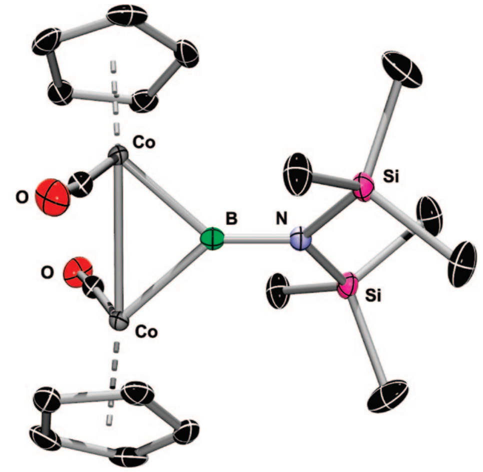
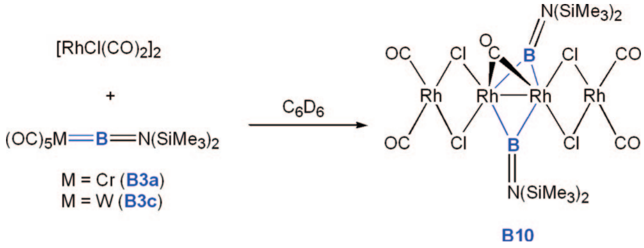


Figure 8. Molecular structure of **B9a**. Thermal ellipsoids are set at the 50% probability level.

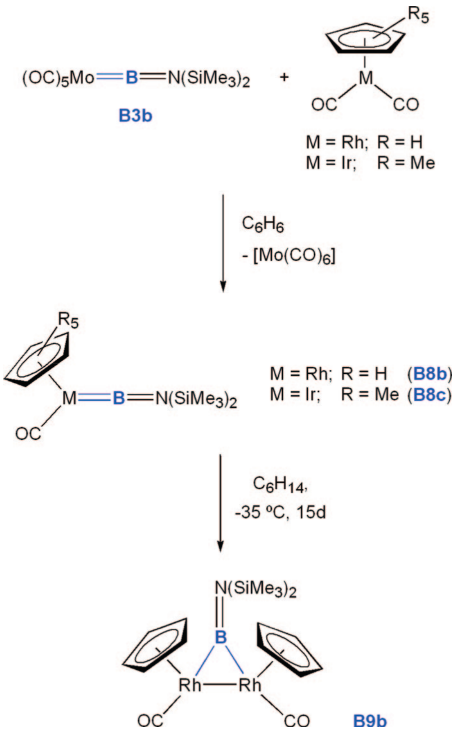
Scheme 12. Aminoborylene Transfer to [{RhCl(CO)$_2$}$_2$]



One principal limitation associated with the photoinduced transfer of the aminoborylene fragment from complexes of the type **B3a−c** is that the use of photochemically active substrates is precluded, and this has spurred investigation into alternative (i.e., nonphotolytic) methodologies for the synthesis of these “second-generation” borylene complexes. Treatment of **B3a** or **B3c** with the reactive rhodium dimer [RhCl(CO)$_2$]$_2$ at ambient temperature rapidly afforded an unusual tetranuclear rhodium complex that contains two bridging aminoborylene moieties, the first example of a doubly bridged borylene complex (Scheme 12).[41] The observed ^{11}B NMR spectroscopic resonance attributed to [Rh$_4${μ-BN(SiMe$_3$)$_2$}$_2$(μ-Cl)$_4$(μ-CO)(CO)$_4$] (**B10**) was surprisingly upfield-shifted in comparison to that of the parent borylene complexes (**B10**, δ_B: 74 ppm; **B3a**, δ_B: 92 ppm; **B3c**, δ_B: 87 ppm). The molecular structure of **B10** revealed that the internal metal atoms are bridged by two aminoborylene units alongside a bridging carbonyl moiety. The short B−N bond distances noted in both borylene fragments [1.369(4) Å] indicate significant B−N multiple bond character, while the close proximity [2.5786(3) Å] of the two internal Rh atoms (along with their formal odd-electron count) indicates the presence of a Rh−Rh bond.

In an alternative approach to intermetallic borylene transfer reactions, it was found that treatment of [(η^5-C$_5$R$_5$)M(CO)$_2$] (M = Rh, R = H; M = Ir, R = Me) with the more reactive complex **B3b** at ambient temperature afforded the first terminal borylene complexes of rhodium and iridium (Scheme 13).[42] The reaction of **B3b** with [(η^5-C$_5$H$_5$)Rh(CO)$_2$] was found to afford initially the terminal borylene complex [(η^5-C$_5$H$_5$)(OC)Rh═B═N(SiMe$_3$)$_2$] (**B8b**), as demonstrated by its ^{11}B NMR spectral data (**B8b**, δ_B: 75 ppm; **B3b**, δ_B: 91 ppm), which represents the first example of a terminal borylene complex of Rh. In a situation reminiscent of the related compound [(η^5-C$_5$H$_5$)(OC)Co═B═N(SiMe$_3$)$_2$] (**B8a**), [(η^5-C$_5$H$_5$)(OC)Rh═B═N(SiMe$_3$)$_2$] (**B8b**) was found to be of limited stability by its slow conversion to the borylene-bridged complex [{(η^5-C$_5$H$_5$)(OC)Rh}$_2${μ-BN(SiMe$_3$)$_2$}] (**B9b**) (Scheme 13, Figure 9). The dirhodium species exhibits a resonance in its ^{11}B NMR spectrum at δ_B 90 ppm, which is consistent with other complexes of this type. Additionally, the moderate isolated yield of **B9b** (37%) was again in line with the nonstoichiometric formation of this complex.

Scheme 13. Transfer of the “B═N(SiMe$_3$)$_2$” Fragment to [(η^5-C$_5$R$_5$)M(CO)$_2$] (M = Rh, R = H; M = Ir, R = Me)



In related studies, treatment of **B3b** with [(η^5-C$_5$Me$_5$)Ir(CO)$_2$] at ambient temperature cleanly formed [(η^5-C$_5$Me$_5$)Ir═B═N(SiMe$_3$)$_2$] (**B8c**) (Figure 10), the first example of a terminal borylene complex of Ir (**B8c**, δ_B: 67 ppm; **B3b**, δ_B: 91 ppm)

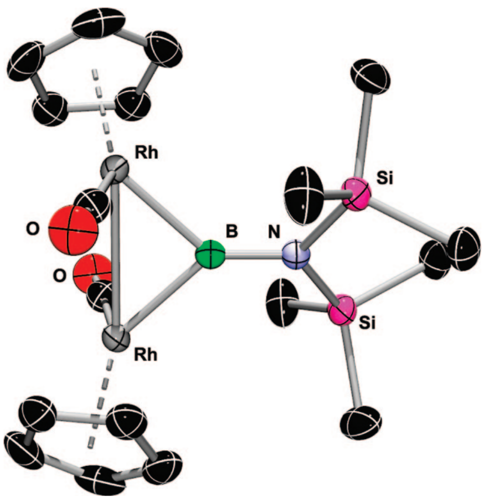


Figure 9. Molecular structure of **B9b**. Thermal ellipsoids are set at the 50% probability level.

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[41] Braunschweig, H.; Forster, M.; Radacki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2132–2134.

[42] Braunschweig, H.; Forster, M.; Kupfer, T.; Seeler, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 5981–5983.

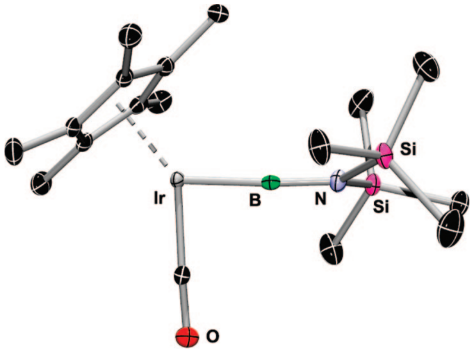

Figure 10. Molecular structure of **B8c**. Thermal ellipsoids are set at the 50% probability level.

(Scheme 13).[42] In contrast to what had been found for the related complex, $[(\eta^5\text{-}C_5H_5)Rh{=}B{=}N(SiMe_3)_2]$ (**B8b**), the desired monometallic Ir borylene complex (**B8c**) was found to be unreactive in terms of scavenging a second $[(\eta^5\text{-}C_5Me_5)Ir(CO)]$ fragment, a situation probably due to the relatively high steric shielding of the Ir metal atom by the bulky, electron-rich (η^5-C_5Me_5) ligand. The Ir−B bond length of **B8c** is short, 1.892(3) Å, which is as expected for a terminal borylene of this type. The use of the more reactive molybdenum borylene complex **B3b** represents a breakthrough in the syntheses of borylene complexes which suffer from photolytic and/or thermal instability and thus opens new synthetic avenues for the preparation of a wider scope of transition metal borylene complexes.

4. Summary and Outlook

Timms' prediction that transition metal-carbenoid complexes may be used as sources of the carbenoid[2b] has only recently been fulfilled in the case of borylenes, approximately thirty years after the prediction was made. The chemistry of transition metal borylene complexes still lags behind that of some neighboring main-group analogues, and the current repertoire of "first-generation" borylene complexes (i.e., those not prepared from borylene complexes themselves) is still limited to only a few families of complexes (see Scheme 2). However, the blossoming of examples of second-generation borylene complexes provides reassurance that in many cases metal−boron double bonds are indeed stable and that constructing them from simple starting materials is merely a question of finding a more general synthetic method. In terms of transfers to main-group substrates, the borylene insertion into alkenyl C−H bonds is a particularly exciting result, and one can envisage similar reactions with other "unactivated" C−H bonds, as well as main-group X−H bonds.[43] In addition to these less reactive targets, a wealth of more obvious unsaturated molecules and electron-rich transition metal complexes invite borylene transfer, and from the latter may arise previously unknown M═B linkages. In any case, the transfer of a borylene fragment has been found to be a surprisingly powerful technique for introducing boron into a substrate. Given future advances in the synthesis of the borylene-donor complexes, the borylene transfer reaction could find true application in the functionalization of simple chemical feedstocks.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. R.D.D. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship. H.B. is very much indebted to his present and past co-workers, in particular the late Dr. Daniela Rais, all of whom took up the challenge to develop the chemistry of borylene complexes over the past 15 years to its present stage.

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(43) During the reviewing process the reversible transfer of a borylene unit from ruthenium to dihydrogen was reported by Sabo-Etienne and co-workers. Upon addition of H_2 to *trans*-$[(Cy_3P)_2RuHCl({=}BMes)]$, a mixture of a borane adduct of ruthenium (*trans*-$[(Cy_3P)_2RuHCl(H_2BMes)]$), mesityl borane, and $[RuHCl(H_2)_2(PCy_3)_2]$ was obtained. When this mixture was placed under vacuum, the borylene complex was re-formed. Alcaraz, G.; Helmstedt, U.; Clot, E.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2008**, *130*, 12878–12879.