Electron-Precise Coordination Modes of Boron-Centered Ligands

Holger Braunschweig,* Rian D. Dewhurst, and Achim Schneider

Institut für Anorganische Chemie, Bayerische Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Received October 7, 2009

Contents

1. Introduction and Scope

1.1. The Transition Metal−Boron Bond

With the exception of those to boron, two-center covalent and dative bonds between transition metals and the first-row p-block elements have been known since the mid-1800s or before. As transition metals are most commonly electrophilic species, it is intuitive that such bonds have been more difficult to construct with those elements with less propensity toward nucleophilicity, i.e. carbon and boron. The dye known as Prussian blue (or *Berliner blau*) and the alkylzinc complexes prepared by Frankland in 1849 are considered the earliest known synthetic examples of complexes containing transition metal−carbon two-center bonds.[1,2] Similar M−C bonds also exist in biological systems such as vitamin B12 and complexes of cyanide and carbon monoxide with metalloenzymes.[3] In comparison, transition metal boryl complexes were first proposed in 1963[4] and structurally confirmed in 1990.[5,6] Reagents containing nucleophilic boron atoms were unknown until very recently, in marked contrast to those of boron's first-row neighbors carbon, nitrogen, oxygen, and fluorine. This, combined with the relatively late isolation and identification of elemental boron (in 1808),[7] has presumably contributed to the belated arrival of "bora-metallic" chemistry.

The steadily growing number of compounds with electron-precise transition metal−boron single bonds which are stable at room temperature (and above) is a clear sign that there is no inherent instability of such a linkage. Thus, it follows

---

* To whom correspondence should be addressed. E-mail: h.braunschweig@mail.uni-wuerzburg.de. Fax: (+ 49) 931-888-4623.

10.1021/cr900333n

Holger Braunschweig (born 1961 in Aachen) obtained his Ph.D. (1991) and Habilitation (1998) from the RWTH Aachen with P. Paetzold and stayed for a Postdoc with M. F. Lappert, FRS, at the University of Sussex, Brighton. After 2 years at Imperial College as Senior Lecturer and Reader, he moved to a chair for inorganic chemistry at the Julius-Maximilians-University Würzburg in 2002. In 2009 he was awarded the Gottfried Wilhelm Leibniz prize of the DFG and elected as a member to the Bavarian Academy of Sciences. His research interests lie in the area of boron chemistry, organometallic synthesis, and catalysis and are currently focused on borametallocenophanes, boron heterocycles, and transition metal complexes of boron.

Rian Dewhurst obtained his B.Sc. (Hons) (University of Canterbury, New Zealand) degree in 2002 and his Ph.D. (Australian National University) in 2006 after completion of his research with Professor Anthony F. Hill, for which he was awarded the The J. G. Crawford Medal of the ANU. After a postdoctoral stay in the research group of Professor Guy Bertrand (2006−2007, University of California, Riverside), he took up an Alexander von Humboldt Postdoctoral Fellowship in the group of Professor Holger Braunschweig (2007−2009, University of Würzburg). Since this time, Dr. Dewhurst has been an independent researcher at the University of Würzburg, funded by a grant from the Deutsche Forschungsgemeinschaft (DFG), and he has recently been awarded a Queen Elizabeth II Fellowship from the Australian Research Council. His research interests include the organometallic chemistry of furans and related biomass-derived heterocycles.

Achim Schneider graduated with a diploma degree in chemistry from the University of Würzburg in 2007, and for this he received the award of the Faculty of Chemistry and Pharmacy. Supported by the Fonds der Chemischen Industrie with a fellowship, he is currently working toward his doctoral degree with Professor Holger Brauschweig in the field of late transition metal complexes of boron-centered ligands featuring boron-element multiple bonds. In 2009 he suspended his studies in order to undertake an internship at BASF corporation in Ludwigshafen on the alternative syntheses of boron-containing compounds.

that any disparity between the transition metal complexes of boron and those of the other first-row elements must mainly be due to synthetic considerations. Until very recently, synthesis of such M−B bonds has relied exclusively on the presence of a metal fragment with sufficient nucleophilicity to attack the boron atom, for instance an anionic metalate salt or a low-valent, late transition metal complex. This, of course, severely limits the range of viable metal-containing precursors, as well as complicating practical aspects of their synthesis by precluding various solvents and reaction conditions. For one section of the transition metals, this difficulty is particularly salient: M−B bonds were unknown for the electron-poor transition metals of groups 3 and 4 (including lanthanides and actinides) until the very recent report of boryl complexes of Ti and Hf (vide infra). Presumably, this and other paucities may only be fully remedied with the future use of nucleophilic boron reagents.

Since the comprehensive 1998 review of Lesley, Marder, Norman, and Roper in this journal,[8] which focused mainly on transition metal boryl complexes, the areas of M−B multiple (borylene) and dative (borane or "boratrane") bonding have witnessed exceptional research interest. Just as E. O. Fischer's discovery of alkylidene (1967)[9] and alkylidyne (1973)[10] complexes reinvigorated the field of organometallic chemistry, the discovery of metal−boron multiple bonding has complemented the rapidly maturing field of transition metal boryl (i.e., "single bond") chemistry. Current synthetic routes to transition metal borylene and boride species lack generality and convenience, yet their fascinating reactivity more than compensates for the investment. On the other hand, the surprising discovery of the so-called "Z-type" borane ligands featuring direct M → B dative bonding was unprecedented in transition metal chemistry, and new families of these ligands are being uncovered regularly.

1.2. Scope of This Review

This review takes as its focus molecular compounds featuring "electron-precise" two-center metal−boron bonds (as shown in Figure 1). A number of areas of boron transition metal research exist outside this definition, i.e. ionic borides,[11] compounds with multicenter M−X−B interactions (e.g., σ-hydroborane,[12,13] σ-hydroborate,[14] polyborane, and carborane[15–17] complexes), and transition metal π-complexes of boron-containing heterocycles.[18] Each of these research fields is far too diverse in its own right to be covered comprehensively in this review, and each perhaps warrants reviewing independently.

As previously mentioned, a comprehensive 1998 review on transition metal *boryl* complexes exists in this journal,[8] and these complexes have been covered extensively with respect to their intermediacy in catalytic processes.[19] Thus, we have confined the section on boryl ligands to the recent

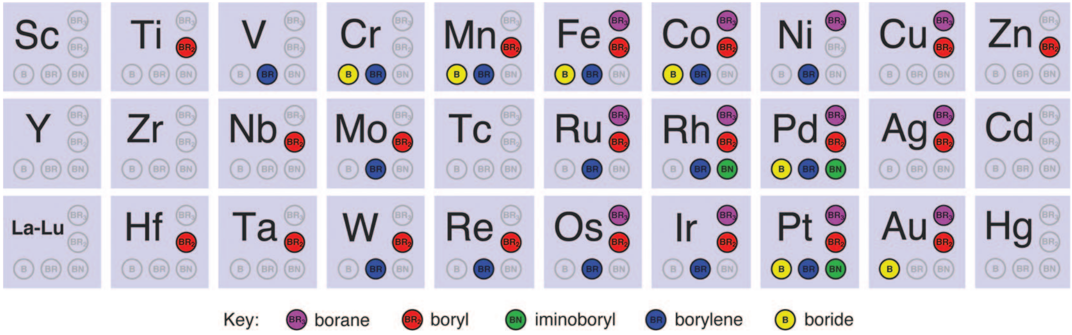


Figure 1. Section of the periodic table showing the transition metals, indicating their known complexes with electron-precise boron−metal bonds.

progress made in late-transition metal boryl complexes, a field which has seen a number of exciting developments in the past couple of years. Reviews covering other forms of metal−boron covalent and dative interactions have since appeared in a number of publications.[20–32] We have attempted to comprehensively cover the remaining sections regarding complexes with two-center M → B dative interactions ("borane"), B−R fragments as terminal or bridging ligands ('borylene'), and a lone boron atom as ligand ("boride").

2. Borane Ligands

2.1. Introduction

In 1963 Shriver reported a metal−boron dative bond in a complex formulated as $[(\eta^5\text{-}C_5H_5)_2WH_2(BF_3)]$.[33] However, these findings were refuted around 30 years later when differing products of the reaction of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ with alkylboranes were reported in a series of papers from this laboratory.[34–36]

At this time, the concept of transition metal basicity was a young one; as Shriver noted, "[transition metal] basicity toward acids other than the proton has never been demonstrated". His program of screening transition metal complexes for reactivity with boranes was nevertheless a prescient one, and it led to the development of metal basicity as a synthetic concept by the groups of Vaska, Werner, and others.[37] Shortly after the findings of Shriver, Parshall reported a number of transition metal complexes of BH_3 prepared by the action of borane−ether adducts on anionic transition metal carbonyls.[38]

Subsequently, a broad range of transition metal complexes of borane and halo- and arylboranes were reported, and their constitution (including direct M → B dative bonds) was based on infrared and NMR data.[39] However, it is perhaps telling that, even now, direct $L_nM \rightarrow BR_3$ (BR_3 = *unsupported* borane ligand) bonding is unsubstantiated structurally. The most plausible evidence for such a complex comes from the reaction of $[NEt_4][(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with BPh_3. Among other promising data, a ^{11}B NMR signal at δ −28.8 was observed, indicative of tetracoordinate boron. However, upon dissolution in THF, the purported borane ligand underwent migration to the cyclopentadienyl ring.[40]

It was not until 1999 when structural confirmation of a M → B bond was reported, consisting of a borane supported by three thione donor groups, by the group of Hill.[41] In marked contrast to the unsupported examples, a large number of supported complexes have since been structurally characterized in a relatively short time frame (see Table 1), containing a variety of different metal centers and supported by tethered sulfur, phosphorus, and nitrogen donor groups.

2.2. Borane Complexes with Sulfur Donor Groups

2.2.1. Borane Complexes of Group 8 Metals

The tris- and bis(azolyl)borates[42,43] (Tm^R and Bm^R, respectively, Figure 2) were the first species to act as proligands to the now well-represented family of boratrane complexes. The unique topology of the Tm^R and Bm^R ligands provides one extra atom in each binding arm (when bound: M−S−C−N−B) relative to the archetypal scorpionate ligands, the tris- and bis(pyrazolyl)borates (when bound: M−N−N−B). The effect of this extra atom is dramatic: the pyrazolyl arms of the (pyrazolyl)borates conspire to prevent propinquity of the metal and boron atoms, allowing at best a small amount of boron−metal interaction through B−H agostic bonds. In contrast, the geometry of the (methimazolyl)borate ligands grants the B−H group proximity to the metal such that in many cases the B−H bond is ruptured.

The first examples of boratrane complexes came in combination with Ru(II)[41] and Os(II)[44] species containing vinyl or aryl ligands which, when protonated, make relatively poor ligands and are easily lost by the metal. The net effect of boratrane formation in these cases is that both anionic ligands of the precursor are lost, providing a formally reduced complex of Ru(0) or Os(0), regarding the borane moiety as a neutral ligand.

In a number of cases the intermediate κ^3-Tm^R complex could be isolated: in the case of $[(\kappa^3\text{-}Tm^{tBu})Fe(CH_2SiMe_3)]$, application of CO induced loss of $SiMe_4$ and furnished the dicarbonyl boratrane complex **2.1a** (Figure 2).[45] Iron boratrane **2.1a** exhibited a relatively short Fe−B distance of 2.108(6) Å. Among the series of group 8 borane complexes, complex **2.1a** remains an outlier in terms of structural parameters, presumably due to perturbations from both the iron center and the considerably bulkier *t*Bu-substituted methimazolyl arms of the ligand.

Ruthenium tris(methimazolyl)borate complexes $[(\kappa^3\text{-}Tm^{Me})Ru(R')(CO)(PPh_3)]$ (R′ = CH=CH$_2$, CH=CHC(OH)Ph$_2$, CH=CHTol, Ph) were obtained in good yields by the addition of $Na[Tm^{Me}]$ to the corresponding ruthenium complexes $[RuCl(R')(CO)(PPh_3)_2]$ if the reaction was performed in diethyl ether.[41] If CH_2Cl_2 was used, or the intermediate borate complexes were dissolved in CH_2Cl_2, loss of R′H occurred, providing pseudooctahedral boratrane **2.1b**. The ^{11}B NMR spectra of **2.1b** showed a single peak at δ 17.1 and a Ru−B separation of 2.161(5) Å, similar to those of known boryl and borylene complexes of Fe and Os.

Addition of ligands such as CO and isocyanides to **2.1b** effected exclusive substitution of the L_{trans} phosphine ligand, allowing isolation of boratranes **2.1c**−**f**.[46] The ligand substitution was found in the case of CO to be

Table 1. List of M−B Distances and ^{11}B NMR Shifts for Borane Complexes Mentioned Herein

complex	M−B dist (Å)	δ_B	complex	M−B dist (Å)	δ_B
2.1a	2.108(6)		**2.9e**	2.050(8)	
2.1b	2.161(5)	17.1	**2.9f**		1.5
2.1c			[**2.10a**]Cl	2.157(4)	1.6
2.1d	2.176(7)	14.6	**2.10b**		0.4
2.1e			**2.10c**		2.1
2.1f	2.146(4)		**2.10d**	2.119(4)	5.1
2.1g	2.154(5)		**2.10e**		4.3
2.1h	2.171(8)	12.4	[**2.10f**]Cl		3.0
2.3a			**2.11**	2.073(4)	
2.3b			**2.13a**	2.903	80.1
2.3c	2.210(5)	−4.5	**2.13b**	2.663(8)	55.2
2.4a		3.2	**2.14**	2.306(3)	20.0
2.4b	2.179(4)		**2.15**	2.295(5)	19.4
2.4c	2.183(3)		**2.16**	2.374(3)	26.7
2.5a	2.132(6), 2.122(7)	1.7	**2.17a**	2.650(3)	47.0
[**2.5b**]Cl		3.1	**2.17b**	2.429(3)	22.8
[**2.5c**]Cl	2.155(7)	9.0	**2.18a**	2.309(8)	24.6
[**2.5d**]Cl			**2.18b**	2.335(5)	28.5
[**2.5e**]Cl		8.7	**2.19a**	2.168	15.9
[**2.5f**]Cl	2.146(3)	8.9	**2.19b**	2.254	27.3
[**2.5g**]Cl		−2.0	**2.19c**	2.220	18.2
[**2.5h**]Cl		9.1	**2.19d**	2.508	53.8
[**2.5i**]Cl		8.8	**2.19e**	2.540	59.1
[**2.5j**]Cl	2.153(11), 2.148(10)	9.5	**2.19f**	2.318	27.7
2.5k			[**2.19g**][GaCl$_4$]	2.448	56.6
2.5l	2.095(3)		**2.20a**		5.8
2.5m	2.15(2), 2.18(2)		**2.20b**	2.222(3)	4.3
[**2.6**]Cl	2.098(6), 2.091(5)		**2.20c**		3.7
[**2.7**][BPh$_4$]	2.132(4)		**2.21**	2.196(6)	−9.3
[**2.8**][PF$_6$]	2.155(5)	−7.5	**2.25a**	2.49(2)	
2.9a	2.108(4)		**2.25b**	2.51(2)	
2.9b	2.112(3)		**2.26**	2.444(9)	35.0
2.9c	2.079(13)		**2.27**	2.062(4), 2.090(4)	72.2
2.9d	2.112(3)				

reversible; addition of PPh$_3$ to **2.1c** regenerated the phosphine−carbonyl complex **2.1b**. The ligand substitution was found to have only minimal effect on the Ru−B bond length and ^{11}B NMR signal for those complexes examined (**2.1d**,**f**). Analogous chemistry with Na[Tm^{Me}] provided CS-ligated and osmium derivatives **2.1g** and **2.1h** from [RuCl(CH=CH$_2$)(CS)(PPh$_3$)$_2$][46] and [OsCl(Ph)(CO)(PPh$_3$)$_2$],[44] respectively. Complexes **2.1g** and **2.1h** also exhibited little deviation from the structural and spectroscopic parameters of boratranes **2.1b**−**f**.

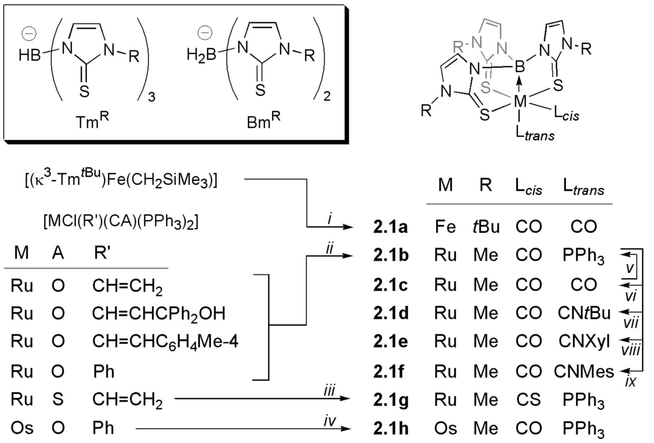


Figure 2. Synthesis of complexes of group 8 transition metals with thione−borane ligands. Key reagents and reaction conditions: (i) excess CO; (ii) K[Tm^{Me}], CH$_2$Cl$_2$; (iii) Na[Tm^{Me}]; (iv) Na[Tm^{Me}]; (v) PPh$_3$; (vi) excess CO; (vii) CNtBu; (viii) CNXyl; (ix) CNMes.

2.2.2. Borane Complexes of Group 9 Metals

It was with group 9 metals that the first tridentate borane complexes were prepared, comprising two sulfur-donor arms and a borane group, to which is attached either a hydrogen or another sulfur-donor arm. In the case of the latter, the third buttress is effectively prevented from forming by the presence of strongly bound ligands *cis* to the borane group (Figure 3).

Addition of Na[Bm^{Me}] to *trans*-[MCl(CA)(PPh$_3$)$_2$] (M = Rh, A = O, S; M = Ir, A = O) provides the first five-coordinate metal complexes, **2.2a**−**c**, containing an agostic interaction between the B−H bond and the metal, with loss of chloride and one phosphine ligand.[47,48] Upon standing at room temperature, complexes **2.2a**−**c** gradually undergo metal insertion into the B−H bond, affording doubly strapped borane complexes **2.3a**−**c**. Iridium complex **2.3c** was found to contain an Ir−B distance of 2.210(5) Å, with an ^{11}B NMR shift of δ −4.5.

Upon treatment of Vaska's complex *trans*-[IrCl(CO)(PPh$_3$)$_2$] with various salts of the anions [Tm^R]$^-$, similar doubly strapped borane complexes, **2.4a**−**c**, were obtained in which one arm of the ligand points away from the metal.[49] The strongly bound hydride and CO ligands which lie *cis* to the borane site presumably prevent binding of the third sulfur-donor arm, while the phosphine ligand now sits *trans* to the borane. Complex **2.4a** exhibited a broad ^{11}B NMR signal at δ 3.19, slightly downfield of that of related doubly strapped complex **2.3c** but still upfield with respect to signals of ruthenium boratranes (vide supra). Complexes **2.4b** and **c** showed slightly contracted Ir−B distances (2.179(4) and

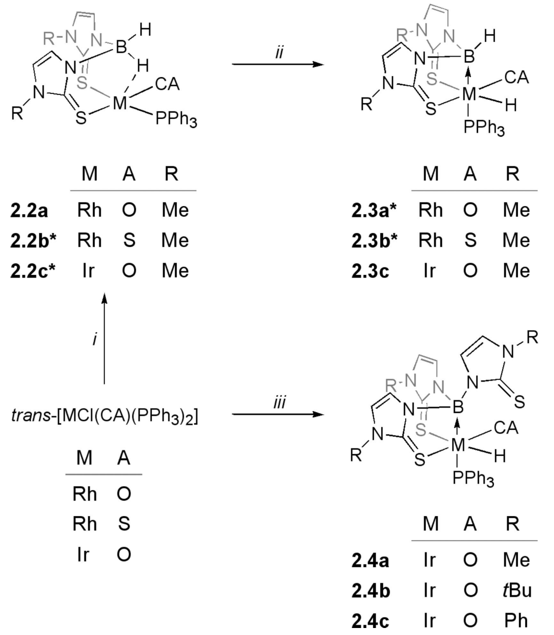


Figure 3. Synthesis of complexes of group 9 transition metals containing tridentate thione−borane ligands. Key reagents and reaction conditions: (i) Na[Bm^{Me}]; (ii) room temperature; (iii) Na[Tm^{Me}]/K[Tm^{tBu}]/Tl[Tm^{tBu}]/Li[Tm^{Ph}]. An asterisk denotes complexes that were detected but not isolated.

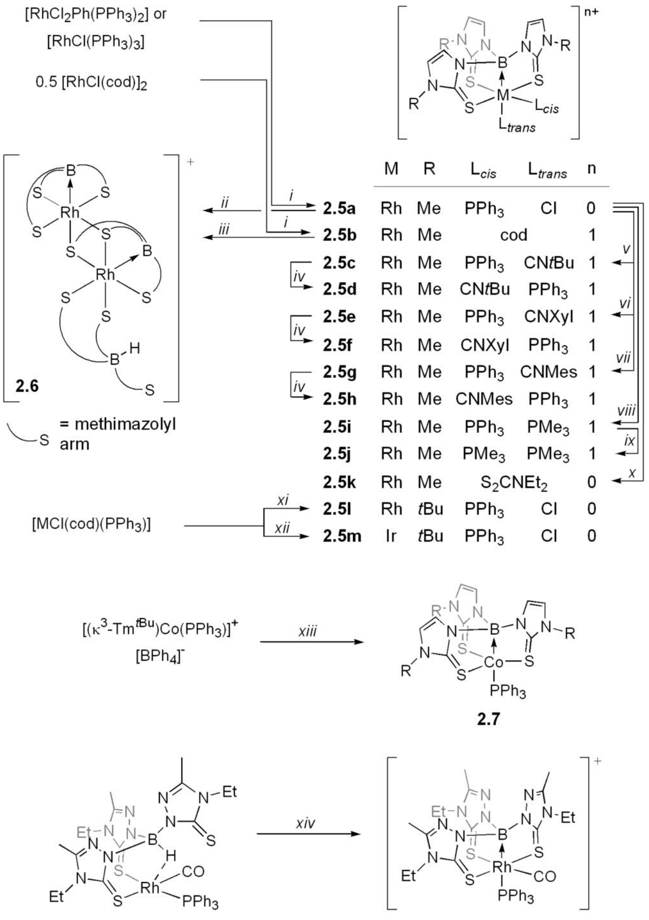


Figure 4. Synthesis of complexes of group 9 transition metals containing tetradentate thione−borane ligands. Key reagents and reaction conditions: (i) Na[Tm^{Me}]; (ii) room temperature; (iii) Na[Tm^{Me}]; (iv) refluxing CH_2Cl_2/ethanol (20:1); (v) CN*t*Bu; (vi) CNXyl; (vii) CNMes; (viii) PMe_3; (ix) excess PMe_3, refluxing CH_2Cl_2/THF (10:1); (x) Na[S_2CNEt_2]; (xi) M = Rh, K[Tm^{tBu}]; (xii) M = Ir, K[Tm^{tBu}]; (xiii) reaction conditions not specified; (xiv) [(η^5-C_5H_5)$_2$Fe][PF_6] (2 equiv).

2.183(3) Å, respectively) when compared with hydroborane complex **2.3c**.

Treatment of [$RhCl_2Ph(PPh_3)_2$] or [$RhCl(cod)_2$] with Na[Tm^{Me}] generates neutral and cationic boratrane complexes **2.5a** and [**2.5b**]Cl, respectively (Figure 4).[50,51] The latter reaction is presumed to occur with assistance from 1 equiv of a source of HCl, presumably from the chlorinated solvent. However, both **2.5a** and [**2.5b**]Cl can be converted to the dinuclear, cationic bis(borane) species [**2.6**]Cl, in both cases through loss of the L$_{cis}$ and L$_{trans}$ ligands. Boratrane **2.5a** converts to [**2.6**]Cl spontaneously at room temperature through a presumed disproportionation reaction, while [**2.5b**]Cl requires the addition of an extra equivalent of Na[Tm^{Me}] to complete conversion.

The L$_{trans}$ chloride ligand of **2.5a** is readily substituted by isocyanides "CNR" (R = *t*Bu, Xyl, Mes), or 1 equiv of trimethylphosphine, to obtain L$_{trans}$-substituted products [**2.5c,e,g,i**]Cl.[52] Heating of the isocyanide complexes [**2.5c,e,g**]Cl in a refluxing mixture of CH_2Cl_2/ethanol (20:1) effected exchange of the ligands L$_{cis}$ and L$_{trans}$, affording the thermodynamic products [**2.5d,f,h**]Cl. The more strongly bound L$_{cis}$ triphenylphosphine ligand can also be substituted by addition of a further equivalent of trimethylphosphine to [**2.5i**]Cl, providing [**2.5j**]Cl, or by addition of 1 equiv of a chelating diethyldithiocarbamate ligand to **2.5a**, providing **2.5k**. X-ray crystallographic analyses of related borane complexes **2.5a** (Rh−B: 2.132(6), 2.122(7) Å), [**2.5c**]Cl (2.155(7) Å), [**2.5f**]Cl (2.146(3) Å), and [**2.5j**]Cl (2.153(11), 2.148(10) Å) showed little variation in the Rh−B distance.

A similarly complex mechanism is noted in the synthesis of neutral boratrane complexes **2.5l** and **2.5m**, by addition of K[Tm^{tBu}] to [$MCl(PPh_3)(cod)$] (M = Rh, Ir, respectively).[49] A metal hydride signal is briefly observed in the former reaction mixture by ^{1}H NMR spectroscopy, suggesting the initial formation of a neutral hydride analog of **2.5l**, followed by replacement of the hydride ligand with chloride. This hydride complex was independently synthesized by addition of Li[BH_4] to **2.5l**, and the ^{1}H NMR hydride signal was found to be identical to that observed in the reaction mixture.

An unusual five-coordinate boratrane complex [**2.7**][BPh_4] was observed by the group of Rabinovich, by reduction of a cationic Tm^{tBu} complex of Co(II).[53] Although experimental details were not given, the complex was structurally authenticated, with the Co−B distance (2.132(4) Å) being significantly shorter than those in borane complexes of the second- and third-row transition metal elements Rh and Ir, similar to the relationship between Fe, Ru, and Os described in section 2.2.1.

In one interesting case, the metal → boron dative bond was constructed by chemical oxidative cleavage of the B−H bond of a rhodium complex featuring the κ^2-*S*,*S*-hydrotris(4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl)borate ligand.[54] Treatment with oxidant ferrocenium hexafluorophosphate provided triply strapped boratrane complex [**2.8**][PF_6], featuring a tricyclo-3,3,3,0-undecene ring structure similar to that in the methimazolyl-based boratranes above. Despite the altered triazolyl heterocyclic scaffold, the Rh−B distance (2.155(5) Å) is not markedly different from those of other cationic borane complexes of rhodium such as [**2.5c,e,j**]Cl.

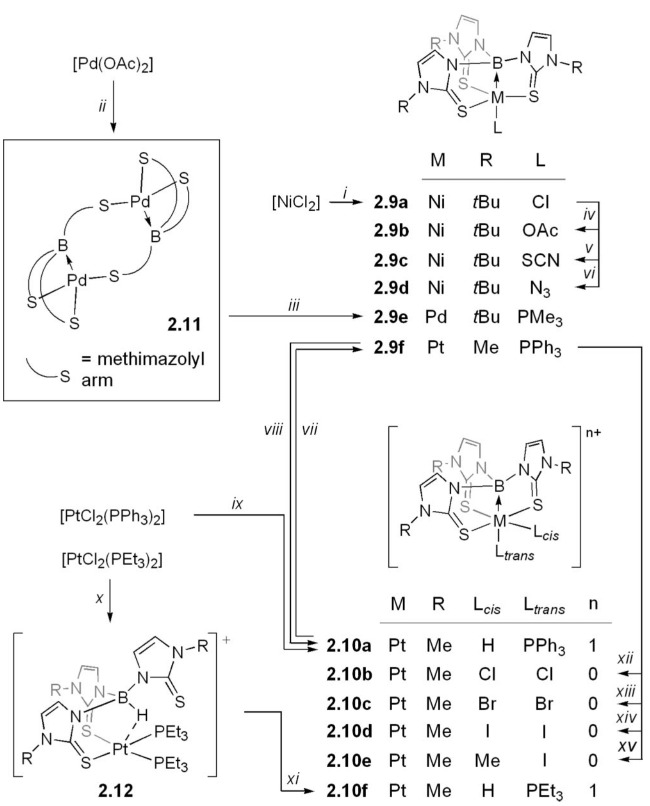


Figure 5. Synthesis of complexes of group 10 transition metals with thione−borane ligands. Key reagents and reaction conditions: (i) K[Tm^{tBu}]; (ii) K[Tm^{tBu}]; (iii) PMe$_3$; (iv) Tl[OAc]; (v) K[SCN]; (vi) Na[N$_3$]; (vii) DBU; (viii) HCl; (ix) Na[Tm^{Me}]; (x) Na[Tm^{Me}]; (xi) room temperature; (xii) Cl$_2$; (xiii) Br$_2$; (xiv) I$_2$; (xv) MeI.

2.2.3. Borane Complexes of Group 10 Metals

Sulfur−donor boratrane complexes of group 10 metals generally fall into two categories: five-coordinate complexes containing low-valent metals (Ni(I), Pd(0), Pt(0)), and six-coordinate complexes containing Pt(II). Addition of Li[Tm^{tBu}] or K[Tm^{tBu}] to [NiCl$_2$] effected reduction of the Ni center and led to Ni(I) borane complex **2.9a** (Figure 5).[55] This work by Tatsumi and co-workers was followed by a report from the group of Parkin in which the chloride ligand of **2.9a** was substituted by monoanionic ligands such as acetate, thiocyanate, and azide, creating complexes **2.9b**, **c**, and **d**, respectively.[56] The short Ni−B distances in complexes **2.9a**−**d** (2.079−2.112 Å) are in line with similar trends seen in borane complexes of Fe and Co and can be ascribed to the smaller radii of the metal atom.

Unlike the one-electron reduction seen in the synthesis of **2.9a**, addition of K[Tm^{tBu}] to [Pd(OAc)$_2$] formally liberates 1 equiv each of acetic acid and potassium acetate, forming the unsual bimetallic bis(borane) complex **2.11**, in which each borane ligand is bound κ^3-*SSB* to one metal and κ^1-*S* to the other.[57] Addition of PMe$_3$ breaks the dimeric system, providing the monomeric complex **2.9e**. Both **2.9e** and **2.11** contain unusually short M−B distances (2.050(8) and 2.073(4) Å, respectively) and remain the only structurally authenticated examples of formally zerovalent group 10 borane complexes.

Addition of Na[Tm^{Me}] to *trans*-[PtCl$_2$(PPh$_3$)$_2$] or *trans*-[PtCl$_2$(PEt$_3$)$_2$] provides, in both cases, cationic hydrido borane complexes ([**2.10a**]Cl and [**2.10f**]Cl, respectively) in which the B−H bond has been added across the Pt center.[58,59] Through base-mediated loss of HCl, [**2.10a**]Cl can be reduced to pentacoordinate complex **2.9f**, while the reverse oxidation reaction occurs readily with addition of HCl.[58] Similarly, **2.9f** can be oxidized by moderate to strong oxidants Cl$_2$, Br$_2$, I$_2$, and MeI, effecting loss of the phosphine ligand and oxidative addition of the reagents across the Pt center.[60] Interestingly, the resulting complexes **2.10b**−**e** were formed without net disruption of the boratrane cage system despite the aggressive conditions.

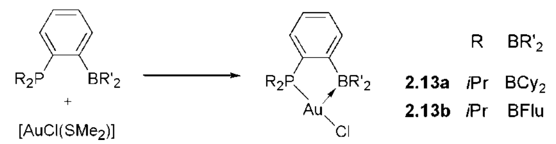


Figure 6. Synthesis of transition metal complexes containing bidentate phosphine−borane ligands.

2.3. Borane Complexes with Phosphorus Donor Groups

2.3.1. Complexes with Bidentate (κ^2-PB) Borane Ligands

The phosphorus-donor family of borane complexes is young in comparison to their sulfur-donor cousins, despite the relative simplicity of the phosphine−phenylene−borane skeleton and the absence of a B−H bond, which must be broken as a prerequisite for M → B bond formation. But like the sulfur-donor examples, the resulting structural motif is a five-membered ring containing D → M → B (D = donor atom) and closed with two sp^2-hydridized P-block atoms (C,N or C,C), which presumably provide the rigidity necessary to hold the borane in the metal coordination sphere.

The simplest supported borane ligand is that with only one donor moiety, and this was targeted by Bourissou and co-workers through design of phenylene-based phosphine−boranes iPr$_2$P(1,2-C$_6$H$_4$)BCy$_2$ and iPr$_2$P(1,2-C$_6$H$_4$)BFlu (Figure 6).[61] Addition of [AuCl(SMe$_2$)] to these phosphine−boranes provided the borane complexes **2.13a**,**b**. Formation of **2.13a** is accompanied by a very small downfield movement of the ^{11}B NMR signal (from $\delta = 76-80$) when compared to the free ligand, while the corresponding signal of **2.13b** is found significantly high-field-shifted at $\delta = 55$. The contrast between the two complexes **2.13a** and **2.13b** is reflected also in their Au−B distances, as determined by X-ray crystallographic analysis. The Au−B distance of **2.13a** (2.90 Å) is significantly longer than that of **2.13b** (2.663(8) Å), yet both remain shorter than the sum of the van der Waals radii of the two atoms. Interestingly, both metal−boron distances are much longer than those of the sulfur-donor borane complexes (2.0−2.2 Å, vide supra).

Given their bidentate architecture, complexes **2.13a**,**b** are the least supported of all structurally authenticated borane complexes, and are thus conceptually the closest known approximations to the long-sought-after "unsupported" borane systems. This feature may also play a part in the observation of long M−B distances.

2.3.2. Complexes with Tridentate (κ^3-PPB) Borane Ligands

The diphosphine−borane PhB{(1,2-C$_6$H$_4$)PiPr$_2$}$_2$ reacts with the rhodium(I) dimer [RhCl(NBD)]$_2$ to replace the diene ligand, retaining the bis(chloro) bridged dimer structure and providing the *fac*-κ^3-*PPB* bis(borane) complex **2.14** (Figure 7).[62] The monometallic derivative **2.15** was prepared by addition of the donor ligand DMAP to **2.14**, breaking the

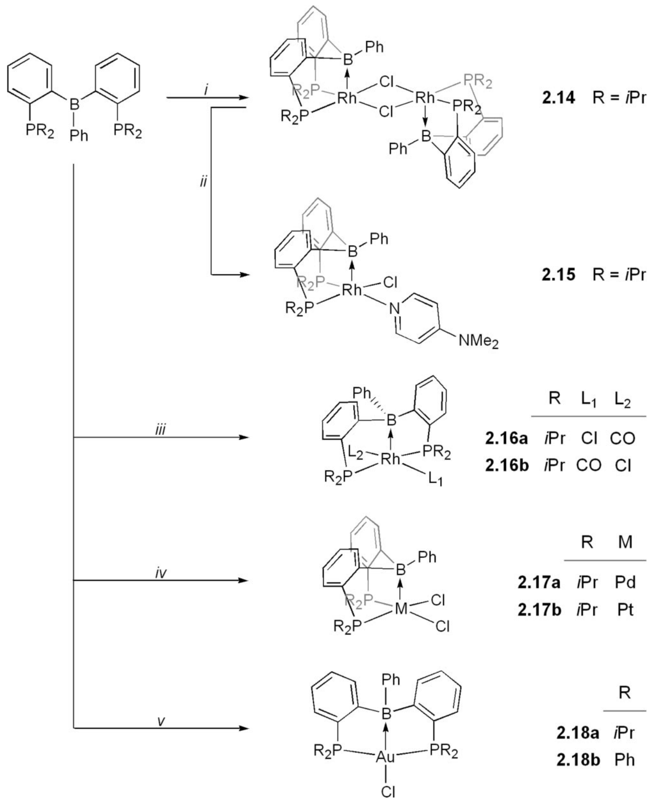


Figure 7. Synthesis of transition metal complexes containing tridentate phosphine−borane ligands. Key reagents and reaction conditions: (i) $[RhCl(NBD)]_2$ (0.5 equiv); (ii) DMAP; (iii) $[RhCl(CO)_2]_2$ (0.5 equiv); (iv) $[MCl_2(cod)]$ (M = Pd, Pt); (v) $[AuCl(SMe_2)]$.

chloro bridges without net disruption of the M → B bond. The conversion of **2.14** to **2.15** was accompanied by statistically negligible changes in both their ^{11}B NMR spectra ($\delta = 20.0$ to 19.4) and Rh−B distances (2.306(3) to 2.295(5) Å). The conversion was however noted unmistakably in the ^{31}P NMR spectrum, in which the doublet signal of the equivalent phosphorus nuclei of **2.14** (d, $\delta = 76.9$, $J_{PRh} = 167$ Hz) split into a double−doublet pattern in **2.15** ($\delta = 66.8$, $J_{PRh} = 170$ Hz, $J_{PP} = 31$ Hz; $\delta = 65.3$, $J_{PRh} = 145$ Hz, $J_{PP} = 31$ Hz) with coupling to both ^{103}Rh and ^{31}P nuclei. However, the similarity of the two complexes is supported by the relatively similar ^{31}P NMR chemical shifts and $^{103}Rh-^{31}P$ coupling constants.

Through addition of PhB{(1,2-C_6H_4)P*i*Pr_2}$_2$ to dimer $[RhCl(CO)_2]_2$, Dyer, Miqueu, Bourissou, and co-workers were able to construct a Rh → B bond with loss of one CO ligand per metal center (Figure 7).[63] In this case, however, the phosphine donor groups of the resulting complexes **2.16** were found situated mutually *trans*, with the boron atom sitting at the apex of the square-pyramidal complex. This *mer-*κ^3*-PPB* binding mode of the ligand enforces such rigidity on the phenylene spacers such that two noninterconverting isomers were obtained, one in which the B-Ph group points toward the CO ligand (**2.16a**, 80%) and one toward the chloride ligand (**2.16b**, 20%). The two isomers were found to be inseparable via fractional crystallization, and an X-ray crystallographic study displayed disorder of the Cl and CO ligands in a similar ratio of 85:15 (**2.16a/2.16b**). Despite this disorder, the Rh−B distance (2.374(3) Å) was found to be slightly longer than those of the related *fac-*κ^3*-PPB* borane complexes **2.14** and **2.15**.

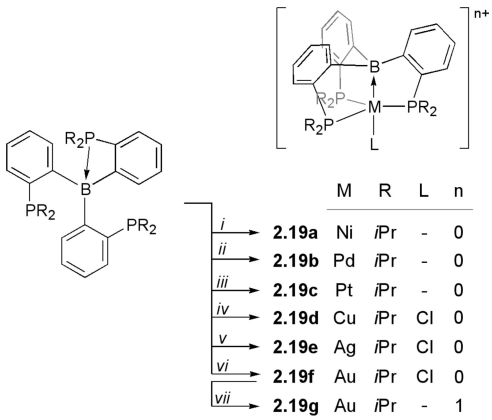


Figure 8. Synthesis of transition metal complexes containing tetradentate phosphine−borane ligands. Key reagents and reaction conditions: (i) $[Ni(cod)_2]$; (ii) $[Pd(PtBu_3)_2]$; (iii) $[Pt(PtBu_3)_2]$; (iv) CuCl; (v) AgCl; (vi) $[AuCl(SMe_2)]$; (vii) $GaCl_3$.

Similarly, diphosphine−borane ligand PhB{(1,2-C_6H_4)P*i*Pr_2}$_2$ replaces the diene ligand of $[MCl_2(cod)]$ (M = Pd, Pt), providing the square pyramidal *fac-*κ^3*-PPB* borane complexes **2.17a**,**b**, respectively (Figure 7).[63] The ^{11}B NMR signals of **2.17a**,**b** were found at $\delta = 47.0$ and 42.8, while the Pd−B distance of **2.17a** (2.650(3) Å) was found to be much longer than the Pt−B distance of **2.17b** (2.429(3) Å). Both M−B distances are significantly longer than those of structurally determined sulfur-donor Pd and Pt borane complexes, regardless of their oxidation states (vide supra).

Doubly strapped borane complexes of gold were also found to be accessible, utilizing the ligands PhB{(1,2-C_6H_4)PR_2}$_2$ (R = *i*Pr, Ph) (Figure 7).[64] As in the synthesis of **2.13a**,**b**, reaction of the appropriate diphosphine−borane afforded κ^3*-PPB* borane complexes **2.18a**,**b**. The complexes are described as square planar, as the P−Au−P and B−Au−Cl angles, although significantly bent, indeed suggest that the complexes are closer to square planar than tetrahedral. The Au−B distances of **2.18a**,**b** (2.309(8) and 2.335(5) Å, respectively) are strongly contracted in relation to those of the κ^2*-PB* borane complexes **2.13a**,**b**, which is unsurprising given the extra phenylene−phosphine buttress in the ligand. The ^{11}B NMR signals of **2.18a**,**b** ($\delta = 25$ and 29, respectively) are also found at much higher field than those of singly strapped complexes **2.13a**,**b** ($\delta = 80.1$ and 55.2, respectively).

2.3.3. Complexes with Tetradentate (κ^4-PPPB) Borane Ligands

In 2008 the phosphine−borane motif was extended to its logical limit by the groups of Maron, Ozerov, and Bourissou, in the synthesis of tetradentate κ^4*-PPPB* boratrane complexes of group 10 and 11 metals (Figure 8).[65,66] Complexes **2.19** are analogous to the archetypal κ^4*-SSSB* boratrane complexes described earlier, yet their synthesis is conceptually simpler and no formal oxidation state change of the metal occurs. Tris(phosphino)borane B{2-*i*Pr_2P(C_6H_4)}$_3$ was treated with group 10 metal complexes $[Ni(cod)_2]$, $[Pd(PtBu_3)_2]$, and $[Pt(PtBu_3)_2]$ to prepare neutral boratrane complexes **2.19a**−**c**, with concomitant displacement of both ligands from each respective precursor complex. Treatment of B{2-*i*Pr_2P(C_6H_4)}$_3$ with group 11 complexes CuCl, AgCl, and $[AuCl(SMe_2)]$ afforded the neutral boratrane complexes **2.19d**−**f**, where in each case the chloride ligand was retained and bound *trans* to the borane moiety. The somewhat related

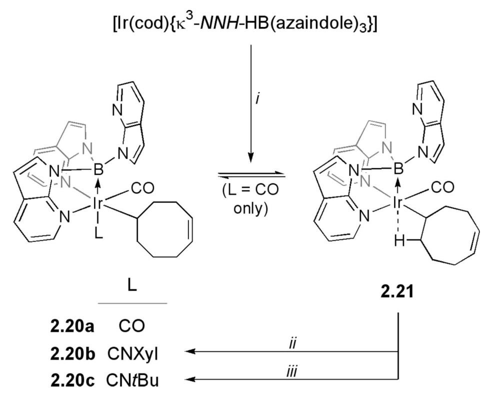


Figure 9. Synthesis of transition metal complexes containing tridentate azaindole−borane ligands. Key reagents and reaction conditions: (i) excess CO; (ii) CNXyl; (iii) CN*t*Bu.

complexes **2.19a−f** provided an excellent basis for comparison of their structural parameters. Group 10 complexes **2.19a−c** displayed somewhat longer M−B distances than their κ^4-*SSSB* counterparts. Within each group, the second-row metal complex (Pd, **2.19b**, 2.254 Å; Ag, **2.19e**, 2.540 Å) possessed the longest M−B distance. Chloride abstraction from gold boratrane **2.19f** with $GaCl_3$ provided the salt [**2.19 g**][$GaCl_4$], in which the Au−B distance has lengthened considerably (2.448 Å) and the ^{11}B NMR signal has shifted almost 30 ppm downfield ($\delta = 57$).[66]

2.4. Borane Complexes with Nitrogen Donor Groups

The first borane complexes supported by nitrogen-donor arms were reported recently from the group of Owen (Figure 9).[67,68] The promising poly(azaindole)borate system (in which the pyrollic nitrogen is bound to the boron atom) shares many characteristics with the sulfur and phosphorus borane systems, including the ring size when bound to the metal and a rigid construction based on fused ring azaindole side arms.

Addition of CO to [Ir(cod){κ^3-*NNH*-HB(azaindole)$_3$}] effects release of one olefin arm of the cod ligand, and hydrometalation of the other (with cleavage of the B−H bond). The end result is an equilibrium between the mono- and dicarbonyl borane complexes **2.20a** and **2.21**. In both cases one azaindole arm is pendent and noncoordinating. Dicarbonyl complex **2.20a** could not be isolated even under CO atmosphere, while slow loss of the CO ligand *trans* to the borane yielded the monocarbonyl complex **2.21**, in which the "empty" coordination site is partially satisfied by an agostic β-C−H−M interaction from the σ-bound cyclooctene ligand. The ^{11}B NMR signals of the two complexes differ noticeably (**2.20a** $\delta = 5.8$; **2.21** $\delta = -9.3$); however, both signals were determined to arise from hydrogen-free boron atoms. X-ray crystallographic analysis of **2.21** showed an unremarkable Ir−B distance of 2.196(6) Å. The apparent hydrometalation route to **2.20a** and **2.21** suggests a mechanism involving the insertion of the metal center into the B−H bond, creating a hydride ligand, and this is consistent with proposals of Hill and Parkin for the sulfur-donor borane complexes of section 2.2.

Addition of isocyanides CNXyl or CN*t*Bu to the mixture results in addition to the position *trans* to the borane ligand, affording complexes **2.20b** and **2.20c**, respectively. The ^{11}B NMR signals of the two complexes (**2.20b** $\delta = 4.3$; **2.20c** $\delta = 3.7$) were found, as expected, close to that of the structurally related dicarbonyl complex **2.20a**. X-ray crystallographic structural analysis of **2.20b** revealed a slightly lengthened Ir−B distance, presumably a result of the increased coordination number of the Ir center.

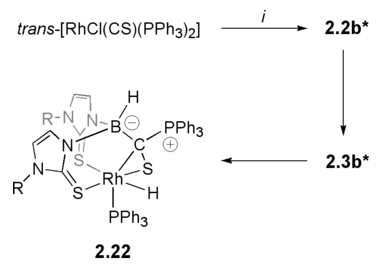


Figure 10. Insertion of CS into the rhodium−boron bond of a borane complex, followed by attack of PPh_3. Key reagents and reaction conditions: (i) Na[Bm^{Me}]. An asterisk indicates presumed intermediate complexes that were not detected.

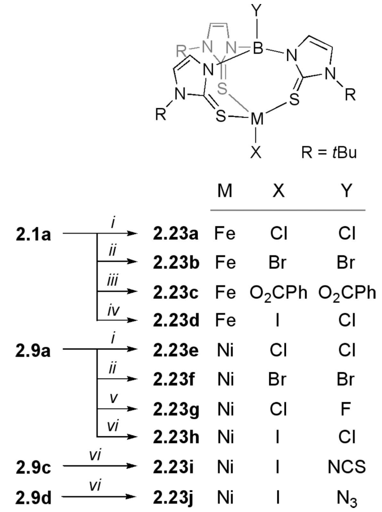


Figure 11. Oxidative cleavage of the M−B bonds of iron and nickel borane complexes. Key reagents and reaction conditions: (i) $CHCl_3$; (ii) $CHBr_3$; (iii) $[PhC(O)O]_2$; (iv) $CHCl_3/I_2$; (v) XeF_2; (vi) I_2.

2.5. Further Reactivity of Boratrane-Style Borane Complexes

While Vaska's complex *trans*-[IrCl(CO)(PPh$_3$)$_2$] and its rhodium analog *trans*-[RhCl(CO)(PPh$_3$)$_2$] undergo classical borane ligand construction when treated with Na[Bm^{Me}], the thiocarbonyl derivative *trans*-[RhCl(CS)(PPh$_3$)$_2$] takes one further step (Figure 10).[47] Presumed intermediate complexes **2.2b** and **2.3b** were not detected, and the final product of the reaction is **2.22**, which contains a side-bound η^2-CS group, which is in turn bound through the carbon atom to the boron. One originally Rh-bound phosphine ligand is found bound instead to the carbon of the CS group, while a hydride is found at the Rh center. The unusual exchange of the hydride and CS ligands on Rh and B suggests that initial transfer of the hydride to the Rh occurs, followed by migration of CS to the boron.

Cleavage of the metal−boron bond of borane complexes has only been reported in a small number of cases, with both moderate and strong oxidants (Figure 11).[45,56] The relatively weak oxidants $CHCl_3$ and $CHBr_3$ cleave the Fe−B bond of iron borane complex **2.1a** with loss of both CO ligands, providing a haloborate κ^3-*SSS* ligand and a tetrahedral Fe center in the complexes **2.23a**,**b**. Similarly, dibenzoylperoxide or a $CHCl_3/I_2$ mixture oxidizes **2.1a**, providing the tetrahedral κ^3-*SSS* complexes **2.23c**,**d**, respectively.

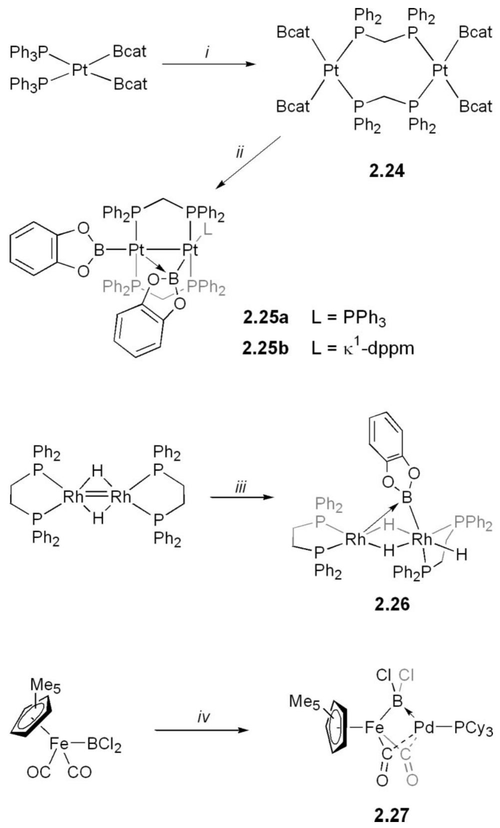


Figure 12. Synthesis of bimetallic borane/boryl complexes. Key reagents and reaction conditions: (i) 1.1 equiv dppm; (ii) crystallization; (iii) HBcat; (iv) [Pd(PCy$_3$)$_2$].

With oxidants CHCl$_3$, CHBr$_3$, and XeF$_2$, the Ni−B bond of **2.9a** is broken, forming κ^3-*SSS* haloborato complexes **2.23e**, **2.23f**, and **2.23g**, respectively.[56] As mentioned earlier, the chloride ligand of borane complex **2.9a** can be replaced with other monoanionic ligands such as acetate (**2.9b**), isothiocyanate (**2.9c**), and azide (**2.9d**). Treatment of **2.9a**,**c**,**d** with I$_2$ brought about cleavage of the Ni−B bond, and in each case the original ligand had migrated to the boron atom, leaving an iodide ligand at the Ni center of the complexes **2.23h**, **i**, and **j**, respectively.

2.6. Bimetallic Complexes with Bridging Borane/Boryl Ligands

In addition to the unequivocal borane complexes mentioned above, there exists a number of bimetallic systems in which borane-type (M → B) bonding may be inferred.

In 1999, Norman and Orpen disclosed the unexpected synthesis of a bimetallic framework based on the short-chain diphosphine dppm, known for its proclivity toward bridging two metal centers and platinum. Addition of dppm to *cis*-[Pt(Bcat)$_2$(PPh$_3$)$_2$] resulted in a species which was characterized in solution as the diplatinum tetraboryl complex **2.24**. However, upon crystallization two different species were observed as samples of red (**2.25a**) and orange (**2.25b**) crystals, both of which were crystallographically characterized (Figure 12).[69] Both complexes contain only two boryl ligands, with the other two presumably being lost as the B$_2$cat$_2$ diborane(4) via reductive elimination. One remaining boryl ligand of each complex **2.25** is terminally coordinated to one Pt center, while the other was found to be asymmetrically bridging. The boron atom of the bridging boryl ligand is essentially planar and appears to be terminally bound to the proximal Pt center (boryl Pt−B: 2.12(2) Å, **2.25a**; 2.14(2) Å, **2.25b**) while the second Pt−B distance is significantly longer (borane Pt−B: 2.49(2) Å, **2.25a**; 2.51(2) Å, **2.25b**) and resembles the slightly longer platinum−borane distances, as mentioned above.

A similar asymmetrically bridging borane/boryl Bcat ligand was observed by the groups of Westcott, Marder, Baker, and Lin, when HBcat was added to the rhodium hydride dimer [Rh(μ-H)(dppe)]$_2$, forming the bridging boryl species **2.26** (Figure 12).[70] The bis(hydride) bridge between the two rhodium atoms of the starting material was retained in the reaction, while the rhodium centers had become inequivalent. Oxidative addition of the BH bond of HBcat to a single metal center meant that one rhodium atom of **2.26** is trivalent, six-coordinate, octahedral and is ligated by a terminal boryl ligand (boryl Rh−B: 2.057(8) Å). The remaining rhodium atom conversely is monovalent and square-planar, albeit with a dative interaction to the bridging boryl ligand (borane Rh−B: 2.444(9) Å). As in the case of the diplatinum complex **2.25** above, this longer M−B distance fits well with other borane complexes, as previously described.

The addition of relatively strong metal-bases to preisolated boryl complexes was found by this group to be another route to such borane/boryl complexes. Addition of [Pd(PCy$_3$)$_2$] to the iron boryl complex [(η^5-C$_5$Me$_5$)(OC)$_2$Fe(BCl$_2$)] provided the bridging boryl complex **2.27** (Figure 12).[71] Crystallographic analysis of **2.27** showed two distinct molecules in the unit cell, one in which the boron atom is more closely bound to the Fe atom than the Pd atom (Fe−B: 2.078(4) Å; Pd−B: 2.090(4) Å) and another with the opposite relationship (Fe−B: 2.095(4) Å; Pd−B: 2.062(4) Å). Unlike the aforementioned bridging boryl complexes, the overall impression gained from **2.27** is that the boryl ligand is unusually symmetrical, yet given the binding of the neutral Pd(0) fragment to the boron center, it can be thought of as a borane (Pd → B) complex.

2.7. Theory and Bonding of Borane Complexes

2.7.1. Formalisms and Qualitative Descriptions of M → B Bonding

The metal−boron bonding in the borane and boratrane complexes described above is in some ways extremely simple. Each borane boron atom is pyramidalized (to differing extents) with its three nonmetal substituents pointing away from the metal; thus, the M−B interaction is almost exclusively a two-center one. Since a free borane has no free electrons and lacks appropriate orbitals for π-bonding with a fourth substituent, the electrons in the M−B bond can be thought to originate exclusively from the metal, and said interaction is exclusively σ in nature. Given the fact that many phosphine-donor borane complexes are prepared from neutral (tricoordinate) borane precursors, the former supposition is undisputed. Where variation exists in borane M−B bonds, it is invariably in the *extent* of the electron donation to the boron atom and thus manifested in the M−B distance.

In terms of oxidation states, as the metal center releases electrons to form the M−B bond, the metal is partially oxidized and will lie somewhere between M^{n+} and M^{n+2} while the boron atom will be partially reduced upon electron acceptance and lie somewhere between B^{3+} and B^{+}. However, since the electronegativities of the metals concerned are all higher than that of boron, the formalism dictates that the two bonding electrons are assigned to the metal center and that both the metal and boron atoms remain in their original M^{n+} and B^{3+} oxidation states. In any case, the concept of oxidation states is ill equipped for describing such variable bonding and is of little use other than in rationalizing the reaction pathway by which the borane complex is formed. This and other qualitative aspects of the M → B bond are discussed in two 2006 correspondence articles by Hill[72] and Parkin.[73] Notably, the former article includes the proposal of a notation to be added after the formula of a borane complex of $(M \rightarrow B)^n$ (where n = "the total number of electrons associated with metal d orbitals and the M → B group"), based on the acceptance of a similar notation for nitrosyl complexes.

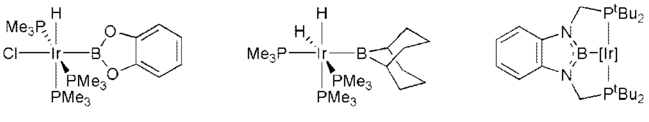
A listing of M−B distances derived from X-ray crystallography and ^{11}B NMR signals of borane complexes can be found in Table 1.

2.7.2. Insights into Metal−Borane Bonding from Computation

Density functional theory (DFT) calculations on palladium borane complex **2.9e** (Figure 5)[57] and a simplified derivative of the iridium complex **2.5m** (R = H, $L_{cis} = PH_3$, Figure 4)[49] were carried out by the group of Parkin. In both complexes, two high-lying occupied orbitals were found with M−B bonding interactions, one with a high degree of B-character and low degree of participation from the *trans* ligand, and the other with the opposite paradigm. The boron-dominated occupied orbital in **2.9e** resembles a Pd p(z) orbital (M−B bonding, $M-L_{trans}$ antibonding), while the orbital dominated by the *trans* ligand resembles a Pd d(z^2) orbital (M−B and $M-L_{trans}$ bonding). In the **2.5m** derivative complex, both the boron-dominated (with Ir d(z^2) symmetry) and *trans*-ligand-dominated (with Ir p(z) symmetry) orbitals appear to be bonding in both directions. LUMO orbitals were found in both complexes, which feature antibonding interactions in both directions.

The most intriguing borane system for computational study is perhaps that of the κ^2-*PB* borane complexes **2.13a**,**b** (Figure 6) which, given their bidentate nature, feature the lowest degree of conformational rigidity of all known borane ligands.[61] This allows the borane moiety more freedom to bind to the metal at its discretion—a feature that is apparent in the large difference between the Au−B distances in **2.13a** (2.90 Å) and **2.13b** (2.66 Å). Through DFT and Natural Population Analysis (NPA) methods, Miqueu and Bourissou showed that, within the four-atom core of the molecule (Au, P, Cl and B), the NPA charges on the P and Cl atoms of **2.13a** and **2.13b** remain constant, while the charges on the Au and B atoms vary greatly. In **2.13a** the longer Au−B bond is reflected in a lower positive charge on the Au atom and higher positive charge on the B atom. In **2.13b**, the charge on the Au atom has increased and the charge on the B atom has decreased, which is consistent with the shorter bond length and a greater degree of Au → B electron donation.

Tridentate borane gold complexes **2.18a**,**b** (Figure 7) showed similar positive charge depletion on boron and accumulation on gold, when the Au → B borane complex was compared with the nonbound fragments in their Natural Bond Order (NBO) analysis.[64] Complexes **2.13a**,**b** differ from **2.18a**,**b** in the position of the chloride ligand, with the former being approximately *cis* to the borane and the latter approximately *trans*. Consequently, the DFT-generated frontier orbitals of **2.18a**,**b** showed a somewhat interconnected relationship between the borane and chloride ligands. The HOMO orbitals contained primarily Au−B bonding and Au−Cl antibonding interactions, while the LUMO orbitals contained antibonding Au−B and bonding Au−Cl interactions.



3.1 **3.2** **3.3a-c**

Figure 13. First structurally characterized boryl complexes **3.1** and **3.2** and the first boryl based pincer complexes **3.3** ([Ir] = IrHCl, **a**; IrHCl(CO), **b**; Ir(η^2-C_2H_4), **c**).

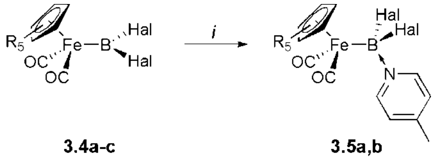
A comprehensive NBO analysis of tridentate κ^3-*PPB* borane complexes of rhodium (*fac* **2.15** and *mer* **2.16a**,**b**), palladium (*fac* **2.17a**), and platinum (*fac* **2.17b**) showed large differences in the strength of the metal−boron interaction (Figure 7).[63] The NBO stabilization energy associated with the M−B bond decreased in the order **2.15** (Rh) > **2.17b** (Pt) ≈ **2.16b** (Rh) ≈ **2.16a** (Rh) > **2.17a** (Pd), and similar trends were apparent in related metrics such as the charge on the boron atom, the calculated M−B bond order, and the relative electronic contribution of the M and B atoms to the corresponding NLMO (the contribution of the boron atom decreases, while that of the metal increases, as the bonding weakens).

Similar NBO analysis was performed on the tetradentate κ^4-*PPPB* borane complexes **2.19a**−**f** and [**2.19g**][$GaCl_4$] (Figure 8), showing a similar trend toward stronger M−B bonding with the heavier transition metals.[66] The calculated NBO stabilization energy for the M−B bond was found to decrease in the order **2.19c** (Pt) > **2.19b** (Pd) ≈ **2.19a** (Ni) > **2.19f** (Au) > [**2.19g**][$GaCl_4$] (Au^+) > **2.19e** (Ag) > **2.19d** (Cu). As expected, upon M−B coordination the charge on the boron atom becomes more negative and that on the metal atom more positive, consistent with the donation of electron density from the metal center. The magnitude of these charge differences roughly follows the trend of the calculated bond strengths.

3. Boryl Ligands

3.1. Introduction

As early as 1970, the first of a number of different types of compounds featuring electron precise bonds between transition metals and the element boron was described.[74] However, as mentioned above, the first structural authentication of such two-center−two-electron bonds did not take place until 1990 (**3.1** and **3.2**; Figure 13).[5,6] Apart from the transition metal fragment, the boron centers bore two more substituents, and therefore, these compounds were classified as boryl complexes. Since then, numerous studies have dealt with the synthesis and reactivity of those boryl ligands coordinated to mainly mid-transition metals.[8,20,22,24,27,28,31] Furthermore, the nature of the transition metal−boron bonding was intensively investigated, revealing, inter alia, remarkably strong σ-donation abilities.[75−78] The significant degree of π-backdonation could be determined experimentally only recently for the first time by occupation of the vacant p-orbital of iron dihaloboryl complexes by a Lewis base and monitoring the change in the M−B linkage beyond what would be expected for a simple sp^2−sp^3 rehybridization (Figure 14).[79,80]



3.4a-c **3.5a,b**

Figure 14. Conversion of iron dihaloboryl complexes **3.4** (R = H, Hal = Cl, **a**; R = Me, Hal = Cl, **b**; Hal = Br, **c**) into the corresponding Lexis-base adducts **3.5** (R = H, Hal = Cl, **a**; R = Me, Hal = Br, **b**). Key reagents and reaction conditions: (i) 4-pic.

For a long time, boryl complexes have been known to participate in the functionalization of organic substrates. Since the first description of catalytic hydroboration,[81] which was accomplished utilizing a rhodium catalyst, numerous publications were related to this topic.[82-87] Furthermore, involvement of later transition metals in diboration[19,88-98] as well as in stoichiometric[99-103] and catalytic C−H[104-113] and C−F[114] bond activation processes underlines their importance. Most of these examples once more emphasize the outstanding role that the pinacolato and to an even larger extent the catecholato moiety play in transition metal boryl chemistry.

In most of the above-mentioned systems, the boryl group is a rather labile—if not the most labile—ligand, a fact commonly used in transition metal mediated borylation processes. But it also prevented application of a boryl moiety and its unique electronic features in other functionalization reactions. Most recently, stabilization of the boryl moiety was accomplished by incorporation in tridentate ligand systems, yielding different boryl-based pincer complexes (Figure 13).[115,116]

The outstanding importance of later transition metals in metal-mediated borylation processes stimulated great efforts in extending the understanding of the involved species. Therefore, the most recent progress in the chemistry of boryl complexes has been achieved in this area and we put our main focus on boryl complexes of group 10 metals, which account for the largest proportion of the latest publications. Afterward, we turn our attention to group 11 boryl complexes, a class of compounds, which five years ago contained not a single well-characterized example. A new synthetic approach, however, has now made complexes of the whole triad accessible.

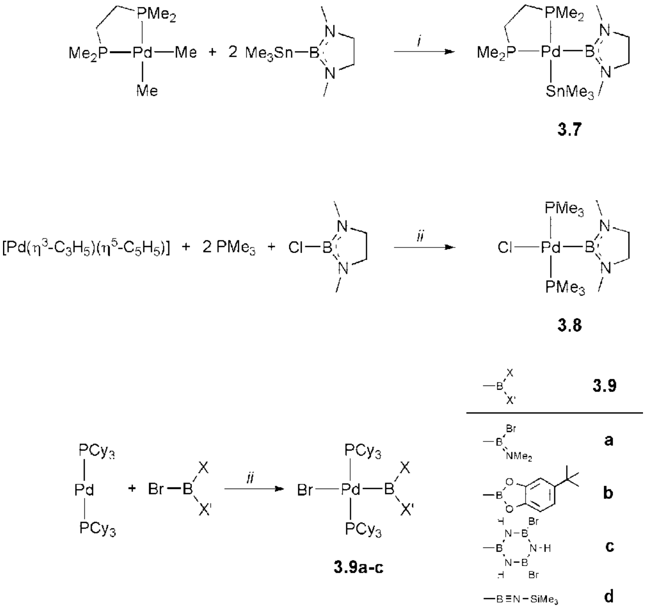


Figure 16. Synthesis of structurally characterized palladium boryl complexes **3.7**−**3.9**. Key reagents and reaction conditions: (i) 130 °C, − MeB(NMe)$_2$C$_2$H$_4$ − SnMe$_4$; (ii) RT.

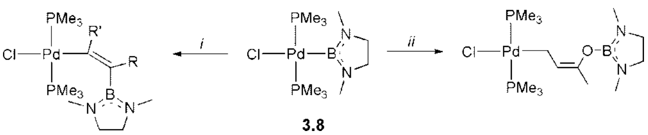


Figure 17. Insertion reactions of unsaturated substrates with **3.8**. (i) RC≡CR (R = H, R′ = Me, Hex; R = R′ = Me, CO$_2$tBu); (ii) H$_2$C=CHC(=O)CH$_3$.

3.2. Group 10 Boryl Complexes

The outstanding importance of the Suzuki coupling in organic synthesis gives enormous significance to group 10 metals in boron-based chemistry. It represents a powerful protocol for generation of carbon−carbon bonds via palladium catalyzed cross-coupling of organoboranes with organic electrophiles.[117,118] Beyond this, the metals of group 10 also play a prominent role in the borylation of organic compounds. In this area, diboration of unsaturated organic substrates accounts for the largest proportion,[19,88-95,97,98] but many other borylation processes have been reported.[119-132]

Several studies dealing with nickel-mediated borylation of unsaturated organic substrates suggest an intermediary

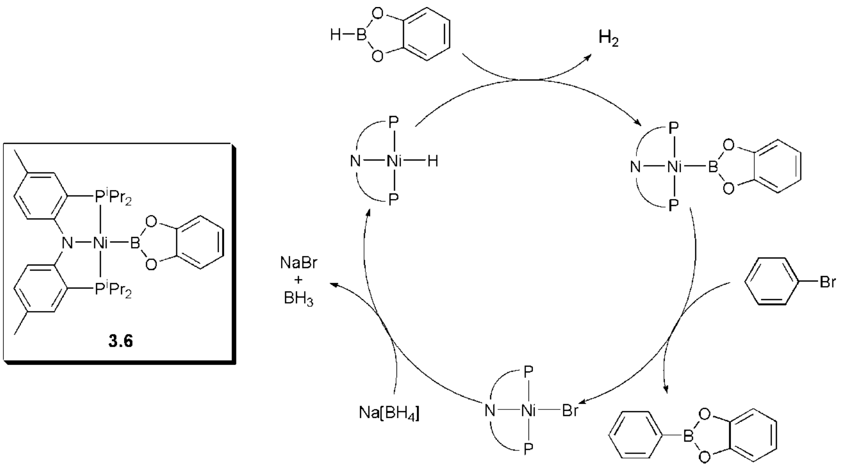


Figure 15. First structurally characterized boryl complex of nickel **3.6** and its application as a recyclable borylation agent.

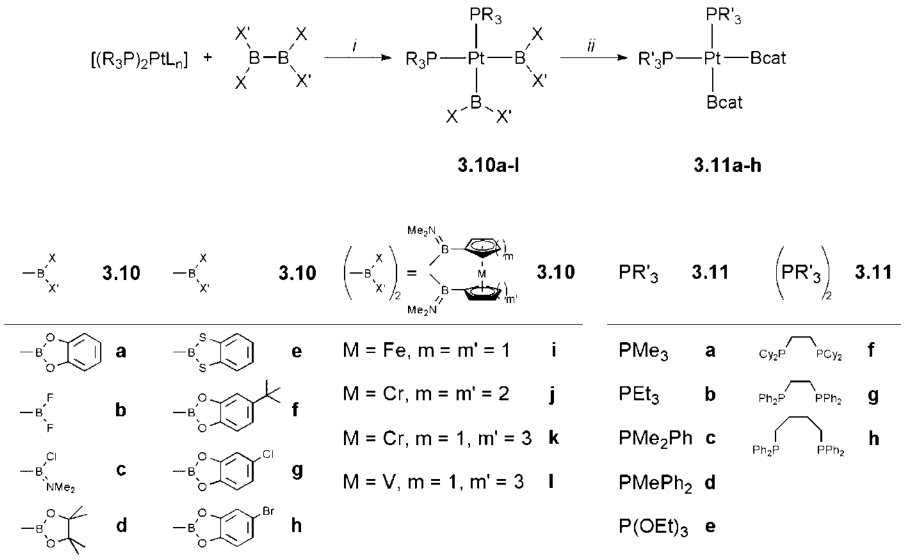


Figure 18. Preparation of bis(boryl) complexes. Key reagents and reaction conditions: (i) − *n*L (**3.10a**: $PR_3 = PPh_3$, L = PrC≡CPr, *n* = 1, $PR_3 = L = PMe_3$, *n* = 2; **3.10a−h**: $PR_3 = PPh_3$, $L = \eta^2\text{-}C_2H_4$, *n* = 1; **3.10i,j**: $PR_3 = L = PEt_3$, *n* = 1; **3.10k,l**: $PR_3 = L = PEt_3$, *n* = 2); (ii) $2PR'_3 - 2PR_3$.

transition metal boryl species to be involved.[123,128,133,134] However, only one boryl complex of nickel has been structurally characterized so far.[135] This compound can be used to transfer the boryl moiety to bromobenzene, and the nickel reagent can be recycled (Figure 15).

The first structural elucidation of a palladium boryl complex, however, was accomplished in the past decade.[119] This mixed boryl (stannyl) palladium(II) compound **3.7** (Figure 3.4) catalyzes addition of the corresponding stannylborane to 1-octyne, and therefore, such species were suggested to be involved in the catalytic cycle of stannaboration. Meanwhile, oxidative addition of boron−halogen bonds to coordinatively unsaturated palladium fragments has become a useful protocol to prepare this type of compounds (Figure 16).[136-139] In this manner, a whole series of complexes were prepared, such as an unusual η^1-borazine complex **3.9c**[139] and an unprecedented iminoboryl complex **3.9d** (see section 3.2.1 for the synthesis of **3.9d** and more details about this subclass of boryl complexes).[137] Theoretical calculations predicted the palladium−boron bond to be rather labile.[140,141] Hence, unsaturated organic substrates, such as differently substituted alkynes as well as 3-buten-2-one, were shown to undergo insertion reactions (Figure 17),[136] and several catalytic carboboration reactions involving boron−chlorine bond activation by nickel or palladium complexes have been established recently.[128,130,131]

3.2.1. Platinum Boryl Complexes

In contrast to the lighter metals of group 10, platinum exhibits a rather robust metal−boron bond, and hence, both the number of boryl complexes and the studies concerning their reactivity dominate in number by far. The method of choice to prepare these compounds, as is the case for most late transition metals, is oxidative addition of boron−element bonds. Thus, a variety of bis(boryl) complexes was prepared from diborane(4) compounds,[28,88-92,95,142-145] and it could be demonstrated that those complexes undergo phosphine exchange reactions (Figure 18).[29,91] Not only boron−boron bonds but also group 14 element−boron bonds undergo oxidative addition to platinum.[146,147] The boryl silyl complexes represent isolated intermediates in catalytic silaboration and undergo insertion reactions with phenylacetylene exclusively into the platinum−boron bond. While the pina-

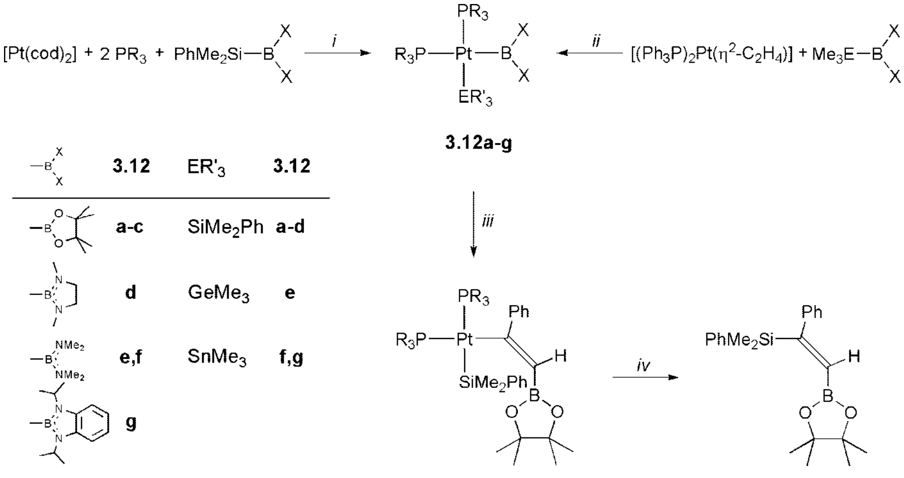


Figure 19. Preparation of mixed boryl group 14-yl complexes **3.12a−g** ($PR_3 = PMe_3$: **a,d**; PMe_2Ph: **b**; PEt_3: **c**; PPh_3: **e−g**) and reaction of the pinacolatoboryl silyl complexes **3.12a−c** with phenyl acetylene. Key reagents and reaction conditions: (i) − 2cod (**a–d**); (ii) − C_2H_4 (**e−g**); (iii) PhC≡CH (**a−c** only); (iv) − $Pt(PR_3)_2$; **a,b**: 60 °C; **c**: RT.

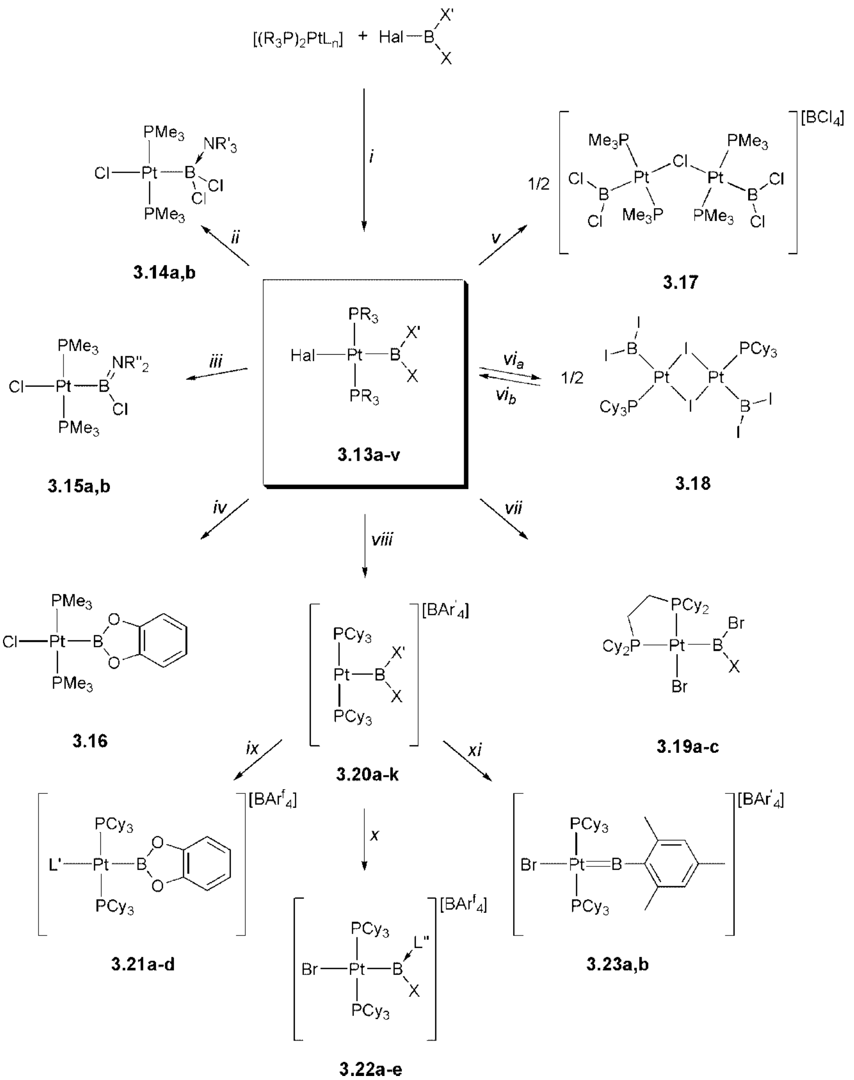


Figure 20. Synthesis and reactivity of platinum halo (boryl) complexes. Key reagents and reaction conditions: (i) − *n*L (see Table 2 for ligands and substituents for **3.13a**−**v**); (ii) NR'_3 (from **3.13d**; $NR'_3 = NEt_3$: **3.14a**, pyr: **3.14b**); (iii) $4HNR''_2 - [H_2NR''_2]Cl$ (from **3.13d**; $NR''_2 = NEt_2$: **3.15a**, pip: **3.15b**); (iv) $catH_2$ + excess $NEt_3 - 2[HNEt_3]Cl$ (from **3.13d**); (v) $^1/_2BCl_3$ (from **3.13d**); (vi_a) $BI_3 - Cy_3P \rightarrow BI_3$ (from **3.13v**); (vi_b) PCy_3; (vii) dcpe − $2PCy_3$ (from **3.13k**−**m**; X = Fc: **3.19a**, Mes: **3.19b**, pip: **3.19c**); (viii) $M[BAr'_4] - MBr$ (from **3.13k**−**t**: M = Na, $Ar' = Ar^f$; from **3.13l**: M = K, $Ar' = C_6F_5$); (ix) L′ (from **3.13t**; L′ = thf: **3.21a**, H_3CCN: **3.21b**, pyr: **3.21c**, quinoline: **3.21d**); (x) L″ (from **3.13k,m,n,q**: L″ = 4-pic; from **3.13 m**: L″ = NC_5H_4-4-*t*Bu); (xi) RT (X = Mes, X′ = Br, $Ar' = C_6F_5$: **3.23a**, Ar^f: **3.23b**).

colyl substituted complexes **3.12a**−**c** readily react even at ambient temperature, the amino analogue **3.12d** is inactive toward insertion. Carbon−silicon reductive elimination can be initiated by heating the corresponding insertion products **3.12a** and **b**, or in the case of **3.12c** the elimination follows successively after insertion of the acetylene even at room temperature, yielding α,β-silaborated styrene (Figure 19).[146]

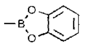
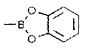
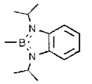
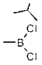
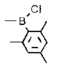
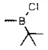
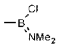
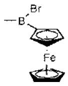
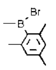
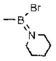
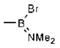
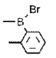
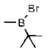
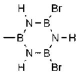
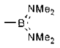
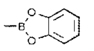
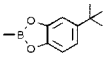
In all of the above-mentioned examples, the products obtained by oxidative addition exhibit the anionic ligands in a mutually *cis* arrangement, whereas reactions of haloboranes yield the corresponding *trans* complexes (**3.13a**−**v**, Figure 20).[137,139,142,147−155] The halide ligand in the *trans* position enables a systematic investigation of the *trans*-influence of the boryl ligands, and the predicted dependence on σ-donating ability[156] was experimentally confirmed.[149]

Utilizing the B−Br oxidative addition protocol also allowed unusual boron-centered ligands to be generated. Thus, this protocol enabled the preparation of η^1-borazine complexes of both platinum (**3.13r**) and palladium (**3.9c**).[139] Furthermore, reaction of 1,4-bis(dibromoboryl)benzene yielded a dinuclear platinum complex bridged by a bidentate boryl ligand (**3.24f**, Figure 21).[154] These coordination modes previously were only known for a few iron complexes prepared by salt elimination reactions.[157,158]

As in the case of the iron analogues mentioned above,[79,80] the vacant p-orbital of *trans*-$[(Me_3P)_2Pt(BCl_2)Cl]$ (**3.13d**) can be occupied by Lewis bases (**3.14a,b**). Furthermore, reaction with secondary amines gives the corresponding amino(chloro)boryl complexes (**3.15a,b**). Substitution of both boron bound chlorine atoms could be achieved by reaction with catechol in the presence of triethylamine (**3.16**), and treatment with boron trichloride leads to the dinuclear complex *trans,trans*-$[\{(Me_3P)_2(Cl_2B)Pt\}_2(\mu\text{-}Cl)]$ (**3.17**), obtained via initial formal halogen abstraction.[152] In contrast, reaction of *trans*-$[(Cy_3P)_2Pt(BI_2)I]$ (**3.13v**) with boron triiodide results not in halogen abstraction but in reversible dissociation of one phosphine ligand, and the corresponding product forms the dimeric structure $[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$ (**3.18**).[151]

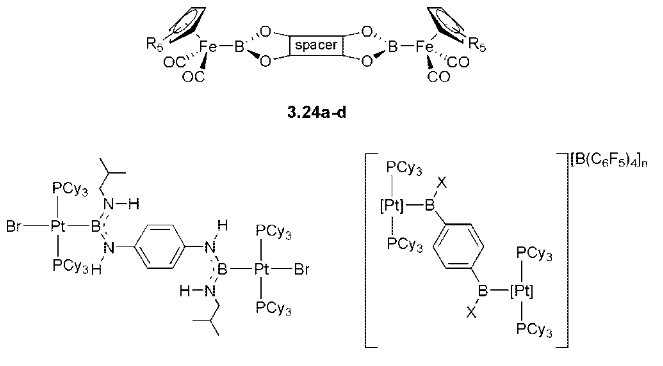
Conversion of different complexes of the general formula *trans*-$[(Cy_3P)_2Pt\{B(X)Br\}Br]$ (**3.13k**−**m**) to their *cis*-analogues (**3.19a**−**c**) could be accomplished upon reaction with the chelating bisphosphine bis(dicyclohexylphosphino)-

Table 2. Ligands and Substituents for 3.13a−v[a]

PR_3	L	n	Hal	$-B(X')X$	**3.13**
PPh_3	C_2H_4	1	Cl		**a**
PPh_3	C_2H_4	1	Br		**b**
PPh_3	C_2H_4	1	Br		**c**
PMe_3	PMe_3	2	Cl		**d**
PPh_3	*	*	Cl		**e**
$PMePh_2$	*	*	Cl		**f**
PMe_2Ph	*	*	Cl		**g**
PCy_3	-	0	Cl		**h**
PCy_3	-	0	Cl		**i**
PCy_3	-	0	Cl		**j**
PCy_3	-	0	Br		**k**
PCy_3	-	0	Br		**l**
PCy_3	-	0	Br		**m**
PCy_3	-	0	Br		**n**
PCy_3	-	0	Br		**o**
PCy_3	-	0	Br		**p**
PCy_3	-	0	Br		**q**
PCy_3	-	0	Br		**r**
PCy_3	-	0	Br		**s**
PCy_3	-	0	Br		**t**
PCy_3	-	0	Br		**u**
PCy_3	-	0	I		**v**

[a] * indicates generated in situ from $[Pt(nbe)_3]$ and 2 equiv of PR_3.

ethane.[159] Formal bromide abstraction from platinum complexes of the general formula *trans*-$[(Cy_3P)_2Pt(BXX')Br]$ (**3.13k−t**, **3.24f**) upon treatment with alkaline boronates yields T-shaped boryl complexes with platinum in coordination number three (**3.20a−k**, **3.24g**).[154,160,161] The vacant coordination site at platinum can be occupied by Lewis bases (**3.21a−d**), and if at least one of the boron bound substituents is a bromide atom, addition of pyridine derivatives leads to base-stabilized borylene complexes (**3.22a−e**, **3.24h**).[154,160] In the case of the mesityl(bromo)boryl analogue, this 1,2-shift of the bromide from boron to platinum even takes place without addition of a Lewis base. Addition of alkaline boronates to a solution of *trans*-$[(Cy_3P)_2Pt\{B(Br)Mes\}Br]$ (**3.13l**) at room temperature causes immediate formation of *trans*-$[(Cy_3P)_2Pt(BMes)Br][BAr^f{}_4]$ (**3.23a,b**), which is the first example of a platinum borylene complex with boron in the coordination number of two.[150] The corresponding T-shaped boryl complex could be spectroscopically observed only at low temperature.[161]



3.24a-d

3.24e

3.24f-h

Figure 21. Bis(boryl) bridged dinuclear iron (**3.24a−d**; spacer = C_6H_2, R_5 = H_5: **a**; H_4Me: **b**; Me_5: **c**; spacer = C_5H_8, R_5 = H_5: **d**) and platinum complexes (**3.24e−g**; [Pt] = PtBr, X = Br, *n* = 0: **f**; [Pt] = Pt, X = Br, *n* = 2: **g**) as well as the first dinuclear doubly base-stabilized bis(borylene) complex (**3.24h**; [Pt] = PtBr, X = 4-pic, *n* = 2).

Oxidative addition of silylamino(dibromo)boranes to coordinatively unsaturated metal fragments and subsequent elimination of bromosilane yielded the unprecedented iminoboryl complexes (**3.9d**, **3.25a−c**), once more underlining the ability of platinum fragments to stabilize boron in low coordination numbers (Figure 22).[137,153] The substitution pattern could be varied with respect to the substituent at nitrogen, the metal bound coligands, and the metal itself. In such a manner, not only iminoboryl complexes of the heavier group 10 metals but also the rhodium species *cis*,*mer*-$[(Br)_2(Me_3P)_3Rh(B{\equiv}NSiMe_3)]$ (**3.26**) could be prepared. The elimination of bromosilane remarkably proceeds rapidly even at ambient temperature and seems to be facilitated by the steric demands of the substituents at nitrogen. Hence, in the case of the isobutyl substituted compound **3.25b**, the intermediate "classical" boryl complex with tricoordinate boron, which previously was only postulated, was observed spectroscopically.

Iminoboryl complexes, in contrast to their main group substituted counterparts, display a remarkable reluctance toward cyclo-oligomerization, and the platinum complexes cleanly react with both Lewis (**3.27**) and moderately Brønsted acidic reagents.[153,162] This protocol provides facile access to transition metal complexes bearing mixed boryl ligands (**3.28a−c**) and additionally allowed for the preparation of the boryl-bridged dinuclear complex (**3.24e**) by using a bifunctional reagent. Furthermore, the bromide ligand can be substituted by an acetylide, giving **3.29** with the two isoelectronic ligand species bound to the same metal center.[153]

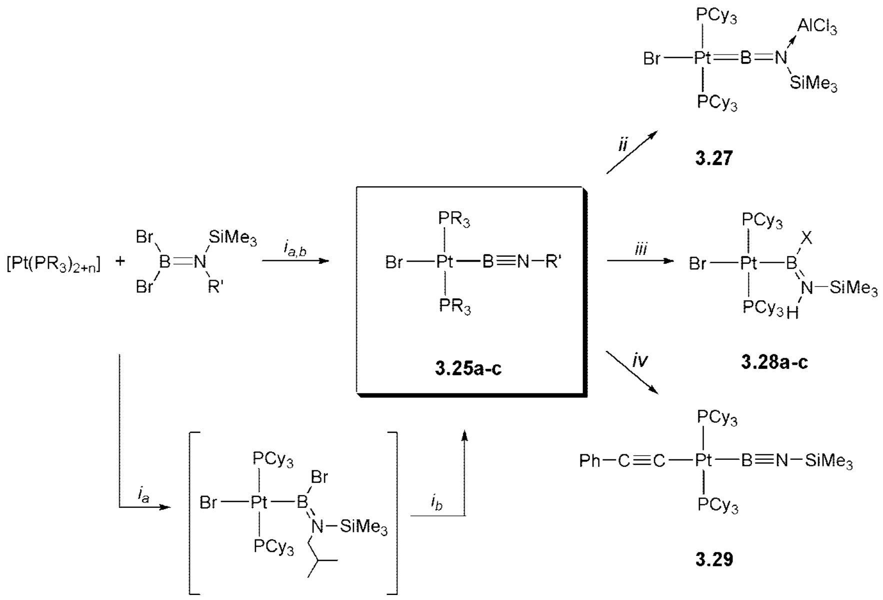


Figure 22. Preparation and reactivity of iminoboryl complexes. Key reagents and reaction conditions: (i$_a$) − nPR$_3$ (PR$_3$ = PCy$_3$, n = 0, R′ = SiMe$_3$: **3.25a**; R′ = iBu: **3.25b**; PR$_3$ = iPr, n = 1, R′ = SiMe$_3$: **3.25c**); (i$_b$) − BrSiMe$_3$; (ii) AlCl$_3$ (from **3.25a**); (iii) HX (cat. H$^+$ for X = OH; from **3.25a**; X = OMe: **3.28a**; N(H)Ph: **3.28b**; OH: **3.28c**); (iv) NaC≡CPh (from **3.25a**).

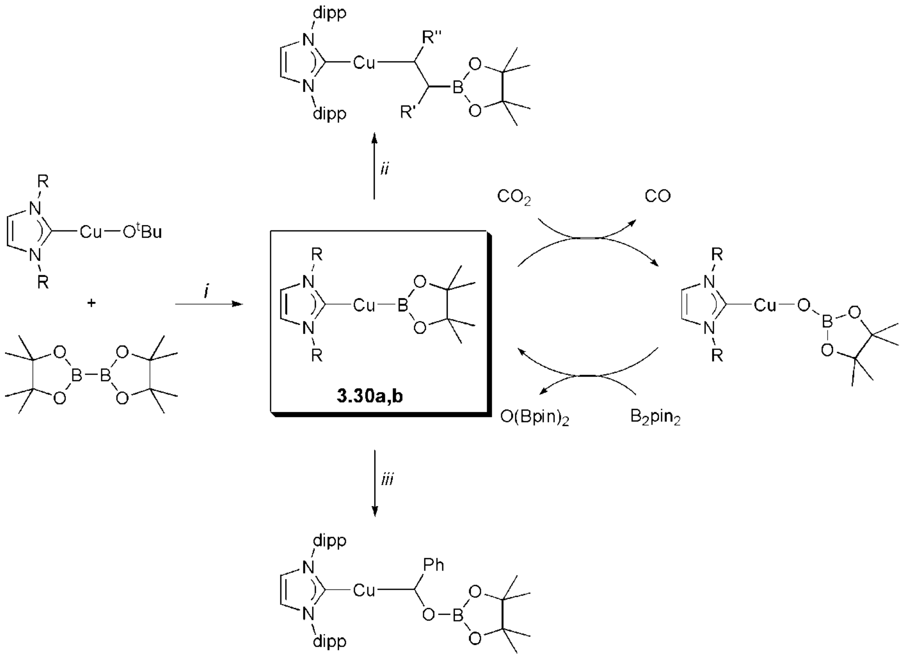


Figure 23. Preparation of the first well characterized copper boryl complexes and their reactivity (R = dipp: **3.30a**, Cy: **3.30b**). Key reagents and reaction conditions: (i) − tBuOBpin; (ii) R′(H)C=C(H)R″ (from **3.30a**: R′ = H, R″ = H, Ph, 4-C_6H_4F, 4-C_6H_4Me, 4-C_6H_4OMe, 4-$C_6H_4NMe_2$; R′ = R″ = Ph: E and Z); (iii) Ph(CO)H (from **3.30a**).

3.3. Group 11 and 12 Boryl Complexes

As in the case of boryl complexes of lighter group 10 metals, copper boryl species initially have been suggested to be important key intermediates in borylation processes,[163–170] and incorporation of these species in several functionalization reactions, most recently also leading to optically active products,[171–174] induced intense theoretical work.[175,176] However, it was not until 2005 when the first well-characterized examples of this type (**3.30a,b**) could be isolated. They have been shown to act as catalysts in the reduction of CO_2,[177] and additionally, **3.30a** undergoes interesting insertion chemistry with alkenes[178] and aldehydes (Figure 23).[179]

Meanwhile, the availability of both boryllithium[180,181] and borylmagnesium[182] species, which both exhibit the characteristic reactivity of a boryl anion, opened a new approach in preparing complexes of boron-centered ligands by introducing the boryl moiety via nucleophilic attack and substitution of halides. In this manner, boryl complexes of the whole group 11 triad **3.31a–i** were made accessible,[183,184] as well as zinc analogues **3.32a–c** (Figure 24).[183] The latter exhibit the first examples of post-transition-metal boryl species, and in contrast to boryl lithium, both the copper and the zinc species cleanly react by 1,4-addition with α,β-unsaturated ketones and therefore prove themselves as soft nucleophiles.[183] Prior to the preparation of these zinc boryls, the

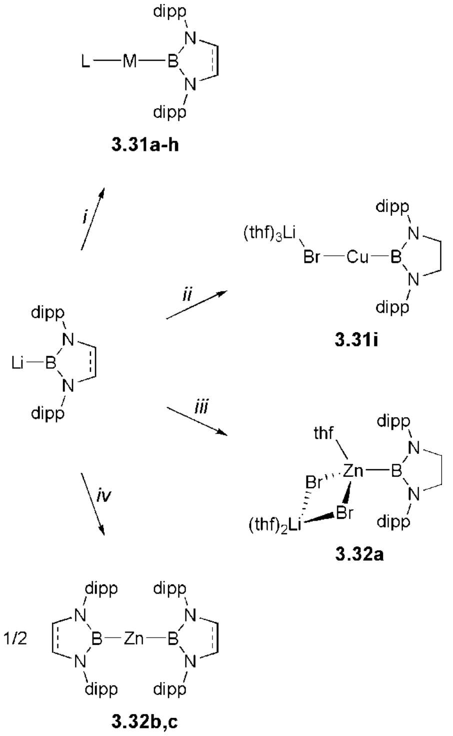


Figure 24. Preparation of boryl complexes from boryl lithium reagents. Key reagents and reaction conditions: (i) [(L)M(Cl)] − LiCl (L = IMes, M = Cu, from $LiB(Ndipp)_2C_2H_2$: **3.31a**; from $LiB(Ndipp)_2C_2H_4$: **3.31b**; L = IMes, M = Ag, from $LiB(Ndipp)_2C_2H_2$: **3.31c**; from $LiB(Ndipp)_2C_2H_4$: **3.31d**; L = IMes, M = Au, from $LiB(Ndipp)_2C_2H_2$: **3.31e**; from $LiB(Ndipp)_2C_2H_4$: **3.31f**; L = PPh_3, M = Au, from $LiB(Ndipp)_2C_2H_2$: **3.31g**; from $LiB(Ndipp)_2C_2H_4$: **3.31h**); (ii) CuBr, THF; (iii) $ZnBr_2$, THF; (iv) $^1/_2ZnHal_2$ − LiHal (from $LiB(Ndipp)_2C_2H_2$, Hal = Cl: **3.32b**; from $LiB(Ndipp)_2C_2H_4$, Hal = Br: **3.32c**).

range of compounds featuring interactions between group 12 metals and boron was restricted to complexes of hydroborates[185–187] as well as borane[188–190] and carborane clusters.[191–195]

3.4. Conclusion

Considering that not even 20 years have passed since the first structural confirmation of an electron-precise two-center transition metal−boron bond, the diversity of boryl complexes as well as their applications has grown at a staggering rate. In particular, those of the late transition metals owe their importance to their role as key intermediates in catalytic borylation processes and, therefore, have been extensively investigated in the past decade. Not only do they allow at most highly selective introduction of boryl moieties into organic substrates, which in turn can be converted into a whole series of other functionalities,[196] but also they exhibit a rich and interesting chemistry in their own right.

Great progress has been made in expanding the variety of examples and gaining a deeper understanding of those compounds. However, there are still blank spots on the periodic table. Thus, chromium fragments, for example, have proven to be especially adeopt at stabilizing borylene ligands, but nevertheless, no boryl complex of this metal is known. Likewise, until very recently, there actually was not one single example of a boryl ligand coordinated to a metal of groups 3−4, including the whole series of f-block elements. But the new synthetic approach to introduce the boryl moiety via a nucleophilic boryl lithium reagent, successful for the preparation of the first boryl complexes of heavier group 11 metals, seems also to be applicable to the very early transition metals. Thus, the first examples of both titanium and hafnium have been isolated and crystallographically characterized in this way.[197]

Although the chemistry of boryl complexes of transition metals is a rather new field of research, such compounds have demonstrated their relevance for both fundamental research and technical applications. Considering furthermore the frequency with which studies dealing with this topic are published, one can expect the importance of this chemistry to grow strongly in the future.

4. Borylene Ligands

4.1. Introduction

The fluoroborylene species ":BF" has been a subject of fascination for chemists for a long time, given its isoelectronic relationship to the well-known and stable CO and N_2 molecules. The energetically high-lying HOMO of the free BF molecule (relative to CO and N_2) imparts such reactivity that its existence can only be inferred from trapping reactions.[198,199] Borylene species other than BF have since been generated and trapped, although so far none have suggested the possible future isolation of such a species.[200–204]

The stabilization of highly reactive species by transition metals, and their subsequent harnessing for further reactivity, is both a central theme and a driving force of inorganic and organometallic chemistry. Following in the footsteps of many other reactive main-group species, the borylene fragment ":BR" finally succumbed to stabilization in the ligand sphere of a transition metal in the 1990s with the synthesis of bridging (1995) and terminal (1998) examples (vide infra).

Relatively early on, theoretical studies showed that the frontier orbitals of the free borylene species :BF and $:BNR_2$ had higher energy HOMO orbitals when compared to N_2 and CO, yet the LUMO orbitals of all four species remained relatively static energetically.[205,206] Upon binding to a transition metal, the borylene is thus able to donate σ electron density to the metal center almost completely, providing marked thermodynamic stability. Retrodonation from the metal center, while still significant, is often less efficient due to the relatively high-energy LUMO of the borylene fragment. The disparity between these two interactions results in residual positive charge at the boron atom; thus, borylene complexes were predicted to be susceptible to nucleophilic attack at the boron atom, unless protected sterically or stabilized by an electron-donating substituent.

As predicted, the synthesis of terminal borylene complexes has thus far only been achieved with use of either strongly electron-donating amino substituents or relatively bulky substituents such as $Si(SiMe_3)_3$, *t*Bu, Mes, or η^5-C_5Me_5. In many cases, the borylene substituents are compatible with both terminal *and* bridging architectures. Neither the strong donating ability of dialkylamino substituents nor the steric bulk of *t*Bu or Mes groups precludes the accommodation of a second metal center at the M=B bond. However, smaller, nondonating borylene substituents such as hydrogen, halides, phenyl, and CH_3 appear exclusively in bridged dinuclear complexes due to electronic necessity and/or steric opportunity.

Despite the stability of the borylene ligand in a vast range of complexes, their most prolific pattern of reactivity is the complete cleavage of the M−B bonds, both photochemically and thermally induced (vide infra). The borylene ligand has

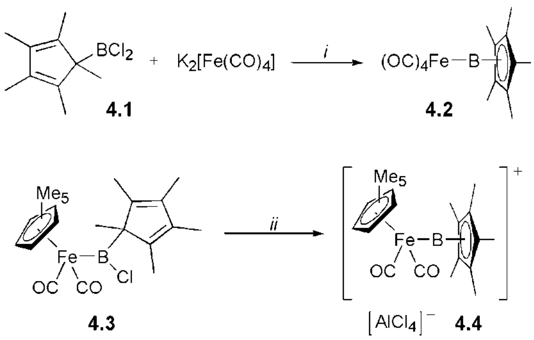


Figure 25. Synthesis of π-cyclopentadienyl-coordinated borylene complexes. Key reagents and reaction conditions: (i) toluene, −78 °C; (ii) $AlCl_3$.

been transferred to other metal centers, alkynes, and CH bonds and undergone metathesis with polar E═E′ bonds. The intermetal borylene transfer reaction, in particular, has emerged as the most useful technique for the synthesis of new borylene complexes, a protocol that has matured from the first adventitious reports to the current state of purposeful application toward this end.

4.2. First Generation Borylene Complexes

4.2.1. Terminal Borylene Complexes

One of the first examples of a terminal borylene complex was the unusual iron species **4.2** (Figure 25), in which the boron atom is coordinated in a η^5 fashion to a C_5Me_5 "ligand", published shortly before the archetypal group 6 borylene complexes (see below).[207] Later, the related borylene complex **4.4** was reported from the same laboratory.[208] The Fe−B distances of the two complexes are similar (**4.2**: 2.010(3); **4.4**: 1.977(3) Å) and are indistinguishable from those of known iron boryl complexes. However, the most clear distinction of **4.2** and **4.4** from other borylene complexes is in their ^{11}B NMR shifts, which are strongly highfield shifted (**4.2**: δ −35.3; **4.4**: δ −37.9) in a region somewhat diagnostic for hypervalent boron nuclei. This is also in accord with the NBO analysis data for **4.4**, in which the Fe−B bond order was found to be unity, belying the complexes "borylene" classification.

Although the structure of **4.2** and **4.4** is atypical of most of the other borylene complexes in this section, the synthetic routes to these complexes are not. Complex **4.2** was prepared by salt elimination from the dianionic $K_2[Fe(CO)_4]$ and dichloroborane **4.1**, while cationic borylene complex **4.4** was prepared via halide elimination from haloboryl complex **4.3**. Both routes are now well established for the synthesis of borylene complexes.

The group 6 pentacarbonyl borylene complexes **4.5a**,**c** (Figure 26) were the first reported terminal borylene complexes, prepared by double salt elimination from the corresponding reactive pentacarbonyl metalate species and a dihaloaminoborane.[209] Later, these were complemented by the synthesis of the molybdenum analogue **4.5b** in a similar manner.[210] The borylene complexes **4.5a**−**c** displayed ^{11}B NMR shifts close to δ 90 (**4.5a**: δ 92.3; **4.5b**: δ 89.7; **4.5c**: δ 86.6) and relatively short M−B distances (**4.5a**: 1.996(6); **4.5b**: 2.152(2); **4.5c**: 2.151 Å).

Similarly, the sterically bulky dichloroborane $Cl_2BSi(SiMe_3)_3$ underwent double salt elimination to form the borylene complex **4.5d** (Figure 26), which lacks the stabilizing influence of the strongly donating amino groups of **4.5a**−**c**.[211] The contrasts between the "supersilyl" derivative and **4.5a**−**c** are glaring, in the strong contraction of the Cr−B distance (1.88(1) Å) and the deshielded ^{11}B NMR signal (δ 204.3), both indicative of a reduced amount of electronic stabilization of the boron atom. The lack of an electron-donating amino-substituent on the boron atom appears to allow (or perhaps necessitate) stronger metal-to-boron π-retrodonation, thus decreasing the bond length. The ^{11}B NMR shift is the lowest-field shift known for a borylene complex and is reminiscent of those of transition metal boride species (covered in section 5).

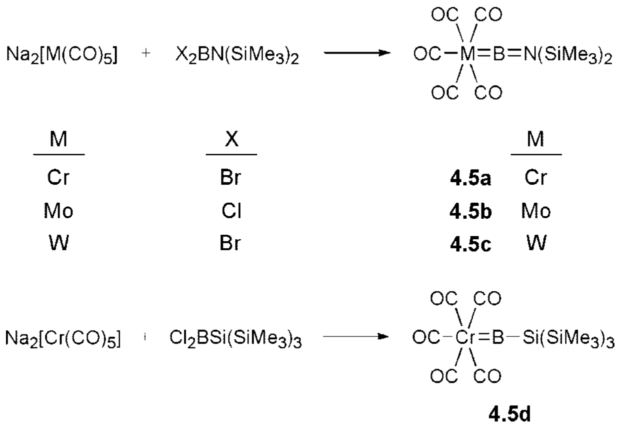


Figure 26. Synthesis of terminal borylene complexes of group 6 metals.

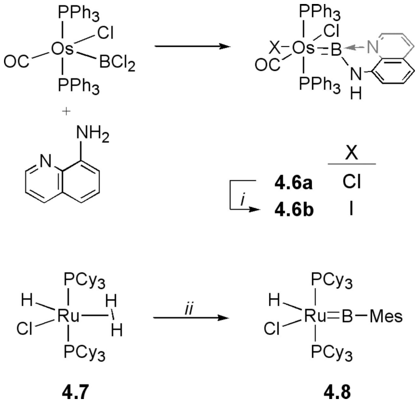
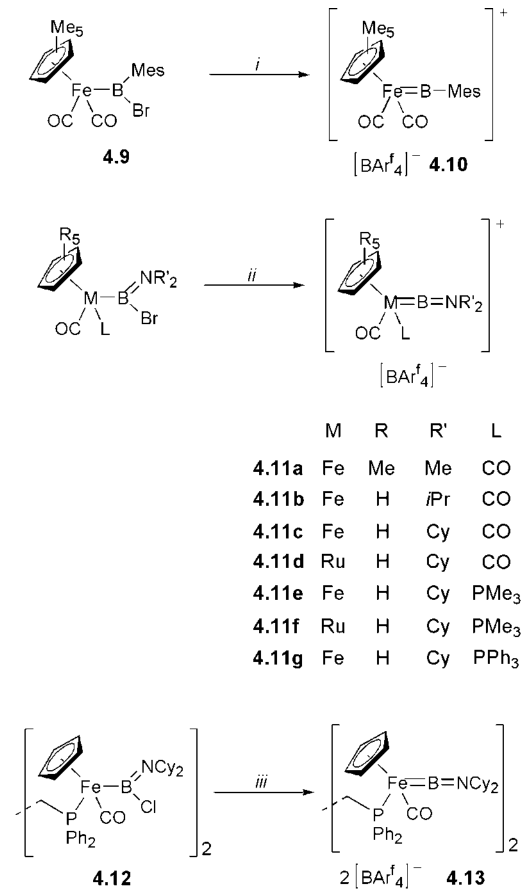


Figure 27. Synthesis of neutral terminal and base-stabilized borylene complexes of group 8 metals. Key reagents and reaction conditions: (i) $[NBu_4]I$; (ii) $MesBH_2$, vacuum.

Among neutral terminal borylene complexes are two base-stabilized examples from the group of Roper and Wright, the chloro- and iodo-substituted Os(II) complexes **4.6a**,**b** (Figure 27).[212] Addition of 8-aminoquinoline to $[OsCl(BCl_2)(CO)(PPh_3)_2]$ effected migration of one halide from the boryl ligand onto the Os center, loss of 1 equiv of HCl, and a quinoline-stabilized aminoborylene ligand in complex **4.6a**. Subsequent addition of $[NBu_4]I$ substituted the chloride ligand *trans* to the borylene with iodide, providing **4.6b**. While ^{11}B NMR and structural data of **4.6a** were unobtainable, the ^{11}B NMR signal of **4.6b** was observed at a boryl-like position (δ 51.7), and the Os−B distance was found to be 2.055 Å.

Somewhat related is the very recent synthesis of Ru(II) borylene complex **4.8** (Figure 27); however, in this case the bulky borylene ligand is not base-stabilized, and the complex lacks a CO ligand.[213,214] The synthesis of borylene **4.8** is particularly novel, starting from the reactive dihydrogen complex **4.7** and $MesBH_2$, through loss of H_2. As in the

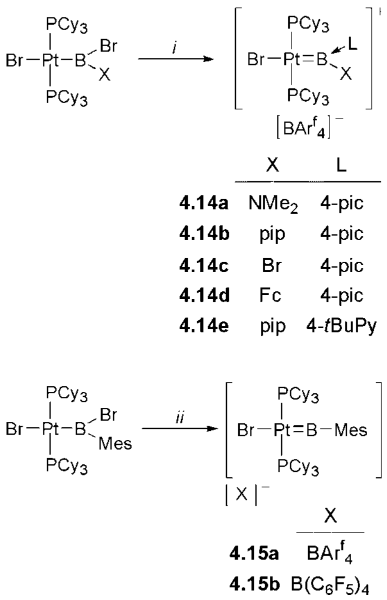


	M	R	R'	L
4.11a	Fe	Me	Me	CO
4.11b	Fe	H	*i*Pr	CO
4.11c	Fe	H	Cy	CO
4.11d	Ru	H	Cy	CO
4.11e	Fe	H	Cy	PMe_3
4.11f	Ru	H	Cy	PMe_3
4.11g	Fe	H	Cy	PPh_3

Figure 28. Synthesis of cationic terminal borylene complexes of group 8 metals. Key reagents and reaction conditions: (i and ii) $Na[BAr^f_4]$; (iii) $2Na[BAr^f_4]$.

“supersilyl” borylene complex **4.5d**, the nonelectron-donating mesityl borylene substituent enforces a short M−B distance (1.780(4) Å). The ^{11}B NMR signal was found at δ 106.0, distinguishing itself from those of bis(σ-borane) complexes, one of which is a possible intermediate in the synthesis. The bis(σ-borane) architecture, as well as possible intramolecular hydride−borylene interaction, was further ruled out through decoupled $^1H\{^{31}P\}$ and $^1H\{^{11}B\}$ NMR experiments, along with DFT calculations. The novel hydrogen-release synthetic method is particularly mild and is surprising in that the reverse reaction is possible upon hydrogen pressurization (vide infra).

In 2003 the group of Aldridge published the first example of a cationic borylene complex, prepared by halide abstraction from a neutral iron boryl complex. Since this time, both the halide abstraction protocol and the group 8 cationic borylene complexes thus prepared have become particularly prolific (Figure 28).[215–220] By employing a noncoordinating borate anion (invariably $[BAr^f_4]$), one halide is abstracted from the boryl ligand, causing the boron atom to become linear. In terms of first-generation complexes, this family contains the mesityl borylene complex **4.10**, a host of Fe and Ru aminoborylene complexes **4.11a**−**g**, and the dinuclear complex **4.13**. The spectroscopic and structural properties of the complexes are mostly as expected: the mesityl complex **4.10** displays a short Fe−B distance (1.792(8) Å), while the remaining iron (**4.11c**: 1.859(6); **4.11e**: 1.821(4); **4.13**: 1.830(7) Å) and ruthenium (**4.11d**: 1.960(6); **4.11f**: 1.928(4) Å) complexes contain relatively long bonds. In terms of ^{11}B NMR shifts, the only outlying complex is **4.10** (δ 145.0), while the signals of complexes **4.11a**−**g** and **4.13** all lie in the narrow range between δ 88 and 94. DFT calculations on **4.10** determined the relative contributions of B → Fe σ-donation and Fe → B π-retrodonation to the Fe−B bond and found them to be very similar to those found in Fischer carbene complexes, thus justifying their classification as true borylene complexes.[217] Results of computations on these cationic complexes suggested that nucleophilic attack may be possible at both the boron and iron centers. So far, reactivity studies of the cationic complexes have borne out this prediction and uncovered a number of other surprising results (vide infra).



	X	L
4.14a	NMe_2	4-pic
4.14b	pip	4-pic
4.14c	Br	4-pic
4.14d	Fc	4-pic
4.14e	pip	4-*t*BuPy

	X
4.15a	BAr^f_4
4.15b	$B(C_6F_5)_4$

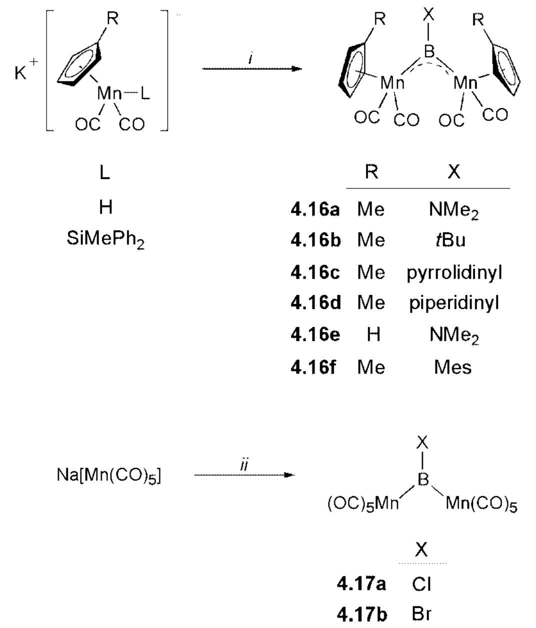
Figure 29. Synthesis of base-stabilized platinum borylene complexes. Key reagents and reaction conditions: (i) $Na[BAr^f_4]$, L; (ii) $Na[BAr^f_4]/K[B(C_6F_5)_4]$.

Shortly after reports of halide abstraction chemistry presented by Aldridge, the analogous technique was used to prepare T-shaped cationic boryl complexes (see section 3) based on platinum.[154,160] In this case, the halide removed was that attached to the Pt center, meaning that borylene complexes were not formed. However, when a strong donor ligand such as 4-picoline or 4-*tert*-butylpyridine was added, the base attacked at the boron atom, forcing migration of the bromide to the Pt center. The result, with a number of boron-subtituents, was base-stabilized borylene complexes **4.14a**−**e** (Figure 29), all displaying relatively long Pt−B distances (**4.14a**: 2.018(4); **4.14b**: 2.046(4); **4.14d**: 2.014(5); **4.14e**: 2.023(5) Å), in agreement with aforementioned base-stabilized borylene complexes.

However, in the case of boryl complex *trans*-$[PtBr(BBrMes)(PCy_3)_2]$, the steric demands of the bulky mesityl substituent induce (net) abstraction of the boron-bound bromide upon treatment with either $Na[BAr^f_4]$ or $K[B(C_6F_5)_4]$.[150] The resulting complexes **4.15a**,**b** (Figure 29) were the first examples of non-base-stabilized platinum borylene complexes. Complex **4.15b** displayed a Pt−B distance of 1.859(3) Å, understandably shorter than those of the structurally determined base-stabilized examples **4.14a**,**b**,**d**,**e**.

4.2.2. Bridging Borylene Complexes

The dimanganese complexes **4.16a**−**f** were the first complexes with definitive borylene character to be prepared (Figure 30).[221–224] They form simply from the reaction of a



L
H
SiMePh$_2$

	R	X
4.16a	Me	NMe$_2$
4.16b	Me	*t*Bu
4.16c	Me	pyrrolidinyl
4.16d	Me	piperidinyl
4.16e	H	NMe$_2$
4.16f	Me	Mes

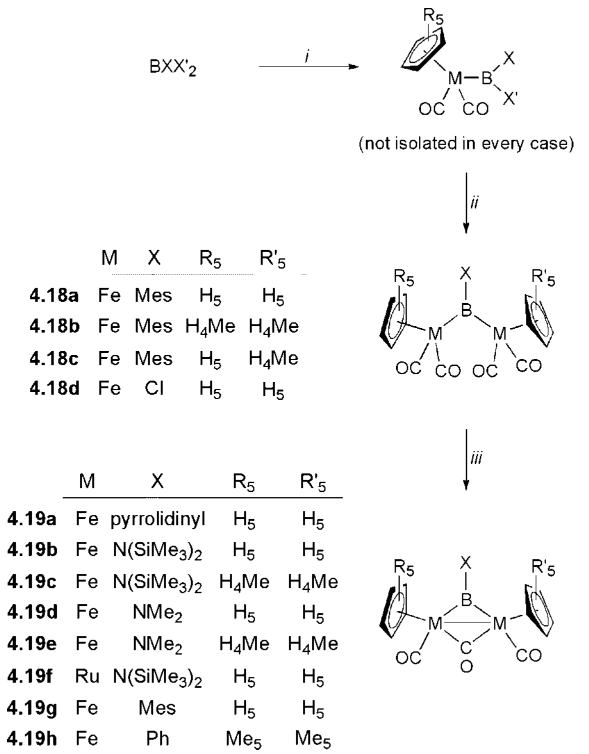
	X
4.17a	Cl
4.17b	Br

Figure 30. Synthesis of bridging borylene complexes based on manganese. Key reagents and reaction conditions: (i) $B_2X_2Cl_2$ (L = H, SiMePh$_2$); (ii) BX_3.

manganese hydride or silane anion (i.e., a "dianion equivalent" complex) with a dihalodiborane(4), liberating 1 equiv of a diborane(6) as a side-product. The ^{11}B NMR signals of the complexes **4.16a–f** vary widely, depending on the borylene substituent. The aminoborylene examples exhibit very similar ^{11}B NMR shifts (**4.16a**: δ 102.8; **4.16c**: δ 100.3; **4.16d**: δ 101.1; **4.16e**: δ 103.0), while the signals for the two carbon-based borylenes can be found at much lower field (**4.16b**: δ 170.0; **4.16f**: δ 165). The M–B bond distances of the bridging borylene complexes are slightly longer than those of many terminal borylene complexes; however, they resemble more closely the distances found in the aforementioned base-stabilized borylene complexes. The results of extensive studies on the reactivity and bonding of these complexes are covered later in this review.

A related group of bridging first-generation borylene complexes are the dimanganese haloborylenes **4.17a**,**b** (Figure 30).[225] Prepared instead via the monoanionic metalate Na[Mn(CO)$_5$], these species do not require the use of a diborane precursor, allowing direct access to the haloborylene architecture (and thus avoiding use of the highly sensitive tetrahalodiborane(4) reagents). The ^{11}B NMR data of the two complexes resembles that of the above bridging alkyl- and arylborylene complexes (**4.17a**: δ 160.1; **4.17b**: δ 163.6), while their Mn–B distances were found to be longer (**4.17a**: 2.164(2), 2.161(2) Å; **4.17b**: 2.149(3), 2.163(3) Å), perhaps indicating a lesser degree of multiple bonding in these complexes as compared to **4.16a–f**.

While group 8 boryl complexes form cationic *terminal* borylenes in the presence of halide abstracting agents, when treated with a second monoanionic metalate species (or alternatively in one pot with 2 equiv of metalate), bridging dinuclear borylene complexes result (Figure 31).[226,227,215,228–230,225] One of the features of the diiron borylene system is that, depending on the substituents on the boron atom and the cyclopentadienyl rings, one of two architectures is possible: the metals-apart tetracarbonyl borylenes **4.18a–d**, and the metals-together tricarbonyl borylenes **4.19a–h**. Only in the mesitylborylene case was it possible to isolate both tri- and tetracarbonyl complexes for the same set of ligands and



	M	X	R$_5$	R'$_5$
4.18a	Fe	Mes	H$_5$	H$_5$
4.18b	Fe	Mes	H$_4$Me	H$_4$Me
4.18c	Fe	Mes	H$_5$	H$_4$Me
4.18d	Fe	Cl	H$_5$	H$_5$

	M	X	R$_5$	R'$_5$
4.19a	Fe	pyrrolidinyl	H$_5$	H$_5$
4.19b	Fe	N(SiMe$_3$)$_2$	H$_5$	H$_5$
4.19c	Fe	N(SiMe$_3$)$_2$	H$_4$Me	H$_4$Me
4.19d	Fe	NMe$_2$	H$_5$	H$_5$
4.19e	Fe	NMe$_2$	H$_4$Me	H$_4$Me
4.19f	Ru	N(SiMe$_3$)$_2$	H$_5$	H$_5$
4.19g	Fe	Mes	H$_5$	H$_5$
4.19h	Fe	Ph	Me$_5$	Me$_5$

Figure 31. Synthesis of bridging borylene complexes with group 8 metals. Key reagents and reaction conditions: (i) Na[(η^5-C$_5$R$_5$)Fe(CO)$_2$], X′ = halide; (ii) Na[(η^5-C$_5$R′$_5$)Fe(CO)$_2$]; (iii) *hν* or Δ.

borylene substituents (M = Fe, X = Mes, R = R′ = H; **4.18a** and **4.19 g**), whereas the loss of carbonyl was not observed if the cyclopentadienyl ligand was any larger (i.e., for **4.18b**,**c**). While this can be ascribed to the greater steric bulk of the cyclic ligand, in the case of **4.18d**, where this bulk is absent, loss of CO was also not observed. In the case of **4.19a–f**,**h**, the loss of carbonyl was spontaneous under the reaction conditions and the tetracarbonyl intermediate was not isolated.

In general, the M–B distances of **4.18** were found to be longer than those of **4.19**, demonstrated well by those of the analogous pair of **4.18a** (2.09(1), 2.09(1) Å) and **4.19g** (1.956(2), 1.966(5) Å). In contrast, the ^{11}B NMR patterns of the two series were found to depend much less on the architecture of the metal fragments (i.e., tri- or tetracarbonyl; Fe or Ru) and more on the boron substituent, with the signals of all complexes **4.18** and **4.19** ranging from δ 161.9 (**4.19g**, X = Mes) to δ 103.5 (**4.19d**, X = NMe$_2$).

Oxidative addition of boron-halide bonds to low-valent transition metal centers has become a reliable method for the synthesis of boryl complexes (see section 3). However, this method was found to be similarly successful when the B–X bond is already part of a transition metal boryl complex (Figure 32).[231] The oxidative addition of a B–Br bond of [(η^5-C$_5$Me$_5$)(OC)$_2$Fe(BBrX)] (X = Fc, Br) to zerovalent palladium complex [Pd(PCy$_3$)$_2$] resulted in the borylene complexes **4.20a** and **b**, respectively. The complexes both feature bridging borylene and carbonyl ligands; however, they differ not only in the borylene substituent but also in the geometry of the ligands around the Pd center. Complex **4.20b** shows the large phosphine ligand to be located *cis* to the borylene ligand, while the sterically encumbered borylene ligand in **4.20a** presumably is the reason for the phosphine ligand being found *trans* to the boron. Likewise, their ^{11}B

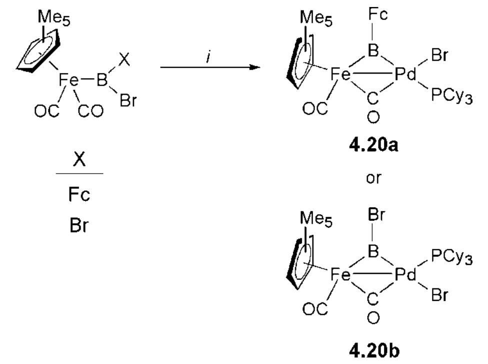


Figure 32. Synthesis of heterodinuclear borylene complexes by oxidative addition. Key reagents and reaction conditions: (i) $[Pd(PCy_3)_2]$.

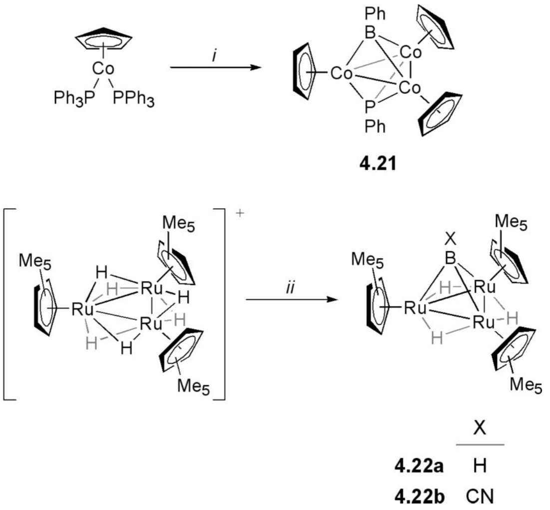


Figure 33. Synthesis of homotrinuclear borylene complexes. Key reagents and reaction conditions: (i) $2BH_3 \cdot THF$; (ii) $Na[BH_3X]$.

NMR signals are found relatively far apart (**4.20a**: δ 136; **4.20b**: δ 118). Crystallographic analysis of **4.20a** showed relatively short metal−boron distances (Fe−B: 1.903(3); Pd−B: 2.090(3) Å), reflecting a contraction of the Fe−B−Pd−C core that is perhaps unsurprising given that the metals are bridged by two ligands.

A number of homotrinuclear borylene complexes were prepared in unusual fashion from both mono- and trinuclear precursors by the groups of Fehlner and Rheingold, and later that of Suzuki (Figure 33).[232,233] Tricobalt complex **4.21** was prepared by addition of borane−tetrahydrofuran complex to $[(\eta^5\text{-}C_5H_5)Co(PPh_3)_2]$, involving a phenyl-group transfer from one (or more) phosphine ligand(s) to the boron. The resulting "phosphacobaltaborane" was presumed to have originated from *ortho* C−H activation by B−H bonds and loss of H_2, followed by cleavage of the P−C bond. Similarly, loss of H_2 accounted for the synthesis of **4.22a**,**b**, however, in this case from a preconstructed trimetallic scaffold. Borates $Na[BH_3X]$ (X = H, CN) provided three hydrogen atoms which combined with three hydride ligands from $[\{(\eta^5\text{-}C_5H_5)Ru\}_3(\mu\text{-}H)_3][BF_4]$, losing 3 equiv of H_2 and $Na[BF_4]$. Complex **4.22a** is the first example of a species containing a spectroscopically characterized hydroborylene ligand (δ_H 8.22, broad); however, this complex was not structurally authenticated. The ^{11}B NMR signal of the complexes **4.21** and **4.22a**,**b** was found in the range δ 116−144, not unusual for multimetallic borylene species.

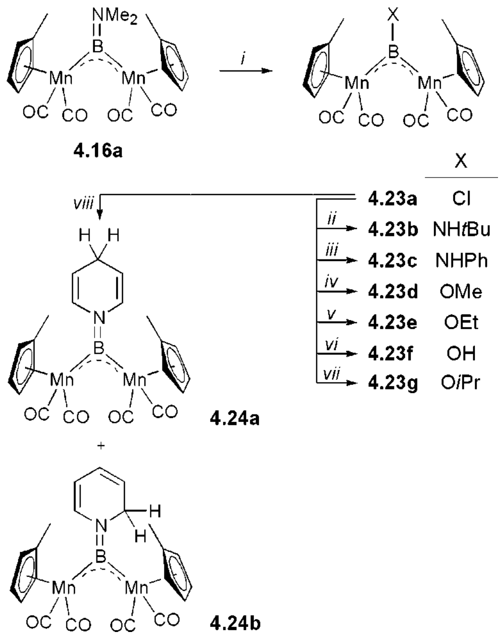


Figure 34. Synthesis of bridging borylene complexes by functionalization at the borylene center. Key reagents and reaction conditions: (i) $2HCl_{(g)}$; (ii) $tBuNH_2$; (iii) $PhNH_2$; (iv) MeOH; (v) EtOH; (vi) H_2O; (vii) *i*PrOH; (viii) pyridine, protic acid.

4.3. Second Generation Borylene Complexes

4.3.1. Borylene Complexes Derived from Bridging Dimanganese Borylene Complexes

Conversion of otherwise unreactive aminoborylene complex **4.16a** to the chloroborylene **4.23a** was achieved with anhydrous HCl, chlorinating the boron ligand and liberating 1 equiv of $HNMe_2$ (as $[H_2NMe_2]Cl$) (Figure 34).[234] The ^{11}B NMR signal of **4.23a** was found at δ 133.5, between the signals of analogous aminoborylenes (δ 100−103) and alkyl/aryl borylenes (δ 165−170).

The reactive B−Cl bond created in the synthesis of **4.23a** opened up a wealth of possibilities for functionalization of the borylene ligand (Figure 34).[235,236] A number of second-generation alkoxy- and aminoborylene derivatives were prepared by simple addition of primary amines (**4.23b**,**c**), alcohols (**4.23d**−**g**), or pyridine (with added protic acid, **4.24a**,**b**). The ^{11}B NMR signals of the new borylene complexes fit well into the paradigm of previously known aminoborylene complexes, with the signals for the aminoborylenes **4.23b**,**c** and **4.24a**,**b** (δ 102−112) being found at slightly lower field than those of the alkoxyborylene complexes **4.23d**−**g** (δ 96−101).

In addition to functionalization at the borylene substituent, dimanganese borylene complexes **4.16b**, **4.23a**, and **4.26** exhibit reactivity of their Mn−B bonds (Figure 35).[224,237] Addition of 2 equiv of $[Pd(PCy_3)_2]$ to **4.16b** or **4.23a** resulted in net loss of one $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2]$ fragment and two phosphines, providing heterotrinuclear borylene complexes **4.25a**,**b**, respectively. As in their starting materials, the ^{11}B NMR signals are found in very different regions (**4.25a**: δ 150; **4.25b**: δ 104), with the contrast stemming purely from the differing natures of the respective borylene substituents. Structurally too, the two complexes vary significantly, with the boron atom found much closer to the Mn center in **4.25a** (Mn−B 1.987(7); Pd−B 2.144(7), 2.128(8) Å) and almost equidistant to all three metals in **4.25b** (Mn−B 2.024(4); Pd−B 2.029(4), 2.031(4) Å).

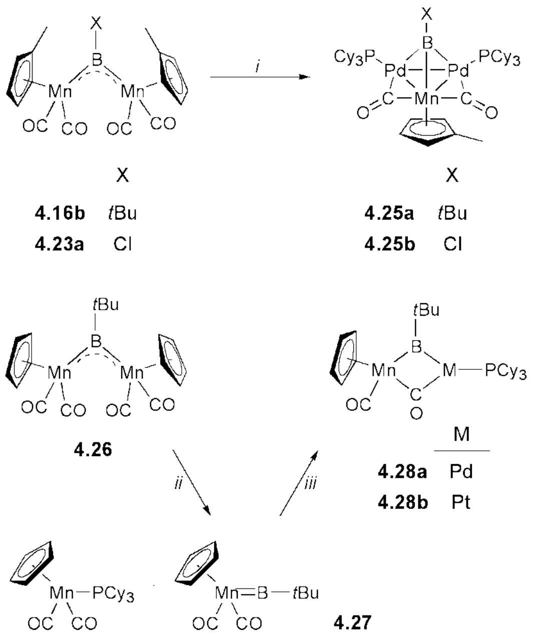


Figure 35. Synthesis of various borylene complexes by functionalization of Mn−B bonds. Key reagents and reaction conditions: (i) [Pd(PCy$_3$)$_2$]; (ii) PCy$_3$; (iii) [M(PCy$_3$)$_2$].

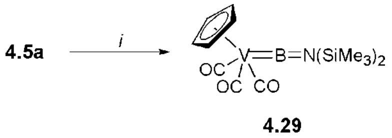


Figure 36. Synthesis of a group 5 borylene complex by intermetal borylene transfer. Key reagents and reaction conditions: (i) [(η^5-C$_5$H$_5$)V(CO)$_3$], *hν*.

Addition of the relatively mild base PCy$_3$ to alkylborylene complex **4.26** also effected loss of one manganese fragment as [(η^5-C$_5$H$_4$Me)Mn(CO)$_2$(PCy$_3$)], providing the terminal alkylborylene complex **4.27** (Figure 35).[238] Along with loss of the metal fragment came a movement of the ^{11}B NMR signal to high field (δ 144) and a large contraction of the Mn−B distance (1.809(9) Å). DFT calculations on the complex **4.27** supported the notion that the absence of π-stabilization from the boron substituent (*tert*-butyl) leads to enhanced Mn → B retrodonation and the very short M−B distance. As in its dimanganese analog, **4.27** reacted with zerovalent group 10 complexes [M(PCy$_3$)$_2$] (M = Pd, Pt) to provide the heterodinuclear borylene complexes **4.28a**,**b**. These complexes exhibited similar ^{11}B NMR spectra (**4.28a**: δ 151; **4.28b**: δ 143) to that of the trinuclear analog **4.25a** (δ 150). Their Mn−B distances (**4.28a**: 1.924(2); **4.28b**: 1.953(2) Å) were found to be somewhat shorter than that in trinuclear analog **4.25a**, yet they were much longer than that of mononuclear precursor **4.27**.

4.3.2. Borylene Complexes Derived from Terminal Group 6 Borylene Complexes

The terminal borylene complexes **4.5a−c** have, since their first reports in the late 1990s, become archetypes in terms of demonstrating borylene reactivity. The intermetal transfer of a borylene ligand is particularly facile with complexes **4.5a−c**, and this is borne out by the fact that the only known boron−ligand complex of vanadium has been prepared in this fashion (Figure 36).[239] Under photolytic conditions, **4.5a** undergoes borylene transfer to [(η^5-C$_5$H$_5$)V(CO)$_3$], with replacement of one V-bound CO ligand. The ^{11}B NMR signal undergoes a small downfield shift from δ 92.3 to δ 98.3, while the V−B distance was found to be 1.959(6) Å.

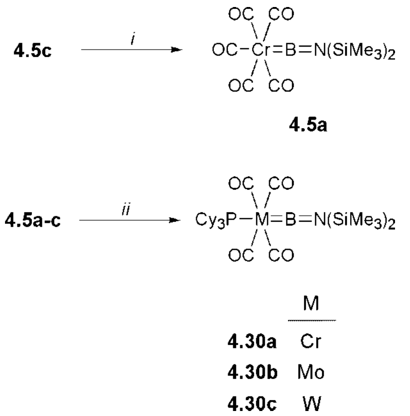


Figure 37. Synthesis of group 6 borylene complexes by intermetal borylene transfer and auxiliary ligand substitution. Key reagents and reaction conditions: (i) [Cr(NMe$_3$)(CO)$_5$], *hν*; (ii) PCy$_3$.

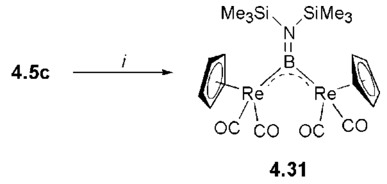


Figure 38. Synthesis of a group 7 borylene complex by intermetal borylene transfer. Key reagents and reaction conditions: (i) [(η^5-C$_5$H$_5$)Re(CO)$_3$], *hν*.

Photolytic borylene transfer within group 6 was found to be possible from the tungsten borylene complex **4.5c** to the labile-ligand precursor [Cr(NMe$_3$)(CO)$_5$] (Figure 37),[240] while the strong *trans*-influence of the borylene ligand in **4.5a−c** was demonstrated by replacement of the unique carbonyl ligand by PCy$_3$ in the synthesis of **4.30a−c**.[210,241] The ligand replacement was heralded by small downfield shifts of the ^{11}B NMR signals (**4.30a−c**: δ 90−94; **4.5a−c**: δ 86−92) and small contractions of the M−B distances (**4.30a−c**: 1.915−2.059 Å; **4.5a−c**: 1.996−2.152 Å).

The first rhenium borylene complex **4.31** was similarly prepared by addition of 2 equiv of [(η^5-C$_5$H$_5$)Re(CO)$_3$] under photolytic conditions (Figure 38).[240] The ^{11}B NMR signal of **4.31** was found at δ 100.4, in full agreement with the corresponding signals of analogous *dimanganese* aminoborylene complexes above (δ 100−108).

One of the most successful forays into the scope of the intermetal borylene transfer reaction has been their partial and complete transfer to group 9 metal complexes (Figure 39).[242−244] Combination of **4.5a** or **4.5c** with [(η^5-C$_5$R$_5$)M′(CO)$_2$] (M′ = Co, R$_5$ = H$_5$, H$_4$Me; M′ = Rh, R$_5$ = H$_5$; M′ = Ir, R$_5$ = Me$_5$) under photolytic conditions led to a number of different borylene architectures: first the *hetero*dinuclear borylenes **4.32a−d**, followed by loss of the group 6 fragment to afford terminal borylenes **4.33a−c**, and the slow disproportionation reaction to form *homo*dinuclear borylenes **4.34a−c**. Only in the case of [(η^5-C$_5$H$_5$)Co(CO)$_2$] was each architecture accessible in series, from heterodinuclear (**4.32d**, δ$_B$ 103) to terminal (**4.33a**, δ$_B$ 79) to homodinuclear (**4.34a**, δ$_B$ 106) examples. Within each structural class, the ^{11}B NMR signals appear to vary significantly with their associated metal centers.

Photolysis of **4.5a** or **4.5c** with [RhCl(CO)$_2$]$_2$ led unexpectedly to the unusual tetranuclear bis(borylene) complex **4.35**, so far the only known example of a complex containing

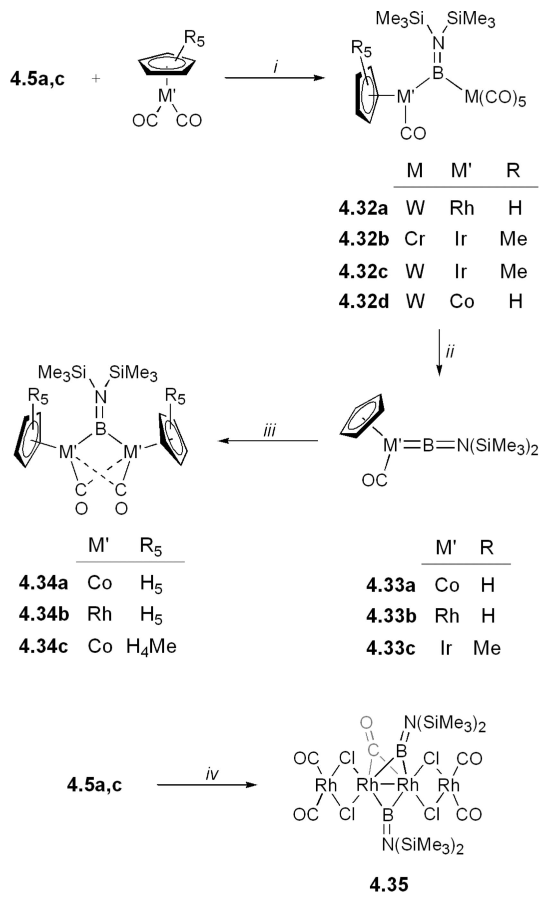


Figure 39. Synthesis of terminal and bridging borylene complexes by reaction with group 9 metal complexes. Key reagents and reaction conditions: (i) *hν*; (ii) RT, C_6H_6 or THF; (iii) −35 °C; (iv) $[RhCl(CO)_2]_2$.

two borylene ligands (Figure 39).[245] The two inner Rh centers are bridged by the two borylene ligands and an additional CO, while the outer two Rh centers connect to the inner centers through double chloride bridges. Spectroscopically, this complex is almost indistingushable from terminal rhodium(I) borylene **4.33b** (**4.35**: *δ* 74; **4.33b**: *δ* 75) despite the vast structural differences. Crystallographic analysis showed each borylene ligand to be slightly biased toward one rhodium center (differences in Rh−B distances within each borylene ligand 0.5−0.7 Å).

As the chemistry of monovalent group 9 metals with borylenes (vide supra) shows, the first mode of action of low valent metal complexes with borylenes **4.5a−c** seems to be coordination to the corresponding metal−boron bond. This mode of action is reiterated with the related zerovalent group 10 complexes $[M(PCy_3)_2]$ (M = Pd, Pt), in that their reaction with borylenes **4.5a−c** produces (depending on the combination of reactants) first the bridging borylenes **4.36a−d** and then with longer reaction times the phosphine derivatives **4.37a−d** (Figure 40).[246,247,241] In both cases, the group 6 and group 10 metal centers are connected through both a borylene and CO ligand. In phosphino derivatives **4.37a−d**, the phosphine is situated *trans* to the borylene ligand, once again highlighting the strong *trans* influence of metal-bound boron ligands. The ^{11}B NMR signals of the complexes **4.36a−d** (*δ* 97−100) and **4.37a−d** (*δ* 97−100) are practically indistinguishable; however, the signals for both sets of compounds are slightly downfield shifted from those of their precursor borylenes **4.5a−c** (*δ* 86−92). Crystallographically examined monophosphine complexes **4.36a** (2.084(2) Å) and **4.36c** (2.235(4) Å) show slight lengthening of their group 6 metal−boron distance relative to their respective parent borylene complexes. However, the corresponding distances of structurally characterized bis(phosphine) complexes **4.37c** (2.138(6) Å) and **4.37d** (2.138(3) Å) are dramatically contracted and shorter even than in the corresponding terminal borylenes **4.5b** and **4.5c**.

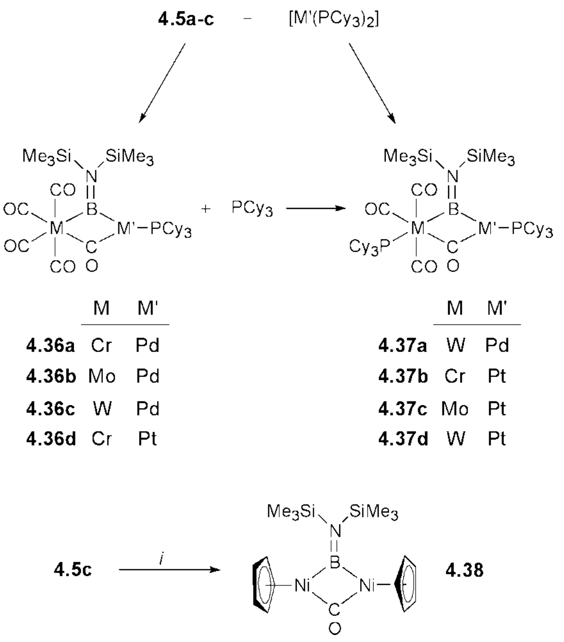


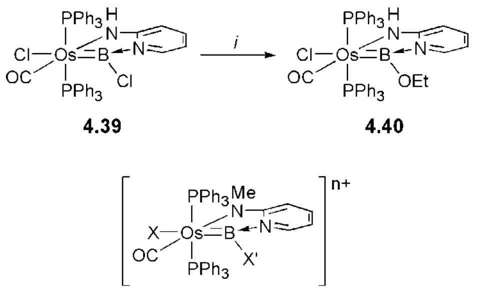
Figure 40. Synthesis of bridging hetero- and homodinuclear borylene complexes by reaction with group 10 metal complexes. Key reagents and reaction conditions: (i) $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$, *hν*.

The first nickel borylene complex **4.38** was prepared similarly, from terminal borylene **4.5c** and dimer $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ under photolytic conditions (Figure 40).[248] The reaction can be seen as a simple borylene-for-carbonyl exchange. Structural analysis revealed the Ni−Ni distance of **4.38** (2.3414(2) Å) to be slightly shorter than that of the precursor nickel complex.

4.3.3. Base-Stabilized Borylene Complexes

The base-stabilized Os(II) borylene complexes of Roper and Wright showed versatile reactivity at both the metal and boron atoms when treated with nucleophiles (Figure 41).[249] Thus, a range of second-generation borylene complexes was prepared from the parent borylene complexes **4.39** and **4.41a**. Addition of ethanol to either of these complexes resulted in ethoxyborylene complexes **4.40** and **4.41d**, respectively. When treated with $Ag[SbF_6]$, acetonitrile, and ethanol, **4.41a** undergoes ethanolysis and chloride abstraction simultaneously, resulting in cationic borylene complex **4.41e**. Alternatively, nucleophilic attack at the Os center by $Na[BH_4]$ converted **4.41a** to hydride complex **4.41b**. Under aqueous conditions, the boron center is hydroxylated while the chloride migrates to the Os center, providing **4.41c**. Overall, the second-generation borylene complexes prepared as above display ^{11}B NMR signals in the small range *δ* 52−55, except hydrido complex **4.41b** (*δ* 84.6).

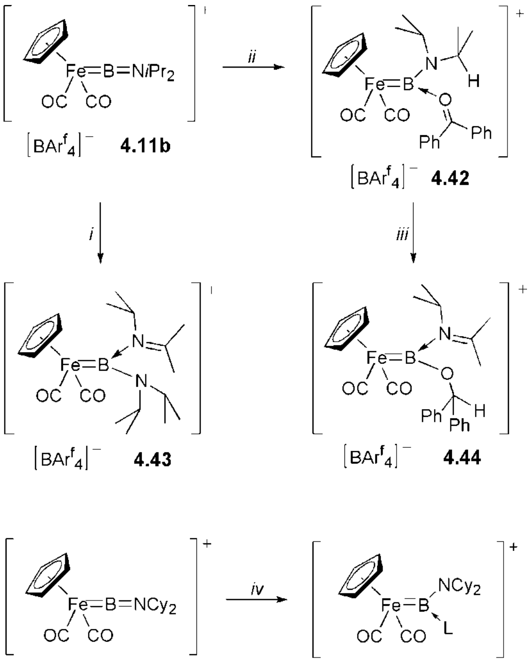
Further base-stabilized borylene complexes were prepared by simple addition of bases to cationic borylenes **4.11b** and **4.11c** (Figure 42).[250,220] Bases such as benzophenone, *i*PrN=CMe_2, THF, and 4-picoline led to base-



4.39 **4.40**

		X	X'	n
	4.41a	Cl	Cl	0
ii	**4.41b**	H	Cl	0
iii	**4.41c**	Cl	OH	0
iv	**4.41d**	Cl	OEt	0
v	**4.41e**	MeCN	OEt	1

Figure 41. Synthesis of base-stabilized borylene complexes by functionalization of boron−halide bonds. Key reagents and reaction conditions: (i) EtOH; (ii) Na[BH$_4$]; (iii) H$_2$O; (iv) EtOH; (v) Ag[SbF$_6$], MeCN, EtOH.

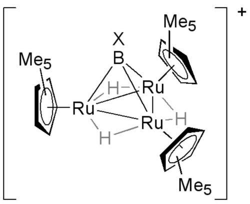


4.11b **4.42** **4.43** **4.44** **4.11c**

	L
4.45a	thf
4.45b	4-pic

Figure 42. Synthesis of a range of base-stabilized borylene complexes by addition of Lewis bases. Key reagents and reaction conditions: (i) iPrN=CMe$_2$; (ii) benzophenone, −78 to −50 °C; (iii) −50 °C to RT; (iv) L.

coordinated complexes **4.42** and **4.43** (from **4.11b**), and **4.45a**,**b** (from **4.11c**), respectively. However, in the case of ketone-stabilized aminoborylene **4.42**, the simple base-adduct was detected only at low temperatures, and upon warming to room temperature it underwent net intramolecular hydrogen transfer from the amine α-carbon to the ketone α-carbon, providing the imine-stabilized alkoxyborylene **4.44**. In all cases a significant upfield shift of the ^{11}B NMR signal was noted, from that of the precursor (**4.11b**: δ 93.5; **4.11c**: δ 93.1) to a region approaching that of boryl complexes (**4.42**: δ 49.0; **4.43**: δ 53.7; **4.44**: δ 64.0; **4.45b**: δ 56.9).



		X
	4.22a	H
i	**4.46a**	OMe
ii	**4.46b**	OEt

Figure 43. Synthesis of homotrimetallic borylene complexes by functionalization of a B−H bond. Key reagents and reaction conditions: (i) MeOH; (ii) EtOH.

4.3.4. Homotrinuclear Borylene Complexes

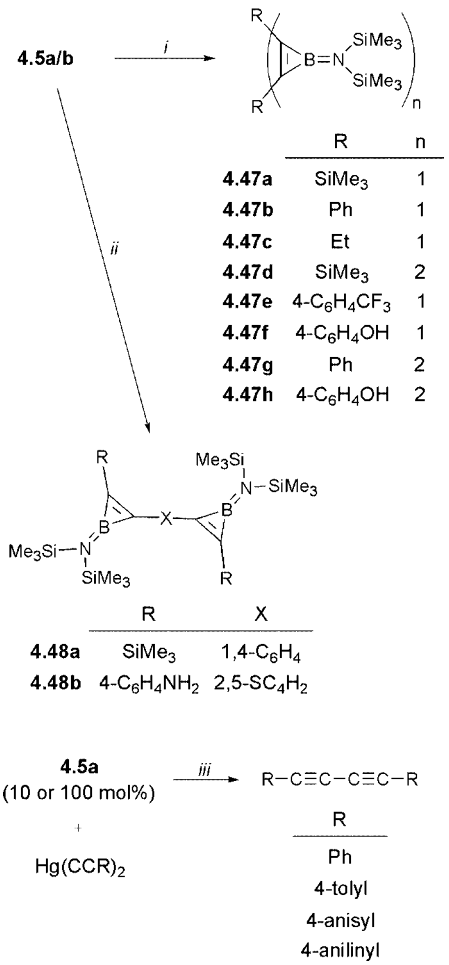
Hydroborylene complex **4.22a** combined with the protic solvents methanol and ethanol to provide the methoxy and ethoxyborylene complexes **4.46a** and **4.46b**, with retention of all three metal−boron bonds (Figure 43).[233] The reaction suggests possible hydridic behavior of the boron-bound hydrogen of precursor **4.22a**; thus, one could describe this family of homotrimetallic borylene complexes as "trimetalloborate" species. The ^{11}B NMR signals of alkoxyborylenes **4.46a** (δ 77.7) and **4.46b** (δ 87.7) were found at much higher field than their first-generation borylene analogues **4.22a** (δ 131.3) and **4.22b** (δ 116.9), yet they are still well outside the region expected for tetravalent boron species (δ < 0).

4.4. Further Reactivity of Borylene Complexes

4.4.1. Reactivity of Group 6 Borylene Complexes

The previous section dealt with borylene reactivity in which a product also contains a borylene ligand; however, a significant amount of borylene reactivity falls outside this category. One of the more unique areas of borylene reactivity is the photochemical borylene transfer from group 6 borylenes **4.5a** and **4.5b** to alkynes, resulting in borirenes **4.7a**−**c** and **4.7e**,**f** and bis(borirenes) **4.7d**,**g**,**h** (Figure 44).[251,252] Later, the bis(borirenes) **4.8a**,**b**, containing spacers between the borirene groups, were prepared analogously. Borirenes, three-membered "BCC" heterocycles first synthesized in 1984,[253] are isoelectronic with the stable, aromatic family of cyclopropenium cations. The aromaticity of the borirenes **4.7a**−**h** and **4.8a**,**b** is a plausible driving force for the efficient transfer of the borylene ligand to the corresponding alkyne, although little is known about the mechanism of the reaction.

A surprising complementary ability of the borylene complex **4.5a** was discovered during the attempted borylene transfer to bis(alkynyl) mercurial reagents. Under thermal conditions (90 °C), the borylene ligand is not transferred to the alkynyl groups; instead the mercurial reagent undergoes demercuration and coupling to form diynes RC$_4$R (R = Ph, 4-tolyl, 4-anisyl, 4-anilinyl) (Figure 44).[254] Surprisingly, a catalytic amount of the borylene (10 mol %) also led to good yields of the diynes. The stoichiometric and catalytic demercuration of bis(alkynyl)mercurials has been known for some time,[255] albeit with late-transition metals. That the reaction occurs without net disruption of the metal−boron bond is surprising, and this reaction is the first to be catalyzed by a borylene complex. In the case of Hg(CCPh)$_2$, photolysis at room temperature led to the corresponding bis(borirene),



	R	n
4.47a	SiMe3	1
4.47b	Ph	1
4.47c	Et	1
4.47d	SiMe3	2
4.47e	4-C6H4CF3	1
4.47f	4-C6H4OH	1
4.47g	Ph	2
4.47h	4-C6H4OH	2

	R	X
4.48a	SiMe3	1,4-C6H4
4.48b	4-C6H4NH2	2,5-SC4H2

R
Ph
4-tolyl
4-anisyl
4-anilinyl

Figure 44. Photochemical and thermal reactions of group 6 borylene complexes with alkynes, diynes, and bis(alkynyl) mercurials. Key reagents and reaction conditions: (i) $R(CC)_nR$, $h\nu$; (ii) R(CC)X(CC)R, $h\nu$; (iii) 90 °C.

with loss of Hg(0), showing that the two reactions can be performed in tandem.

Borylene behavior in the presence of alkenes and UV radiation appears to be somewhat different, however. The possible products, three-membered "bori*ranes*", are unknown and would lack aromatic stabilization. Thus, while such an architecture may be an intermediate of the reaction, there would be little thermodynamic driving force, as in the analogous borirene synthesis. Accordingly, the reaction of **4.5a** with 3,3-dimethylbut-1-ene produced two major products, the alkenyl(amino)borane **4.50** and its chromiumtetracarbonyl adduct **4.49** (Figure 45).[256] The unusual connectivity of **4.50** arises from an apparent activation of a geminal C−H bond of the alkene and insertion of the borylene into this bond, while **4.49** can be ascribed to additional (photolytic) loss of one CO from **4.5a** and coordination of **4.50** in a bidentate (σ,π) fashion. While **4.49** could be crystallized from the reaction mixture, pure samples of **4.50** were prepared by photolysis followed by addition of 2 equiv of tricyclohexylphosphine, with liberation of $[Cr(CO)_4(PCy_3)_2]$.

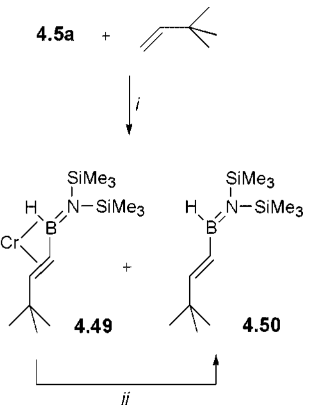


Figure 45. Photochemical insertion of a borylene into a C−H bond of an alkene. Key reagents and reaction conditions: (i) $h\nu$, RT; (ii) $2PCy_3$.

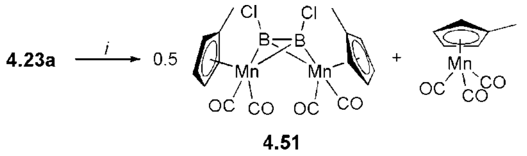


Figure 46. Coupling of two borylene fragments induced by irradiation. Key reagents and reaction conditions: (i) CO, $h\nu$.

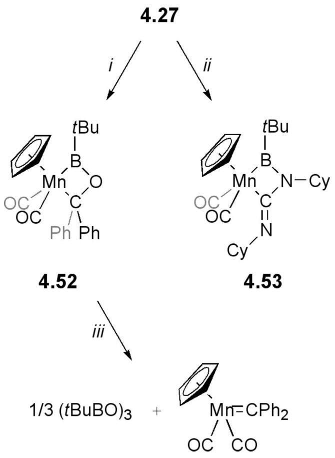


Figure 47. Interrupted and complete metathesis of a terminal borylene with ketones and imines. Key reagents and reaction conditions: (i) benzophenone; (ii) DCC; (iii) RT.

4.4.2. Reactivity of Group 7 Borylene Complexes

While the first terminal manganese borylene complex (**4.27**) was prepared by ligand addition to a dimanganese borylene complex (vide supra), an analogous metal-loss was observed much earlier. Photolysis of a mixture of chloroborylene **4.23a** with CO gave the unusual diborane complex **4.51**, presumably the result of dimerization of 2 equiv of a transient terminal borylene $[(\eta^5\text{-}C_5H_4Me)(OC)_2Mn(BCl)]$ (Figure 46).[257] The formation of the butterfly structure of **4.51** is accompanied by modest elongation of all M−B bonds, and a small downfield shift of the ^{11}B NMR signal (**4.51**: δ 142.2; **4.23a**: δ 133.5).

Somewhat similar 2 + 2 addition is noted in the reaction of terminal borylene complex **4.27** with C−O and C−N double bonds (Figure 47).[258] Addition of benzophenone or DCC to **4.27b** provided cycloaddition products **4.52** and **4.53**, respectively, and both of these were crystallographically characterized. It should be noted, however, that **4.52** must be isolated quickly, as in solution the cycloreversion process to form the completed metathesis products (carbene complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mn(CPh_2)]$ plus boroxine $(tBuBO)_3$) occurs within hours at room temperature.

4.4.3. Reactivity of Group 8 Borylene Complexes

The base-stabilized borylene complex **4.6b** underwent a surprising nucleophilic attack when treated with ethanol,

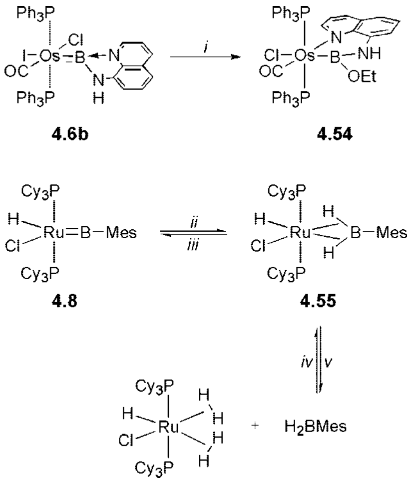


Figure 48. Reactions of group 8 borylene complexes with EtOH and H_2. Key reagents and reaction conditions: (i) EtOH; (ii) H_2; (iii) $-H_2$; (iv) $-$ $2H_2$; (v) $2H_2$.

resulting in disruption of the usually favored BN_2C_2 ring system. Loss of HI and migration of the quinoline nitrogen atom to the Os center provided boryl complex **4.54** (Figure 48).[212] Interestingly, the Os−B distance in both complexes remained unchanged within experimental uncertainty (**4.54**: 2.072(3) Å; **4.6b**: 2.055(8) Å) (see Table 3 for M−B distances), reinforcing the idea that the distinction between boryl and base-stabilized borylene complexes is in most cases a superficial one.

A recent addition to the reactivity of group 8 borylenes, and borylene complexes in general, is the *reversible* single and double insertion of molecular hydrogen into the Ru−B double bond of **4.8** (Figure 48).[213,214] While the synthesis of **4.8** from *trans*-$[RuHCl(H_2)(PCy_3)_2]$ was quantitative upon application of vacuum, the reverse reaction (pressurization with H_2, 3 atm) led to two products. The bis(σ-borane) complex **4.55** and the bis(dihydrogen) hydride complex *cis*,*trans*-$[RuHCl(H_2)_2(PCy_3)_2]$ (resulting from addition of 1 and 3 equiv of H_2, respectively) were identified in the

Table 3. List of M−B Distances and ^{11}B NMR Shifts for Borylene Complexes Mentioned Herein

complex	M−B dist (Å)	δ_B
4.2	2.010(3)	−35.3
4.4	1.997(3)	−37.9
4.5a	1.996(6)	92.3
4.5b	2.152(2)	89.7
4.5c	2.151(7)	86.6
4.5d	1.88(1)	204.3
4.6a		
4.6b	2.055(8)	51.7
4.8	1.780(4)	106.0
4.10	1.792(8)	145.0
4.11a		88.0
4.11b		93.5
4.11c	1.859(6)	93.1
4.11d	1.960(6)	90
4.11e	1.821(4)	93
4.11f	1.928(4)	93
4.11g		92
4.13	1.830(7)	91
4.14a	2.018(4)	
4.14b	2.046(4)	
4.14c		
4.14d	2.014(5)	
4.14e	2.023(5)	
4.15a		
4.15b	1.859(3)	
4.16a		102.8
4.16b		170.0
4.16c		100.3
4.16d		101.1
4.16e	2.031(1), 2.03(1)	103.0
4.16f	2.035(3)	165
4.17a	2.164(2), 2.161(2)	160.1
4.17b	2.149(3), 2.163(3)	163.6
4.18a	2.09(1), 2.09(1)	158.0
4.18b	2.09(2), 2.09(2)	157.9
4.18c		157.6
4.18d	2.019(2), 2.006(2)	146.6
4.19a		115.3
4.19b		118.4
4.19c	2.007(3), 2.002(3)	119.1
4.19d		103.5
4.19e		104.5
4.19f		105.9
4.19g	1.956(2), 1.966(5)	161.9
4.19h	1.934(6), 1.936(6)	159
4.20a	Fe 1.903(3), Pd 2.090(3)	136
4.20b		118
4.21	2.056(8), 2.018(8), 2.031(9)	143.7
4.22a		131.7
4.22b		116.9
4.23a	2.039(11), 1.976(9)	133.5
4.23b		102.4
4.23c		107.6
4.23d		98.9
4.23e	1.988(2), 2.012(2)	97.6
4.23f		101.6
4.23g		96.5
4.24a	2.023(5), 2.007(5)	111.9
4.24b		109.5
4.25a	Mn 1.987(7), Pd 2.144(7), 2.128(8)	150
4.25b	Mn 2.024(4), Pd 2.029(4), 2.031(4)	104
4.27	1.809(9)	144
4.28a	Mn 1.924(2), Pd 2.036(2)	151
4.28b	Mn 1.953(2), Pt 1.998(2)	143
4.29	1.959(6)	98.3
4.30a	1.915(2)	93.7
4.30b	2.059(3)	92.0
4.30c	2.058(6)	90.0
4.31		100.4
4.32a	W 2.423(4), Rh 2.004(4)	95
4.32b	Cr 2.816(8), Ir 1.931(8)	70
4.32c	W 2.848(4), Ir 1.935(5)	73
4.32d	W 2.434(3), Co 1.913(3)	103
4.33a		79
4.33b		75
4.33c	1.892(3)	67
4.34a	1.952(2)	106
4.34b	2.054(2), 2.054(2)	90
4.34c	1.983(2)	104
4.35	B^1 2.004(3), 2.051(3), B^2 2.076(3), 2.003(3)	74
4.36a	Cr 2.084(2), Pd 2.043(2)	100
4.36b		99
4.36c	Mo 2.235(4), Pd 2.065(4)	97
4.36d		98
4.37a		98
4.37b		97
4.37c	Mo 2.138(6), Pt 2.085(6)	100
4.37d	W 2.138(3), Pt 2.090(3)	99
4.38	1.921(14), 1.937(14)	92
4.40	2.066(5)	52.1
4.41a		
4.41b	2.078(4)	84.6
4.41c		
4.41d		53.2
4.41e		54.6
4.42		49.0
4.43		53.7
4.44	2.000(4)	64.0
4.45a		
4.45b	2.049(4)	56.9
4.46a		77.7
4.46b	2.177(6), 2.140(7), 2.146(6)	87.7

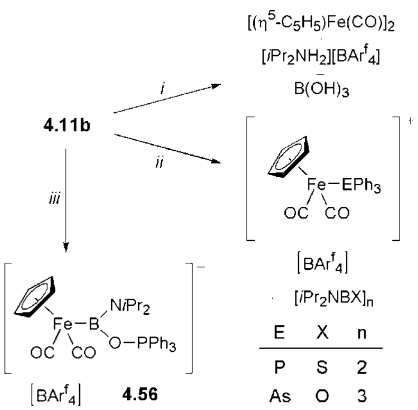


Figure 49. Reactions of a cationic borylene complex with nucleophiles. Key reagents and reaction conditions: (i) H_2O; (ii) Ph_3PS/Ph_3AsO; (iii) Ph_3PO.

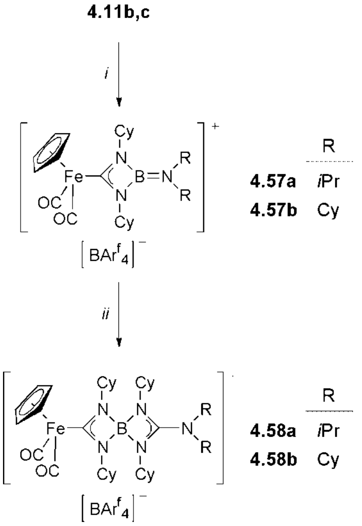


Figure 50. Insertion reactions of DCC into Fe=B and N=B bonds. Key reagents and reaction conditions: (i) DCC, −30 °C; (ii) 20 °C.

reaction mixture based on multinuclear NMR, and independent synthesis of the latter. The reaction is the first example of hydrogenative cleavage of a metal−boron double bond and is particularly surprising given its mildness and reversibility.

A vast range of reactivity has been reported of the prolific family of cationic iron borylene complexes reported by Aldridge et al. with nucleophiles and unsaturated systems. The balance between borylene substitution, borylene abstraction, base adduct formation, metathesis, and insertion appears to be very delicate with these systems, and the outcome of each reaction is far from predictable.

The case of borylene complex **4.11b**, from which a number of these reaction patterns were observed, is demonstrative of this unpredictability (Figure 49).[215,216] With excess H_2O, the usually unreactive B−N double bond was broken along with the M=B double bond, resulting in ammonium salt $[i\mathrm{Pr}_2\mathrm{NH}_2][\mathrm{BAr^f}_4]$, $B(OH)_3$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. Addition of phosphine (Ph_3PS) and arsine (Ph_3AsO) chalcogenides to **4.11b** resulted in mild metathesis of the Fe−B with the E−S or E−O bonds, leading to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(EPh_3)][\mathrm{BAr^f}_4]$ in both cases, with the side products being the cyclic species $[i\mathrm{Pr}_2\mathrm{NBX}]_n$ ($X = S$, $n = 2$; $X = O$, $n = 3$). Conversely, the P−O double bond of Ph_3PO remains intact when treated with **4.11b**, leading to oxygen-donor borylene adduct **4.56**, an indescrepancy ascribed to the greater strength of the P−O double bond over analogous P−S and As−O examples.

Another surprising development in the reactivity of these cationic borylene complexes was the insertion of unsaturated systems into the M=B and B=N double bonds. Bis(dicyclohexyl)carbodiimide (DCC) is known to insert into B−X bonds, and in the case of **4.11b**,**c**, this transformation is a very facile one. At low temperatures, products of the monoinsertion of DCC into the Fe−B bond can be detected in solution (**4.57a**,**b**) and in one case crystallographically characterized (Figure 50).[259,260] At room temperature, double insertion of DCC is noted, providing the spirocyclic boronium complexes **4.58a**,**b**. Both sets of complexes displayed ^{11}B NMR shifts well upfield of those of precursors **4.11b** (δ 93.5) and **4.11c** (δ 93.1). The resonance of monoinsertion product **4.57b** was found within the accepted range of aminoboranes (δ 25), while that of double insertion product **4.58a** lies within the range of tetracoordinate borate species (δ 3.4). DFT calculations on the possible intermediates of the reaction show that the conversion of the initial DCC-stabilized borylene (N → B) to the iron "carbene" product is highly favored energetically, while DCC slippage and insertion into the B−N bond of the former is a slightly endothermic process.

In a number of communications, Aldridge and co-workers reported nucleophilic additions of halides to the boron center of their cationic borylene species **4.10** and **4.11a**,**b** (Figure 51).[217,215,230,218] With salts containing free halides ([PPN]Cl, $[Ph_4P]Br$, $[n\mathrm{Bu}_4\mathrm{N}]I$) or tetrafluoroborate salt $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{BF}_4]$, neutral monohaloboryl complexes **4.59a**−**f** were prepared with ease, with the reaction being in effect the reverse of the halide abstraction by which the borylenes were prepared.

With a number of neutral nucleophiles, yet another reactivity pattern of the borylenes was uncovered (Figure 51).[219,261] With CO, $H_2C{=}CHt\mathrm{Bu}$, or benzophenone, complete loss of the borylene ligand was observed from mesitylborylene complex **4.10**. The neutral ligand was found bound to the Fe center in complexes **4.60a**−**c**, while the borylene ligand was presumed to have undergone insertion into a C−H bond of the dichloromethane solvent. With phenyl, xylyl, or cyclohexyl isocyanates, aminoborylene complex **4.11c** underwent metathesis of the Fe=B and C=O double bonds, resulting in isocyanide complexes **4.60d**−**f** and cyclic boroxine.

Transfer of the borylene ligand to a quinone was also achieved from **4.11c**, thereby aromatizing the carbocyclic system and providing the catecholborane derivative **4.61** (Figure 51).[220] The identity of the Fe-containing product was not mentioned but can be assumed to be $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, as determined for another borylene abstraction reaction (vide supra).

4.5. Major Electronic, Structural, and Mechanistic Studies of Borylene Complexes

4.5.1. Computational and Experimental Electron Density Studies on the Borylene Structure

A pioneering paper by Baerends et al. compared the electronic properties of free and bound (terminal and bridging) isolobal species N_2, CO, BF, BNH_2, and BO^-, with a view to proposing alternatives to CO as a ligand.[205] The energy of the frontier orbitals for these ligands was determined, and the first four were found to have relatively similar

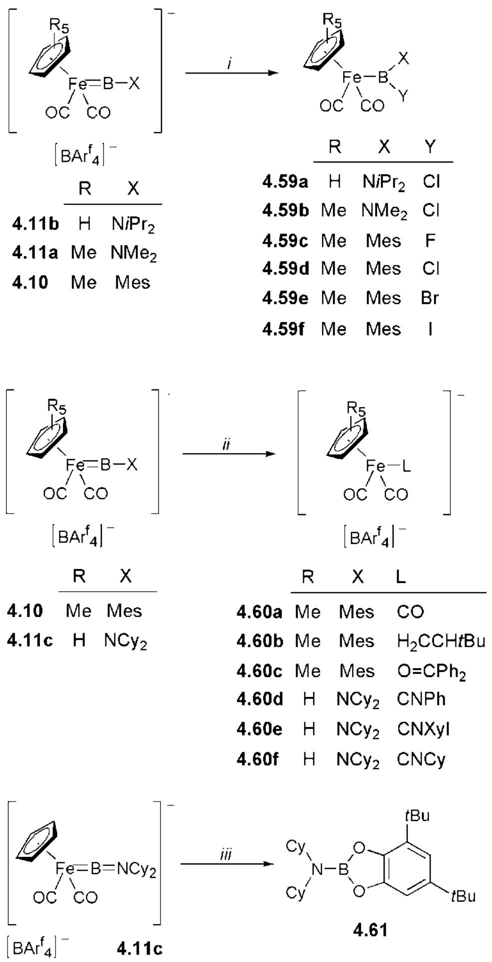


Figure 51. Addition of halides and neutral ligands to cationic borylene complexes. Key reagents and reaction conditions: (i) [nBu$_4$N][BF$_4$]/[PPN]Cl/[Ph$_4$P]Br/[nBu$_4$N]I; (ii) excess L or L=O; (iii) 3,5-di-*tert*-butyl-*ortho*-benzoquinone.

LUMO energies (keeping in mind that the degeneracy of this orbital is lost in BNH$_2$) yet dramatically increasing HOMO energies. The observed strong σ-donor abilities of the borylene ligand, and their resultant accumulation of positive charge, are inextricably linked to this concept. The fifth ligand, BO$^-$, has higher HOMO *and* LUMO energies than the others, providing a reason for the absence of this ligand in current transition metal chemistry.

Cowley and co-workers used DFT to analyze the bonding in group 13 diyl complexes supported by the [Fe(CO)$_4$] fragment, with alteration of the group 13 element (E) and the substituent (R).[262] In general, it was found that the ligand is in all cases a two-electron σ-donor, and it is the electronic properties of the substituent which modulate the amount of retrodonation obtained from the Fe center. Subsequent work on a range of different borylene complexes by Frenking and co-workers supported this and suggested that the retrodonation could in some cases even overwhelm the σ-donation, if the substituent is a very poor π-donor.[263,206] More detailed work from the group of Frenking dealt with the geometry of a range of complexes [(OC)$_4$Fe(BR)] and found that the borylene ligand sits in the equatorial position for R = NH$_2$ and N(SiMe$_3$)$_2$ but the equatorial position is nearly degenerate with the axial when R = H.[264]

Calculations performed by Aldridge and Willock on the relatively new group 8 cationic borylenes showed that, surprisingly, there is little or no decrease of the M−B bond order merely due to the positive charge of the complexes and that they rightfully deserve their classification as "borylenes".[265]

Two recent contributions concerning bridging borylene complexes have called into question the extent of metal−metal bonding in these complexes.[266,267] The combined theoretical/experimental electron density study of Stalke and co-workers concluded in the case of *tert*-butylborylene complex **4.27** that the assumed Mn−Mn bond in the complex does not exist. A bond path was not found between the metal atoms; instead, the coupling of the electrons is accomplished via the boron atom in a delocalized fashion. Subsequently, the group of Kaupp published a comprehensive theoretical study of dimanganese alkyl- and aminoborylenes, in relation to analogous carbene and vinylidene complexes. Through QTAIM and ELF analyses, the absence of the direct metal−metal bond path (suggested by Stalke) was confirmed. Such was the case also for the carbene and vinylidene examples, complexes earlier evoked as containing meaningful Mn−Mn bonds. In addition, both studies favored a bonding picture involving three distinct bonds to boron, with the ligand being described as more dimetalloborane-type than "true" borylene.

4.5.2. Computational Studies on Borylene Reaction Mechanisms

The groups of Jemmis and Aldridge have collaboratively taken up the challenge of elucidating the mechanisms of metathesis of borylene complexes.[268,261,219] In a series of publications, parallels were drawn between the well-known alkene metathesis process and the known borylene metatheses with E=O and E=S (E = C, P, As) double bonds. The metathesis process was found to begin by adduct formation of the electronegative element to the boron center.[268] From this point, four-membered ring formation and metathesis competes with β-hydride transfer, a process observed experimentally in the low-temperature conversion of benzophenone-stabilized aminoborylene **4.42** to imine-stabilized alkoxyborylene **4.44**.

The second study dealt with the metathesis/insertion chemistry observed in the reaction of cationic borylene complexes with carbodiimides and isocyanates.[261,219] Although both reaction patterns are observed in tandem experimentally, insertion of carbodiimides (and, separately, isocyanates) into the Fe=B double bond is preferred over that into the B=N bond. In terms of reactions with isocyanates, net metathesis is plausible via either initial O → B coordination or N → B coordination followed by insertion and cycloreversion. A third study led to the finding that a spirocyclic intermediate akin to the double carbodiimide insertion seen earlier (i.e., isocyanate insertion into both Fe=B and B=N bonds) is not a viable intermediate.

5. Boride Ligands

5.1. Introduction

Multimetallic boride complexes containing a single hypovalent boron atom, along with the iminoboryl complexes described in section 3, have been arguably the two most distinct new classes of boron complex to emerge recently. In just a few years, the variety of boride complexes has increased dramatically and now spans di- (linear) and trinuclear (T-shaped, Y-shaped, trigonal) complexes and

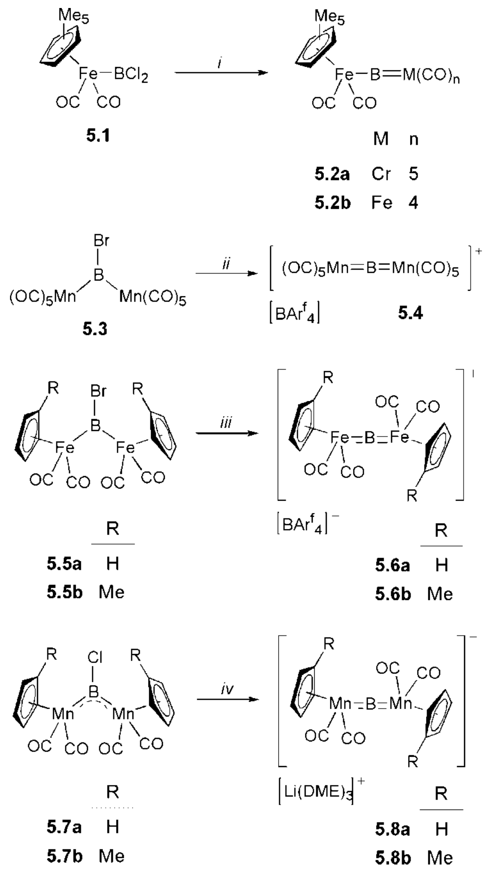


Figure 52. Synthesis of dinuclear boride complexes. Key reagents and reaction conditions: (i) $Na_2[M(CO)_n]$, −100 °C; (ii and iii) $Na[BAr^f_4]$; (iv) Li powder, DME.

includes cationic, neutral, and anionic examples. The metal−boron bonding in these complexes ranges from weak, predominantly metal−base dative bonding to "full" double bonding, and the spectroscopic properties of the complexes vary accordingly.

The synthetic routes to these complexes are equally intriguing. Halide abstraction from boron, oxidative addition of boron−halide bonds, salt elimination, and halide metathesis by a boride anion have now all been shown to be effective toward this end. Thus, boride complexes make an excellent showcase of the new-found versatility of boron reactivity from the traditional polarity B^+/M^- to its opposite, B^-/M^+.

The known reactivity of the smallest boron ligand is currently limited to two reactions (vide infra); however, research into this area is in progress.

5.2. Synthesis and Properties of Boride Complexes

The synthesis of the first boride complexes **5.2a**,**b** was a logical extension of the double salt elimination chemistry used in the synthesis of the original group six pentacarbonyl borylenes from this laboratory (Figure 52).[269] From the dihaloboryl complex $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe(BCl_2)]$, 2 equiv of NaCl are lost upon addition of the metalate dianions $Na_2[M(CO)_n]$ (M = Cr, $n = 5$; M = Fe, $n = 4$) at low temperature. The ^{11}B NMR signals of both boride complexes were found at extremely low field (**5.2a**: δ 204.6; **5.2b**: δ 190.9), and from X-ray crystallographic analyses both complexes were determined to have nearly linear M−B−M′ axes (**5.2a**: 177.8(1)°; **5.2b**: 175.4(1)°). The Cr−B distance of **5.2a** (1.975(2) Å) was found to be slightly shortened when compared to its aminoborylene counterpart $[(OC)_5Cr\{BN(SiMe_3)_2\}]$ (1.996(6) Å), reflecting the lesser ability for π-donation of the iron-based borylene substituent.

As seen earlier, abstraction of halides from boryl ligands can lead to linearization of the boron atom and increase of the M−B bond order. Accordingly, abstraction of bromide from the bromoborylene complexes **5.3** and **5.5a**,**b** also led to the linear, cationic boride complexes **5.4** and **5.6a**,**b**, respectively (Figure 52).[270] The dimanganese boride **5.4** exhibited a significantly low-field resonance in its ^{11}B NMR spectrum (δ 224.9), while those of **5.6a**,**b** (**5.6a**: δ 191.2; **5.6b**: δ 193.7) were found at slightly less extreme positions. Of these complexes, structural data from the two structurally confirmed examples showed M−B distances short enough as to suggest considerable multiple bonding character (**5.4** Mn−B: 1.9096(5) Å; **5.6b** Fe−B: 1.828(5), 1.851(5) Å).

Conversely, reduction of a boron−halide bond has also been demonstrated, leading to the anionic boride complexes **5.8a**,**b** (Figure 52).[271,272] In both cases, stirring chloroborylenes **5.7a**,**b** with Li powder in DME gave strong downfield shifts of the ^{11}B NMR resonance (**5.7a**: δ 196; **5.7b**: δ 195.3) and compounds which crystallized as their $Li(DME)_3$ (ion-separated) salts. Unlike the boryl anions of Yamashita and Nozaki (vide supra), these anionic complexes contain linear boron atoms. Given this fact, the description of **5.7a**,**b** as "boryl anions" appears somewhat misplaced, although they appear to exhibit a modicum of nucleophilic behavior (vide infra).

Trimetalloboride complexes represent the full conceptual metalation of a borane; thus, such complexes were expected to be, effectively, trimetalloboranes. However, the first examples of such a complex did not fit this description in any way. Addition of a zerovalent group 10 complex $[M(PCy_3)_2]$ (M = Pd, Pt) to bridging bromoborylene complex **5.9** resulted in the T-shaped borides **5.10a**,**b** through oxidative addition of the remaining B−Br bond (Figure 53).[273] The unusual geometry at boron, as well as the greatly lengthened M−B (M = Pd, Pt) bond distance compared to the other group 10 centers (**5.10a** M−B: 2.150(4), Pt−B: 1.923(4) Å; **5.10b** M−B: 2.158(4), Pt−B: 1.938(4) Å) meant that a description of the complexes as "trimetalloboranes" would be inaccurate. The ^{11}B NMR data for the complexes (**5.10a**: δ 144; **5.10b**: δ 130) was strongly upfield-shifted in comparison to the previously synthesized boride complexes (δ 190−224), hinting at an unusual bonding situation. Subsequent DFT calculations suggested that the unusual geometry may be partly due to the third metal (M = Pd, Pt) binding strongly to the bridging bromide and CO ligands, yet providing only a dative (M → B) bond to the boron center.

Recently, a number of trimetalloboride complexes have been prepared utilizing two extreme reactivity patterns of the boron center: namely, nucleophilic attack *at* boron (B^+/M^-) and *by* boron (B^-/M^+) (Figure 53).[274,275] Addition of the nucleophilic complex $Na[Co(CO)_4]$ to cationic boride complex **5.3** effected the surprising loss of one CO ligand from cobalt and the trimetalloboride **5.11**. The complex, signified by a characteristic low-field ^{11}B NMR shift of δ 195.8, was found by single-crystal X-ray crystallography to contain two borderline semibridging CO ligands between the Co and one Mn center (heavily biased toward the Mn atom). This structure enforces an inequivalence between the two

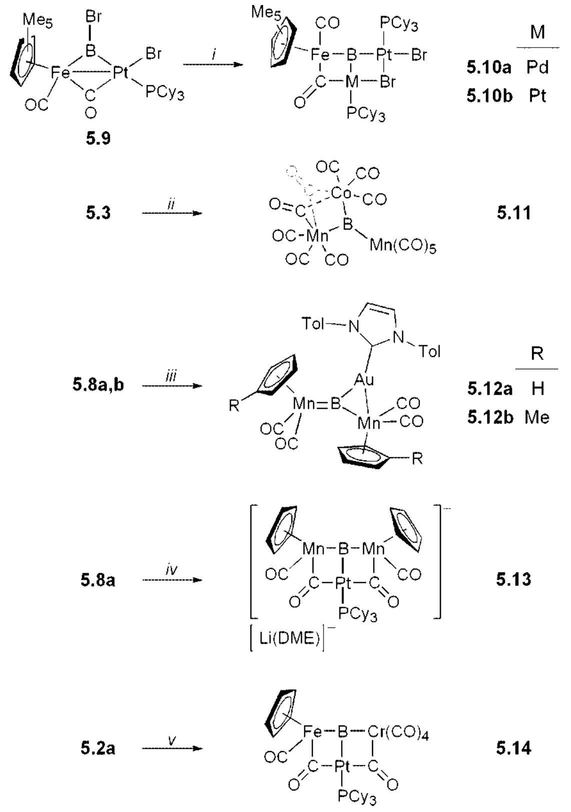


Figure 53. Synthesis of trinuclear boride complexes. Key reagents and reaction conditions: (i) $[M(PCy_3)_2]$; (ii) $Na[Co(CO)_4]$; (iii) [(ITol)AuCl]; (iv and v) $[Pt(PCy_3)_2]$.

Mn centers, and this is seen also in the very disparate Mn−B distances (Mn^{term}−B: 2.129(2) Å; Mn^{br}−B: 2.290(2) Å).

The opposite of this polarity was observed in the nucleophilic halide substitution of [(ITol)AuCl] by anionic boride complexes **5.8a**,**b**. The trimetalloboride complexes thus prepared (**5.12a**,**b**) showed some similarities to complex **5.11**, in that the two Mn centers are inequivalent; however, no interaction was noted between any CO ligands and the Au center. As is the case for **5.11**, the longer Mn−B bond is that to the terminal Mn moiety (Mn^{term}−B: 1.871(3) Å; Mn^{br}−B: 1.964(3) Å) in the complex **5.12b**.

Very recent additions to the family of trimetalloborides include the platinum-containing anionic and neutral borides **5.13** and **5.14**, prepared by addition of $[Pt(PCy_3)_2]$ to the appropriate dimetalloboride **5.8b** or **5.2a**. These complexes bear some resemblance to the original T-shaped complexes **5.10a**,**b** (Figure 53).[276] However, where the group 10 centers in **5.10a**,**b** can be thought of as possessing oxidation states greater than zero due to the two halide ligands, these halides are absent in both **5.13** and **5.14**. Interestingly, the boron-containing anions of the salt **5.13** were found to be linked by $[Li(DME)]^+$ fragments through two oxygen atoms of CO ligands (one terminal, one bridging), suggesting some residual nucleophilicity may remain at the CO ligands.

5.3. Further Reactivity of Boride Complexes

Other than the aforementioned syntheses of trimetalloboride complexes, only two reactions of boride complexes are currently known (Figure 54).[277,271] The first, a dimetallic variation of the borylene transfer to alkynes, resulted in metalloborirene **5.15**—the first transition metal complex of a borirene. Photolysis of boride complex **5.2a** with bis(trimethylsilyl)ethyne resulted in loss of the $Cr(CO)_5$ fragment. Extensive theoretical studies of the complex suggested that little Fe-to-B backbonding exists in the molecule and that the aromaticity of the ring remains intact.

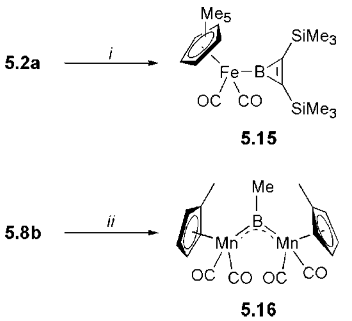


Figure 54. Further reactivity of boride complexes. Key reagents and reaction conditions: (i) bis(trimethylsilyl)ethyne, *hν*; (ii) methyl iodide.

The addition of methyliodide to the anionic boride complex **5.8b** effected a rare example of addition of a nucleophilic boron atom to an electrophile. Methylborylene complex **5.16** was prepared in this manner, giving hope for further mild reactivity of these anionic boron complexes.

6. Recent and in Press Literature

Since this work was submitted for publication, a number of papers relevant to this topic have appeared. A number of tri- and tetradentate mixed sulfur-donor borane complexes were synthesized by Owen and co-workers,[278] a comprehensive full paper from Crossley and Hill elaborated on the synthesis and reactivity of group 9 borane complexes,[279] and a number of slipped-borane complexes of copper(I) were synthesized by Maron, Bouhadir, and Bourissou.[280] New nickel complexes with Ni → B interactions have been synthesized by Stephan, from reaction of $[Ni(COD)_2]$ with “frustrated Lewis pairs”, i.e. alkynyl-bridged phosphine-boranes and their H_2 adducts, phosphonium-borates.[281]

A recent review of carbon−boron bond formation via C−H activation once more demonstrated the extraordinary importance of late transition metal boryl complexes as key intermediates and/or catalytically active species in synthetic chemistry.[282] In this context, the group of Smith examined the steric influence of chelating bisphosphine coligands on the iridium catalyzed borylation of arenes,[283] and extensive mechanistic studies were performed employing time-resolved infrared spectroscopy supported by DFT calculations.[284] Furthermore, adaption of the strategy utilized for the preparation of the first stable boryl complex of copper[177] also allowed for the synthesis of the corresponding nickel and cobalt complexes by metathesis of the corresponding alkoxides with bis(catecholato)diborane(4).[285] Thus, this protocol seems to represent a general applicable route to boryl complexes of the lighter late transition metals, which still are rather limited in number.

In terms of borylene complexes, synthesis of a neutral base-stabilized borylene complex of platinum,[286] and the transfer of a borylene fragment to a platinum(II) σ-alkynyl complex,[287] were both reported by this group. In a compelling duet of papers, Aldridge reported the long-awaited synthesis and characterization of an isolable complex containing a bridging BF ligand (and additionally the abstraction of its fluoride, providing a cationic diruthenium boride complex),[288] while the group of Andrews only weeks later reported the matrix isolation and characterization of the group 4 complexes $F_2M{=}BF$ (M = Ti, Zr, Hf), containing terminal BF ligands.[289] Recently, Pandey, Lledós, Maseras, and Musaev have published two computational studies of borylene complexes, with the first focusing on cationic borylene complexes of the Cowley $[L_nM{-}B{-}(\eta^5\text{-}C_5R_5)]^+$ and Aldridge $[L_nM{=}B(\text{amino/aryl})]^+$ forms[290] and the second focusing on neutral group 9 borylene complexes of the type reported by our group.[291]

7. Conclusions

Borane transition metal complexes have had a tumultuous history: syntheses of complexes containing *unsupported* M → B bonds were reported many times over in the period before about 1990, a number of which were convincingly refuted in the 1990s. Finally the field was somewhat reborn with the unequivocal (and structurally confirmed) synthesis of complexes bearing *supported* borane ligands by Hill and co-workers in 1999. Now, just over 10 years after this rebirth, the field has grown to include a number of interesting ligand architectures with varying Lewis-base donor atoms (S, P, N) and rigid cyclic backbones (based on imidazole, triazole, phenylene, and azaindole). In one case, the degree of "support" of the borane ligand has been decreased to its lower limit—by application of a singly strapped phosphinoborane ligand—while still retaining a well-defined M−B dative bond. Recently, researchers have turned their attention to the reactivity of borane complexes, flexible examples of which have been proposed as mediators of organometallic reactions via their labile M−B bonds.

The field of transition metal boryl complexes contrasts with the remaining chemistry covered in this review, in that the foundational knowledge had been arguably mapped out before the other fields existed. The current maturity of the field can be witnessed in the now-widespread (and relatively well-understood) use of transition metal-catalyzed borylation techniques in areas outside of inorganic chemistry. Despite this, a number of fascinating new reactivity patterns and structures have emerged in the previous decade. In particular, the recent synthesis of a nucleophilic boryl anion has provided a new synthetic route to boryl complexes, and this has already made its mark in the synthesis of novel boryl complexes of group 4 and 11 metals. This breakthrough alone should ensure the field of transition metal boryl complexes remains as compelling as ever.

Since the previous review in this journal regarding transition metal boron chemistry, the field of borylene complexes has exploded with activity. Yet, as in the field of boryl complexes, borylene complexes of a number of transition metal elements are yet to be synthesized, and some may never be. The borylene transfer reaction, useful for preparing novel "second-generation" borylene complexes, has recently been shown to be also effective at functionalizing main-group species. Borylene insertions into H−H and C−H bonds have recently been demonstrated, and a host of other element−element bonds beckon as potential insertion targets. However, many hurdles remain before this protocol is to become broadly used, in particular the harsh conditions or reactive precursors required for the synthesis of the corresponding "first generation" borylene species (via halide abstraction or salt metathesis). This problem has recently shown signs of being solved, with the very mild synthesis of a terminal, reactive borylene complex from $[RuHCl(H_2)(PCy_3)_2]$ and a dihydroborane.

Borides are perhaps the youngest members of the boron−ligand family, yet the variety of examples already available is surprising. The number of known complexes now rivals that of the related family of monocarbon ("carbide") complexes, making borides perhaps the only field of boron−TM complexes to numerically compete with its organometallic counterpart. The manifold reactivity and spectroscopic properties of the known boride complexes depend heavily on their structures, with the latter being exemplified by a range of ^{11}B NMR signals spanning almost 100 ppm.

In all, the field of transition metal boron chemistry has made large steps in the past 10 years, due to synthetic and structural research in conjunction with high-quality computational studies. With continued efforts and imagination, new bonding paradigms and classes of molecule should be accessible. Simpler, milder syntheses of the known classes of complexes should also ensure that promising reactivity patterns such as borylene transfer and insertion can reach closer to their potential widespread application in organic synthesis.

8. Abbreviations

Ac	acetate
Ar^f	3,5-bis(trifluoromethyl)phenyl
atm	atmospheres (pressure)
BFlu	9-borafluorenyl
Bm^R	bis(2-mercapto-1-R-imidazolyl)borate
br	bridging
cat	catechol-diide
cod	1,5-cyclooctadiene
Cy	cyclohexyl
DBU	diaza(1,3)bicyclo[5.4.0]undecane
DFT	density functional theory
dcpe	1,2-bis(dicyclohexylphosphino)ethane
Dipp	2,6-diisopropylphenyl
DMAP	(4-dimethylamino)pyridine
DME	1,2-dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
equiv	molar equivalents
Et	ethyl
fac	facial
Fc	ferrocenyl
Hex	hexyl
hν	photolysis
HOMO	highest occupied molecular orbital
*i*Bu	isobutyl
IMes	*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
*i*Pr	isopropyl
ITol	*N*,*N*′-bis(4-methylphenyl)imidazol-2-ylidene
LUMO	lowest unoccupied molecular orbital
Me	methyl
mer	meridional
Mes	2,4,6-trimethylphenyl
NBD	norbornadiene
NBO	natural bond order
NLMO	natural localized molecular orbital
NPA	natural population analysis
Ph	phenyl
pic	picoline
pip	piperidine
PPN	bis(triphenylphosphine)iminium chloride
pyr	pyridine
RT	room temperature
*t*Bu	*tert*-butyl
*t*BuPy	4-*tert*-butylpyridine

term	terminal
THF	tetrahydrofuran
Tm^{R}	tris(2-mercapto-1-R-imidazolyl)borate
Tol	4-methylphenyl
Xyl	2,6-dimethylphenyl

9. Acknowledgments

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 research fellowship and the Deutsche Forschungsgemeinschaft for an independent research grant. A.S. thanks the Fonds der Chemischen Industrie for a doctoral scholarship.

10. References

(1) Ludi, A. *J. Chem. Educ.* **1981**, *58*, 1013.
(2) Frankland, E. *Liebigs Ann. Chem.* **1849**, *71*, 171.
(3) Beck, W.; Severin, K. *Chem. Unserer Zeit* **2002**, *36*, 356.
(4) Nöth, H.; Schmid, G. *Angew. Chem., Int. Ed.* **1963**, *2*, 623.
(5) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.
(6) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.
(7) Weeks, M. E. *J. Chem. Educ.* **1933**, *10*, 223.
(8) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.
(9) Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445.
(10) Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed.* **1973**, *12*, 564.
(11) Lundström, T. In *Encyclopedia of Inorganic Chemistry*, Vol. 1; King, R. B., Ed.; Wiley: New York, 1994; p 328.
(12) Lin, Z. *Struct. Bonding (Berlin)* **2008**, *130*, 123.
(13) Pandey, K. K. *Coord. Chem. Rev.* **2009**, *253*, 37.
(14) Besora, M.; Lledós, A. *Struct. Bonding (Berlin)* **2008**, *130*, 149.
(15) Fehlner, T. P. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; p 287.
(16) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177.
(17) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.
(18) Siebert, W. *Adv. Organomet. Chem.* **1980**, *18*, 301.
(19) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63.
(20) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786.
(21) Braunschweig, H.; Colling, M. *J. Organomet. Chem.* **2000**, *614−615*, 18.
(22) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.
(23) Braunschweig, H.; Colling, M. *Eur. J. Inorg. Chem.* **2003**, 393.
(24) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535.
(25) Braunschweig, H. *Adv. Organomet. Chem.* **2004**, *51*, 163.
(26) Braunschweig, H.; Rais, D. *Heteroat. Chem.* **2005**, *16*, 566.
(27) Braunschweig, H.; Whittell, G. *Chem.—Eur. J.* **2005**, *11*, 6128.
(28) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254.
(29) Anderson, C. E.; Braunschweig, H.; Dewhurst, R. D. *Organometallics* **2008**, *27*, 6381.
(30) Braunschweig, H.; Kollann, C.; Seeler, F. *Struct. Bonding (Berlin)* **2008**, *130*, 1.
(31) Kays, D. L.; Aldridge, S. *Struct. Bonding (Berlin)* **2008**, *130*, 29.
(32) Vidovic, D.; Pierce, G. A.; Aldridge, S. *Chem. Commun.* **2009**, 1157.
(33) Shriver, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 3509.
(34) Braunschweig, H.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1613.
(35) Braunschweig, H.; Wagner, T. *Z. Naturforsch., B* **1996**, *51*, 1618.
(36) Braunschweig, H.; Kollann, C. *Z. Naturforsch., B* **1999**, *54*, 839.
(37) Werner, H. *Pure Appl. Chem.* **1982**, *54*, 177.
(38) Parshall, G. W. *J. Am. Chem. Soc.* **1964**, *86*, 361.
(39) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1982; Vol. 6, p 880.
(40) Burlitch, J. M.; Burk, J. H.; Leonowicz, M. E.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1702.
(41) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759.
(42) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Poly-(pyrazolyl)borate Ligands*; Imperial College Press: London, 1999.
(43) Garner, M.; Reglinsky, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975.
(44) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913.
(45) Figueroa, J. S.; Melnick, J. G.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 7056.
(46) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J.; Willis, A. C. *Organometallics* **2008**, *27*, 381.
(47) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062.
(48) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2007**, *26*, 3891.
(49) Landry, V. K.; Melnick, J. G.; Buccella, D.; Pang, K.; Ulichny, J. C.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 2588.
(50) Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Willis, A. C. *Organometallics* **2005**, *24*, 4083.
(51) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221.
(52) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289.
(53) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, 1626.
(54) Blagg, R. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Orpen, A. G. *Chem. Commun.* **2006**, 2350.
(55) Senda, S.; Ohki, Y.; Hirayama, T.; Toda, D.; Chen, J.-L.; Matsumoto, T.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **2006**, *45*, 9914.
(56) Pang, K.; Tanski, J. M.; Parkin, G. *Chem. Commun.* **2008**, 1008.
(57) Pang, K.; Quan, S. M.; Parkin, G. *Chem. Commun.* **2006**, 5015.
(58) Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656.
(59) Crossley, I. R.; Hill, A. F. *Dalton Trans.* **2008**, 201.
(60) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2008**, *27*, 312.
(61) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 12056.
(62) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611.
(63) Bontemps, S.; Sircoglou, M.; Bouhadir, G.; Puschmann, H.; Howard, J. A. K.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem.—Eur. J.* **2008**, *14*, 731.
(64) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffron, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8583.
(65) Bontemps, S.; Bouhadir, G.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1481.
(66) Sircoglou, M.; Bontemps, S.; Bouhadir, G.; Saffron, N.; Miqueu, K.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. *J. Am. Chem. Soc.* **2008**, *130*, 16729.
(67) Tsoureas, N.; Haddow, M. F.; Hamilton, A.; Owen, G. R. *Chem. Commun.* **2009**, 2538.
(68) Tsoureas, N.; Bevis, T.; Butts, C. P.; Hamilton, A.; Owen, G. R. *Organometallics* **2009**, *28*, 5222.
(69) Curtis, D.; Lesley, M. J. G.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1687.
(70) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Harlow, R. L.; Calabrese, J. C.; Lam, K. C.; Lin, Z. *Polyhedron* **2004**, *23*, 2665.
(71) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1192.
(72) Hill, A. F. *Organometallics* **2006**, *25*, 4741.
(73) Parkin, G. *Organometallics* **2006**, *25*, 4744.
(74) Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 819.
(75) Musaev, D. G.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 6509.
(76) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.
(77) Cundari, T. R.; Zhao, Y. *Inorg. Chim. Acta* **2003**, *345*, 70.
(78) Lam, K. C.; Lam, W. H.; Lin, Z.; Marder, T. B.; Norman, N. C. *Inorg. Chem.* **2004**, *43*, 2541.
(79) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2004**, *23*, 4178.
(80) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2006**, *25*, 4605.
(81) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878.
(82) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179.
(83) Wadepohl, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2441.
(84) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.
(85) Han, L. B.; Tanaka, M. *Chem. Commun.* **1999**, 395.
(86) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695.
(87) Caballero, A.; Sabo-Etienne, S. *Organometallics* **2007**, *26*, 1191.
(88) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018.
(89) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*, 4403.
(90) Iverson, C. N.; Smith, M. R., III. *Organometallics* **1996**, *15*, 5155.

(91) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137.

(92) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713.

(93) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, 2073.

(94) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2000**, *611*, 392.

(95) Braunschweig, H.; Kupfer, T.; Lutz, M.; Radacki, K.; Seeler, F.; Sigritz, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 8048.

(96) Adams, C. J.; Baber, R. A.; Batsanov, A. S.; Bramham, G.; Charmant, J. P. H.; Haddow, M. F.; Howard, J. A. K.; Lam, W. H.; Lin, Z.; Marder, T. B.; Norman, N. C.; Orpen, A. G. *Dalton Trans.* **2006**, 1370.

(97) Burks, H. E.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 8766.

(98) Braunschweig, H.; Kupfer, T. *J. Am. Chem. Soc.* **2008**, *130*, 4242.

(99) Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357.

(100) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211.

(101) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383.

(102) Waltz, K. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 11358.

(103) Kawamura, K.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8422.

(104) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

(105) Cho, J.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III. *Science* **2002**, *295*, 305.

(106) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3.

(107) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. *Chem. Commun.* **2003**, 2924.

(108) Hartwig, J. F.; Cook, K. S.; Hapke, M.; Incarvito, C. D.; Fan, Y.; Webster, C. E.; Hall, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 2538.

(109) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172.

(110) Chotana, G. A.; Rak, M. A.; Smith, M. R., III. *J. Am. Chem. Soc.* **2005**, *127*, 10539.

(111) Mkhalid, I. A., I.; Coventry, D. N.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Perutz, R. N.; Marder, T. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 489.

(112) Hartwig, J. F. *Nature* **2008**, *455*, 314.

(113) Liskey, C. W.; Wei, C. S.; Pahls, D. R.; Hartwig, J. F. *Chem. Commun.* **2009**, 5603.

(114) Braun, T.; Salomon, M. A.; Altenhoner, K.; Teltewskoi, M.; Hinze, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 1818.

(115) Segawa, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 9201.

(116) Segawa, Y.; Yamashita, M.; Nozaki, K. *Organometallics* **2009**, *28*, 6234–6242.

(117) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(118) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(119) Onozawa, S. Y.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450.

(120) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777.

(121) Ishiyama, T.; Nishijima, K. I.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219.

(122) Onozawa, S. Y.; Hatanaka, Y.; Tanaka, M. *Tetrahedron Lett.* **1998**, *39*, 9043.

(123) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221.

(124) Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *680*, 43.

(125) Suginome, M.; Yamamoto, A.; Murakami, M. *J. Am. Chem. Soc.* **2003**, *125*, 6358.

(126) Suginome, M.; Yamamoto, A.; Murakami, M. *J. Organomet. Chem.* **2005**, *690*, 5300.

(127) Suginome, M.; Yamamoto, A.; Murakami, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2380.

(128) Yamamoto, A.; Suginome, M. *J. Am. Chem. Soc.* **2005**, *127*, 15706.

(129) Suginome, M.; Shirakura, M.; Yamamoto, A. *J. Am. Chem. Soc.* **2006**, *128*, 14438.

(130) Daini, M.; Suginome, M. *Chem. Commun.* **2008**, 5224.

(131) Daini, M.; Yamamoto, A.; Suginome, M. *J. Am. Chem. Soc.* **2008**, *130*, 2918.

(132) Ohmura, T.; Kijima, A.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 6070.

(133) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Organometallics* **2002**, *21*, 1537.

(134) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **1998**, *17*, 5233.

(135) Adhikari, D.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2007**, 4489.

(136) Onozawa, S.; Tanaka, M. *Organometallics* **2001**, *20*, 2956.

(137) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 162.

(138) Braunschweig, H.; Gruss, K.; Radacki, K.; Uttinger, K. *Eur. J. Inorg. Chem.* **2008**, 1462.

(139) Braunschweig, H.; Green, H.; Radacki, K.; Uttinger, K. *Dalton Trans.* **2008**, 3531.

(140) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742.

(141) Sakaki, S.; Kai, S.; Sugimoto, M. *Organometallics* **1999**, *18*, 4825.

(142) Clegg, W.; Lawlor, F. J.; Lesley, G.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Scott, A. J.; Souza, F. E. S. *J. Organomet. Chem.* **1998**, *550*, 183.

(143) Kerr, A.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Timms, P. L.; Whittell, G. R. *Chem. Commun.* **1998**, 319.

(144) Braunschweig, H.; Lutz, M.; Radacki, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5647.

(145) Braunschweig, H.; Lutz, M.; Radacki, K.; Schaumloeffel, A.; Seeler, F.; Unkelbach, C. *Organometallics* **2006**, *25*, 4433.

(146) Sagawa, T.; Asano, Y.; Ozawa, F. *Organometallics* **2002**, *21*, 5879.

(147) Habereder, T.; Nöth, H. *Appl. Organomet. Chem.* **2003**, *17*, 525.

(148) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Organometallics* **2004**, *23*, 5545.

(149) Braunschweig, H.; Brenner, P.; Mueller, A.; Radacki, K.; Rais, D.; Uttinger, K. *Chem.—Eur. J.* **2007**, *13*, 7171.

(150) Braunschweig, H.; Radacki, K.; Uttinger, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3979.

(151) Braunschweig, H.; Radacki, K.; Uttinger, K. *Inorg. Chem.* **2007**, *46*, 8796.

(152) Charmant, J. P. H.; Fan, C.; Norman, N. C.; Pringle, P. G. *Dalton Trans.* **2007**, 114.

(153) Braunschweig, H.; Kupfer, T.; Radacki, K.; Schneider, A.; Seeler, F.; Uttinger, K.; Wu, H. *J. Am. Chem. Soc.* **2008**, *130*, 7974.

(154) Braunschweig, H.; Radacki, K.; Uttinger, K. *Organometallics* **2008**, *27*, 6005.

(155) Braunschweig, H.; Fuss, M.; Radacki, K.; Uttinger, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 208.

(156) Zhu, J.; Lin, Z.; Marder, T. B. *Inorg. Chem.* **2005**, *44*, 9384.

(157) Braunschweig, H.; Kollann, C.; Mueller, M. *Eur. J. Inorg. Chem.* **1998**, 291.

(158) Aldridge, S.; Calder, R. J.; Rossin, A.; Dickinson, A. A.; Willock, D. J.; Jones, C.; Evans, D. J.; Steed, J. W.; Light, M. E.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2020.

(159) Braunschweig, H.; Leech, R.; Rais, D.; Radacki, K.; Uttinger, K. *Organometallics* **2008**, *27*, 418.

(160) Braunschweig, H.; Radacki, K.; Rais, D.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5651.

(161) Braunschweig, H.; Radacki, K.; Uttinger, K. *Chem.—Eur. J.* **2008**, *14*, 7858.

(162) Braunschweig, H.; Radacki, K.; Rais, D.; Schneider, A.; Seeler, F. *J. Am. Chem. Soc.* **2007**, *129*, 10350.

(163) Ito, H.; Yamanaka, H.; Tateiwa, J. I.; Hosomi, A. *Tetrahedron Lett.* **2000**, *41*, 6821.

(164) Takahashi, K.; Ishiyama, T.; Miyaura, N. *Chem. Lett.* **2000**, *29*, 982.

(165) Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2001**, *625*, 47.

(166) Canesi, S.; Bouchu, D.; Ciufolini, M. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 4336.

(167) Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034.

(168) Lee, J. E.; Kwon, J.; Yun, J. *Chem. Commun.* **2008**, 733.

(169) Dang, L.; Lin, Z.; Marder, T. B. *Chem. Commun.* **2009**, 3987.

(170) Kleeberg, C.; Dang, L.; Lin, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5350.

(171) Ito, H.; Kosaka, Y.; Nonoyama, K.; Sasaki, Y.; Sawamura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7424.

(172) Lee, J. E.; Yun, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 145.

(173) Dongwan, N.; Heesung, C.; Junghwan, J.; Jaesook, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 6062.

(174) Lillo, V.; Prieto, A.; Bonet, A.; Mar Diaz-Requejo, M.; Ramirez, J.; Perez, P. J.; Fernandez, E. *Organometallics* **2009**, *28*, 659.

(175) Zhao, H.; Dang, L.; Marder, T. B.; Lin, Z. *J. Am. Chem. Soc.* **2008**, *130*, 5586.

(176) Zhao, H.; Lin, Z.; Marder, T. B. *J. Am. Chem. Soc.* **2006**, *128*, 15637.

(177) Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196.

(178) Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. *Organometallics* **2006**, *25*, 2405.

(179) Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. *J. Am. Chem. Soc.* **2006**, *128*, 11036.

(180) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113.

(181) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 16069.

(182) Yamashita, M.; Suzuki, Y.; Segawa, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 9570.

(183) Kajiwara, T.; Terabayashi, T.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 6606.

(184) Segawa, Y.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6710.
(185) Koutsantonis, G. A.; Iee, F. C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 1975.
(186) Aldridge, S.; Blake, A. J.; Downs, A. J.; Parsons, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1363.
(187) Schaper, T.; Preetz, W. *Inorg. Chem.* **1998**, *37*, 363.
(188) Greenwood, N. N.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc. A* **1971**, 809.
(189) Greenwood, N. N.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 989.
(190) Littger, R.; Englich, U.; Spencer, J. T. *Inorg. Chem.* **1997**, *36*, 6434.
(191) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1979**, 619.
(192) Finster, D. C.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 863.
(193) Zheng, Z.; Diaz, M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 12338.
(194) Zheng, Z.; Knobler, C. B.; Curtis, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 432.
(195) Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Johnson, A. L.; Wade, K. *Chem. Commun.* **1998**, 1713.
(196) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, 1972.
(197) Terabayashi, T.; Kajiwara, T.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14162–14163.
(198) Timms, P. L. *J. Am. Chem. Soc.* **1967**, *89*, 1629.
(199) Timms, P. L. *Acc. Chem. Res.* **1973**, *6*, 118.
(200) Pachaly, B.; West, R. *Angew. Chem., Int. Ed.* **1984**, *23*, 454.
(201) Mennekes, T.; Paetzold, P.; Boese, R. *Angew. Chem., Int. Ed.* **1990**, *29*, 899.
(202) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981.
(203) Ito, M.; Tokitoh, N.; Kawashima, T.; Okazaki, R. *Tetrahedron Lett.* **1999**, *40*, 5557.
(204) Bettinger, H. *J. Am. Chem. Soc.* **2006**, *128*, 2534.
(205) Ehlers, A. W.; Baerends, E. J.; Bickelhaupt, F. M.; Radius, U. *Chem.—Eur. J.* **1998**, *4*, 210.
(206) Boehme, C.; Uddin, J.; Frenking, G. *Coord. Chem. Rev.* **2000**, *197*, 249.
(207) Cowley, A. H.; Lomelí, V.; Voigt, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401.
(208) Vidovic, D.; Findlater, M.; Reeske, G.; Cowley, A. H. *Chem. Commun.* **2006**, 3786.
(209) Braunschweig, H.; Kollann, C.; Englert, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 3179.
(210) Blank, B.; Colling-Hendelkens, M.; Kollann, C.; Radacki, K.; Rais, D.; Uttinger, K.; Whittell, G. R.; Braunschweig, H. *Chem.—Eur. J.* **2007**, *13*, 4770.
(211) Braunschweig, H.; Colling, M.; Kollann, C.; Merz, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4198.
(212) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 948.
(213) Alcaraz, G.; Helmstedt, U.; Clot, E.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2008**, *130*, 12878.
(214) Braunschweig, H.; Dewhurst, R. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1893.
(215) Kays (née Coombs), D. L.; Rossin, A.; Day, J. K.; Ooi, L.-L.; Aldridge, S. *Dalton Trans.* **2006**, 399.
(216) Kays (née Coombs), D. L.; Day, J. K.; Ooi, L.-L.; Aldridge, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7457.
(217) Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911.
(218) Coombs, D. L.; Aldridge, S.; Jones, C.; Willock, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6356.
(219) Pierce, G. A.; Vidovic, D.; Kays, D. L.; Coombs, N. D.; Thompson, A. L.; Jemmis, E. D.; De, S.; Aldridge, S. *Organometallics* **2009**, *28*, 2947.
(220) Aldridge, S.; Jones, C.; Gans-Eichler, T.; Stasch, A.; Kays (née Coombs), D. L.; Coombs, N. D.; Willock, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6118.
(221) Braunschweig, H.; Wagner, T. *Angew. Chem., Int. Ed.* **1995**, *34*, 825.
(222) Braunschweig, H.; Ganter, B. *J. Organomet. Chem.* **1997**, *545*, 163.
(223) Braunschweig, H.; Koster, M. *J. Organomet. Chem.* **1999**, *588*, 231.
(224) Braunschweig, H.; Burzler, M.; Dewhurst, R. D.; Radacki, K.; Seeler, F. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1875.
(225) Bissinger, P.; Braunschweig, H.; Seeler, F. *Organometallics* **2007**, *26*, 4700.
(226) Aldridge, S.; Coombs, D. L.; Jones, C. *Chem. Commun.* **2002**, 856.
(227) Aldridge, S.; Coombs, D. L.; Jones, C. *J. Chem. Soc., Dalton Trans.* **2002**, 3851.
(228) Braunschweig, H.; Kollann, C.; Englert, U. *Eur. J. Inorg. Chem.* **1998**, 465.
(229) Braunschweig, H.; Kollann, C.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 1523.
(230) Coombs, D. L.; Aldridge, S.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **2003**, *22*, 4213.
(231) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F.; Uttinger, K. *J. Am. Chem. Soc.* **2005**, *127*, 1386.
(232) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1988**, *27*, 424.
(233) Okamura, R.; Tada, K.; Matsubara, K.; Oshima, M.; Suzuki, H. *Organometallics* **2001**, *20*, 4772.
(234) Braunschweig, H.; Müller, M. *Chem. Ber.* **1997**, *130*, 1295.
(235) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Inorg. Chim. Acta* **2004**, *357*, 1822.
(236) Braunschweig, H.; Colling, M.; Hu, C. *Inorg. Chem.* **2003**, *42*, 941.
(237) Braunschweig, H.; Burschka, C.; Burzler, M.; Metz, S.; Radacki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4352.
(238) Braunschweig, H.; Burzler, M.; Kupfer, T.; Radacki, K.; Seeler, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 7785.
(239) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 205.
(240) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H. G.; Neumann, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2298.
(241) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Organometallics* **2006**, *25*, 5159.
(242) Braunschweig, H.; Forster, M.; Seeler, F. *Chem.—Eur. J.* **2009**, *15*, 469.
(243) Braunschweig, H.; Forster, M.; Radacki, K.; Seeler, F.; Whittell, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5212.
(244) Braunschweig, H.; Forster, M.; Kupfer, T.; Seeler, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 5981.
(245) Braunschweig, H.; Forster, M.; Radacki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2132.
(246) Braunschweig, H.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 3763.
(247) Braunschweig, H.; Radacki, K.; Uttinger, K. *Eur. J. Inorg. Chem.* **2007**, 4350.
(248) Braunschweig, H.; Christ, B.; Colling-Hendelkens, M.; Forster, M.; Götz, K.; Kaupp, M.; Radacki, K.; Seeler, F. *Chem.—Eur. J.* **2009**, *15*, 7150.
(249) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 4862.
(250) Kays (née Coombs), D. L.; Day, J. K.; Aldridge, S.; Harrington, R. W.; Clegg, W. *Angew. Chem., Int. Ed.* **2006**, *45*, 3513.
(251) Braunschweig, H.; Herbst, T.; Rais, D.; Seeler, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 7461.
(252) Braunschweig, H.; Herbst, T.; Rais, D.; Ghosh, S.; Kupfer, T.; Radacki, K.; Crawford, A. G.; Ward, R. M.; Marder, T. B.; Fernández, I.; Frenking, G. *J. Am. Chem. Soc.* **2009**, *131*, 8989.
(253) Habben, C.; Meller, A. *Chem. Ber.* **1984**, *117*, 2531.
(254) Apostolico, L.; Braunschweig, H.; Crawford, A. G.; Herbst, T.; Rais, D. *Chem. Commun.* **2008**, 497.
(255) Bedford, R. B.; Hill, A. F.; Thompsett, A. R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 1059.
(256) Braunschweig, H.; Dewhurst, R. D.; Herbst, T.; Radacki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5978.
(257) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1359.
(258) Braunschweig, H.; Burzler, M.; Radacki, K.; Seeler, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 8071.
(259) Pierce, G. A.; Aldridge, S.; Jones, C.; Gans-Eichler, T.; Stasch, A.; Coombs, N. D.; Willock, D. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2043.
(260) Pierce, G. A.; Coombs, N. D.; Willock, D. J.; Day, J. K.; Stasch, A.; Aldridge, S. *Dalton Trans.* **2007**, 4405.
(261) De, S.; Pierce, G. A.; Vidovic, D.; Kays, D. L.; Coombs, N. D.; Jemmis, E. D.; Aldridge, S. *Organometallics* **2009**, *28*, 2961.
(262) Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12113.
(263) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571.
(264) Chen, Y.; Frenking, G. *Dalton Trans.* **2001**, 434.
(265) Aldridge, S.; Rossin, A.; Coombs, D. L.; Willock, D. J. *Dalton Trans.* **2004**, 2649.
(266) Flierler, U.; Burzler, M.; Leusser, D.; Henn, J.; Ott, H.; Braunschweig, H.; Stalke, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 4321.
(267) Götz, K.; Kaupp, M.; Braunschweig, H.; Stalke, D. *Chem.—Eur. J.* **2009**, *15*, 623.
(268) De, S.; Parameswaran, P.; Jemmis, E. D. *Inorg. Chem.* **2007**, *46*, 6091.
(269) Braunschweig, H.; Radacki, K.; Scheschkewitz, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1658.
(270) Braunschweig, H.; Kraft, K.; Kupfer, T.; Radacki, K.; Seeler, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 4931.
(271) Braunschweig, H.; Burzler, M.; Dewhurst, R. D.; Radacki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5650.
(272) Östreicher, S. Diploma Thesis, University of Würzburg, 2009.

(273) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 1066.

(274) Braunschweig, H.; Dewhurst, R. D.; Kraft, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5837.

(275) Braunschweig, H.; Brenner, P.; Dewhurst, R. D.; Kaupp, M.; Müller, R.; Östreicher, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9735.

(276) Braunschweig, H.; Kraft, K.; Östreicher, S. Unpublished results.

(277) Braunschweig, H.; Fernández, I.; Frenking, G.; Radacki, K.; Seeler, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5215.

(278) Owen, G. R.; Gould, P. H.; Hamilton, A.; Tsoureas, N. *Dalton Trans.* **2010**, 49.

(279) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2010**, *29*, 326.

(280) Sircoglu, M.; Bontemps, S.; Mercy, M.; Miqueu, K.; Ladeira, S.; Saffon, N.; Maron, L.; Bouhadir, G.; Bourissou, D. *Inorg. Chem.*, published online November 5, 2009, http://dx.doi.org/10.1021/ic901896z.

(281) Zhao, X.; Otten, E.; Song, D.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *4*, 2040−2044.

(282) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

(283) Chotana, G. A.; Vanchura, B. A., II.; Tse, M. K.; Staples, R. J.; Maleczka, R. E., Jr.; Smith, M. R., III. *Chem. Commun.* **2009**, 5731.

(284) Sawyer, K. R.; Cahoon, J. F.; Shanoski, J. E.; Glascoe, E. A.; Kling, M. F.; Schlegel, J. P.; Zoerb, M. C.; Hapke, M.; Hartwig, J. F.; Webster, C. E.; Harris, C. B. *J. Am. Chem. Soc.* **2010**, *132*, 1848.

(285) Tran, B. L.; Adhikari, D.; Fan, H.; Pink, M.; Mindiola, D. J. *Dalton. Trans.* **2010**, 358.

(286) Braunschweig, H.; Brenner, P.; Radacki, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2089.

(287) Braunschweig, H.; Ye, Q.; Radacki, K. *Chem. Commun.* **2009**, 6979.

(288) Vidovic, D.; Aldridge, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 3669.

(289) Wang, X.; Roos, B. O.; Andrews, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 157.

(290) Pandey, K. K.; Lledós, A.; Maseras, F. *Organometallics* **2009**, *28*, 6442.

(291) Pandey, K. K.; Musaev, D. G. *Organometallics* **2010**, *29*, 142.

CR900333N