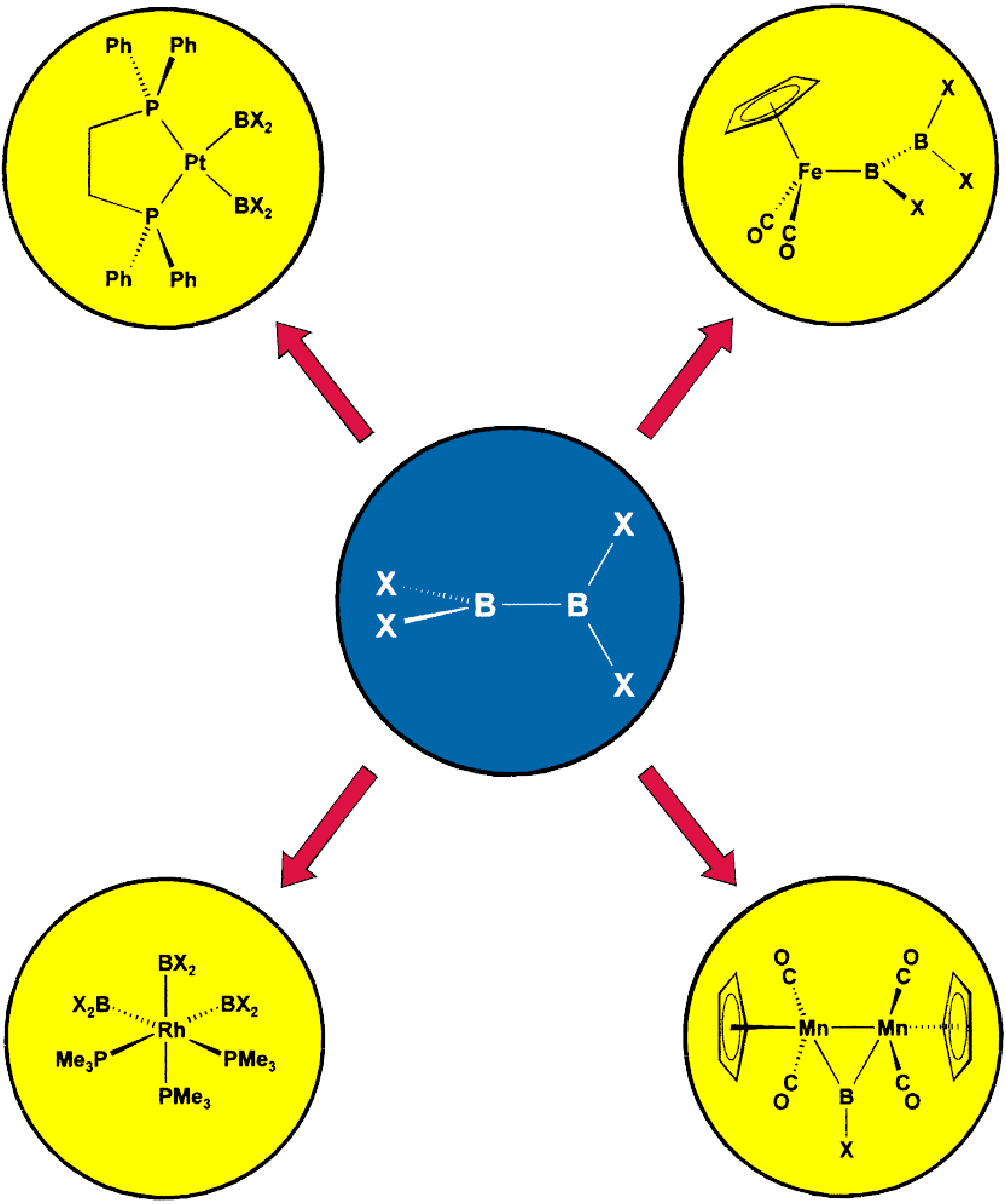

Diborane(4) derivatives as starting materials for various transition metal complexes of boron: bis- and trisboryl complexes (left, top and bottom), complexes with diboran(4)-1-yl and bridging borylene ligands (right, top and bottom).

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Transition Metal Complexes of Boron

Holger Braunschweig*

Borane, boryl, and borylene complexes exhibit two-center, two-electron bonds between the metal and the boron atoms. This differentiates them from other transition metal compounds of boron such as borides or metallaboranes. Although transition metal complexes of boron were first reported between 1963 and 1970, their existence was only proved about thirty years later. This demonstrates the degree of difficulty associated with the synthesis and characterization of these products. This area of research has developed rapidly in the past six years, however, which can be attributed to the interesting application potential of the boryl complexes. Particularly noteworthy are the functionalization of organic compounds by C–H activation and the transition metal catalyzed hydroboration. This review describes synthetic methods which have proven themselves in the preparation of boryl and borylene complexes, and what influence the choice of substituents on boron can have. It is now possible to conduct a more detailed discussion on the nature of the metal–boron bond based on numerous confirmed spectroscopic findings. Preliminary theoretical studies in this field have contributed considerably to the understanding of bonding in boryl complexes as well as to the clarification of the mechanism for the transition metal catalyzed hydroboration.

Keywords: B ligands · boron · hydroboration · transition metal complexes

1. Introduction

Boron, the only nonmetal in Group 13 of the periodic table, forms a number of different compounds with transition metals which display remarkable structural variety. If we restrict ourselves to those compounds in which boron is directly bonded to one or more metal centers, up until 1990 there was confirmed knowledge on borides, metallaboranes, and metallaheteroboranes as well as transition metal complexes with π-bonded ligands containing boron.

The group that has been known the longest is the class of the transition metal borides, for which over 130 structural types and several hundred binary and ternary compounds have been described to date.[1–3] The compositions of the borides range from boron-deficient phases such as $Y_2Co_{14}B$[4] with isolated boron atoms to boron-rich compounds such as YB_{66},[5] which form three-dimensional networks of linked boron clusters. The transition metal borides often demonstrate more interesting physical properties (electrical conductivity or magnetism) than the pure elements. As expected, the bonding in borides cannot be described by a single type of bonding. Instead, the total bonding situation made up of ionic, covalent, and metallic bonding contributions has to be considered; the individual components are dependent on the respective metal and the composition of the boride.

In addition to the transition metal borides, metallaboranes[6–8] and metallacarboranes[9–11] form a further class of boron–transition metal compounds, of which several hundred have been characterized since the middle of the 1960s. As in the case of boranes, these metallaboranes and metallacarboranes are electron-deficient. The central atomic frameworks are stabilized by three-center, two-electron (3c–2e) bonds, and, in most cases, the compounds can also be described as *closo*-, *nido*-, *arachno*-, *hypho*-, *commo*-, or *conjuncto*-boranes in accordance with Wade's rules.[12, 13]

Transition metal complexes with π-bonded ligands containing boron are less numerous than the representatives of the above-mentioned classes of compounds, but have also been known for several decades. These are mainly heterocycles, which contain nitrogen or sulfur in addition to boron and carbon as ring atoms.[14] Among these are borole,[15, 16] diborolene,[17] borabenzene,[18, 19] and borazine.[20, 21] The structures of these compounds show many similarities to those of the corresponding complexes with η^5- or η^6-coordinated carbocyclic ligands; the observed differences are due to the nature of the heteroatoms involved. For example, in the borabenzene complex **A** the π-bonded ligand is displaced to one side such that the ring carbon atom farthest from the boron atom (C4) has the shortest Mn–C distance.[22] In

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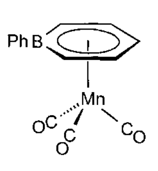
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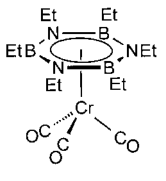
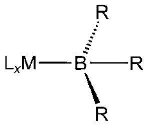

B

contrast to the isoelectronic benzene complex, the π-bonded six-membered ring in the η^6-borazine complex **B** is slightly puckered, which is attributed to the different covalent radii of boron and nitrogen.[21]

In the 1990s the work of several groups led to the establishment of a new class of boron–transition metal compounds: transition metal complexes in which boron is coordinated to the metal through 2c–2e bonds. Such compounds can be systematically classified as borane, boryl, and bridging and terminal borylene complexes. Borane–transition metal complexes **I** can be described as Lewis acid–base adducts between basic metal centers and acidic boranes BR_3; in these compounds boron is four-coordinate. In contrast, boryl transition metal complexes **II** contain a terminal σ-bonded boryl group BR_2, and the coordination number of the boron atom is reduced to three. There are two possible coordination modes for the borylene ligands BR: either bridging between two metal centers (**III**) with three-coordinate boron, or terminal with formation of a metal–boron double bond (**IV**) and boron with the coordination number two.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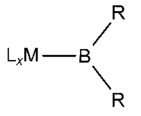
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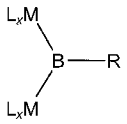
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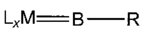
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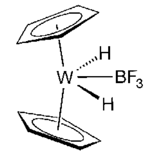
Transition metal complexes with 2c–2e bonds between the metal and a main group element of Groups 14 to 17 have been known for a long time. Silicon, for example, forms numerous silyl[23, 24] and silylene complexes;[25, 26] owing to the diagonal relationship in the periodic table, silicon shows some parallels to boron in its chemical behavior. Until 1990, however, there was no definite knowledge of corresponding boron compounds, although this area of research had been extensively studied between 1963 and 1970. Although numerous compounds—mainly boryl complexes of Mo, W, Mn, Re, Fe, and Co—were described in the course of these early investigations, none could be structurally characterized.[27] Some of the findings from this period have now been disproved by more recent studies.

Today, about thirty years later, these complexes are again being focused on. This is primarily due to the importance of boryl complexes in the functionalization of organic compounds. They appear, for example, as intermediates in the transition metal catalyzed hydroboration, whose application and mechanism has recently been the subject of numerous studies. In addition, use of a special substituent bonded to boron—namely, the phenylene-1,2-dioxy or catechol group—has permitted the synthesis of numerous stable and crystalline boryl complexes of various transition metals within a short time.

2. Borane Complexes

The chemistry of boron-containing compounds is characterized by the fact that boron has only three valence electrons, but four valence orbitals available for bonding. This results in a tendency for many boranes to form multicenter bonds and Lewis acid–base adducts. Thus, the reaction of a suitable borane with a basic transition metal complex could lead to the formation of a corresponding adduct with a metal–boron bond. Reactions of bis(cyclopentadienyl) hydride complexes such as $[(C_5H_5)_2MoH_2]$, $[(C_5H_5)_2WH_2]$, and $[(C_5H_5)_2ReH]$, which all have a basic metal center that can be protonated, with various boranes was studied as early as the 1960s.[28, 29] Based on IR spectra, the presence of the borane–tungsten complex **1** was postulated,[29] which then found its way into textbooks in this form.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Recent studies have shown, however, that no compounds containing tungsten–boron bonds are formed in the reaction of $[(C_5H_5)_2WH_2]$ with boranes. Instead, alkyldichloroboranes such as $t\mathrm{BuBCl_2}$ or $i\mathrm{PrBCl_2}$ react with $[(C_5H_5)_2WH_2]$ under

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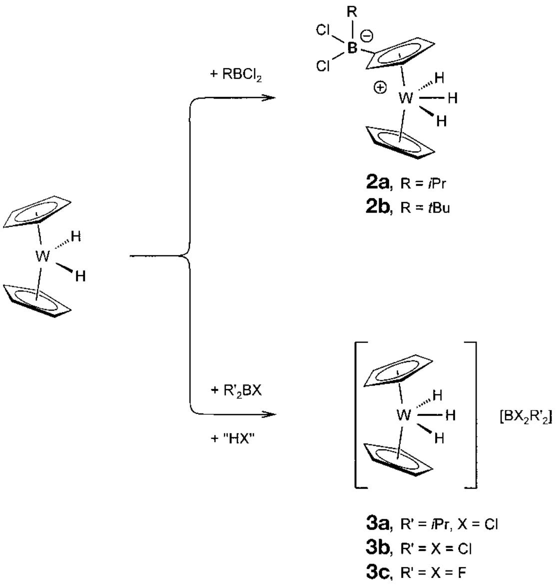
substitution of a hydrogen atom bonded to cyclopentadienyl by the neutral borane and addition of a proton to the tungsten center to give the zwitterionic complexes **2a,b** (Scheme 1).[30]



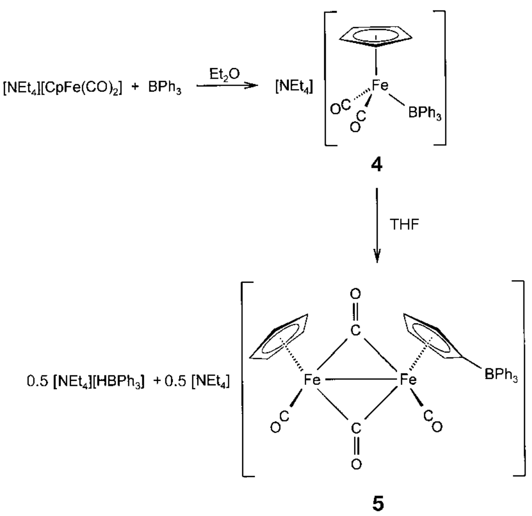
Scheme 1. Reaction of $[(C_5H_5)_2WH_2]$ with boranes.

In contrast, reactions of $[(C_5H_5)_2WH_2]$ with trihaloboranes, such as BCl_3 or BF_3, or $i\mathrm{Pr}_2BCl$ lead to the saltlike compounds **3a–c**.[31]

$[(C_5H_5)_2WH_2(BF_3)]$	**1**
$[(i\mathrm{PrCl_2BC_5H_4})(C_5H_5)WH_3]$	**2a**
$[(t\mathrm{BuCl_2BC_5H_4})(C_5H_5)WH_3]$	**2b**
$[(C_5H_5)_2WH_3][i\mathrm{Pr_2BCl_2}]$	**3a**
$[(C_5H_5)_2WH_3][BCl_4]$	**3b**
$[(C_5H_5)_2WH_3][BF_4]$	**3c**
$[NEt_4][Ph_3BFe(C_5H_5)(CO)_2]$	**4**

In the case of the second reaction, one equivalent of HCl or HF is required per formal conversion for the synthesis of the products. The only possible halide sources are the boranes. Reactions in deuterated solvents[31] and with $[(C_5Me_5)_2WH_2]$[32] show that the required protons are provided by the WH_2 unit. Complexes **2** and **3** were unequivocally identified by spectroscopy in solution and by X-ray structure analysis in the solid state. The original description of the products as borane–tungsten complexes was thus disproved.

In addition to the uncharged basic transition metal compounds, corresponding anionic complexes should also, in principle, be capable of forming adducts with boranes. One example is **4**[33] (Scheme 2), which is isolated as an amorphous solid when synthesized in diethyl ether. However, when dissolved in tetrahydrofuran, **4** spontaneously reacts, with migration of the BPh_3 group to the cyclopentadienyl ligand, to form $[NEt_4][HBPh_3]$ and **5**, whose structure was subsequently characterized by by X-ray crystallography.[34] The composition of **4** in solution was determined from the high-field ^{11}B NMR signal at $\delta = -28.8$, which is typical of compounds with four-coordinate boron, and from the positions of the CO bands in the IR spectrum, which correspond to those of the analogous, structurally characterized alane complex.



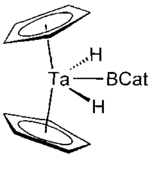
Scheme 2. Synthesis of **4** and its further reaction to **5**.

Since 1963 several other borane–transition metal complexes such as $Na[H_3BRe(CO)_4]$, $Na[H_3BMn(CO)_3PPh_3]$, $Na[H_3BCo(CO)_4]$,[35] $[X_3BRh(PPh_3)_2(CO)X]$ (X = Cl, Br),[36] and $[(Me_2PC_2Me_2BMe_2)_2Rh(CO)Cl]$[37] have been reported. However, because of incomplete spectroscopic studies and the absence of structural characterization the presence of metal–boron bonds in these products cannot be regarded as being certain.

3. Boryl Complexes

3.1. Phenylene-1,2-dioxyboryl Complexes

The use of the phenylene-1,2-dioxy or catechol group (Cat = 1,2-$O_2C_6H_4$) as a substituent on boron has allowed pivotal advances in the study of boryl–transition metal complexes. Of the approximately 30 fully characterized compounds of this type, 20 are phenylene-1,2-dioxyboryl complexes of metals of Groups 5–10 (Table 1).[38] As far as the early transition metals are concerned, only metallocene hydride derivatives of niobium, tantalum, and tungsten—for example, **6a**,[39] **7a**, **b**,[40] **8**,[39, 41] and **9**[41, 42]—are known. In the case of the tantalum compound **7**, the *endo* isomer **7a** and the *exo* isomer **7b** are initially formed. The latter is kinetically favored and dominates slightly, but converts on warming into the thermodynamically more stable *endo* form. Although this



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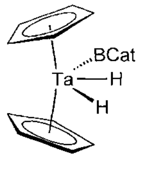

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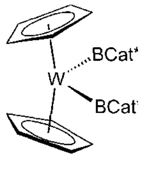

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Table 1. Syntheses, M–B bond lengths, and $\delta(^{11}B)$ values of boryl complexes.

Compound	Synthesis[a]	d(M–B) [pm]	$\delta(^{11}B)$	Ref.
$[(C_5H_5)_2NbH_2(BCat)]$ **6a**	B	229.2(5)	59.0	[39]
endo-$[(C_5H_5)_2TaH_2(BCat)]$ **7a**	A	226.3(6)	70.0	[40]
exo-$[(C_5H_5)_2TaH_2(BCat)]$ **7b**	A	229.6(11)	64.7	[40]
$[(C_5H_5)_2WH(BCat)]$ **8**	A	219.0(7)	57.2	[39, 41]
$[(C_5H_5)_2W\{B(1,2\text{-}O_2\text{-}4\text{-}t\text{Bu}C_6H_3)\}_2]$ **9**	C	219(1), 223(1)	59.3	[41, 42]
$[(CO)_5Mn(BCat)]$ **10a**	A	210.8(6)	49.0	[44]
$[(CO)_5Re(BCat)]$ **10b**	A	–[b]	44.0	[44]
$[(CO)_4Fe\{B(1,2\text{-}O_2\text{-}4\text{-}t\text{Bu}C_6H_3)\}_2]$ **11a**	A, C	202.8(7)	45.0	[45]
$[(C_5H_5)(CO)_2Fe(BCat)]$ **12**	A	195.9(6)	51.8	[46]
$[(Me_3P)_3Co(BCat)_2]$ **13**	C	194.5(11), 197.0(11)	–[c]	[47]
$[(Me_3P)_4Rh(BCat)]$ **14**	C	204.7(2)	49.0	[48]
$[(i\text{Pr}_3P)_2RhCl(H)(BCat)]$ **15**	B	196.1(1)	37.7	[49]
$[(Ph_3P)_2RhCl(BCat)_2]$ **16**	B	195.6(8), 200.8(7)	35.9	[50]
$[(Me_3P)_3RhCl(H)(BCat)]$ **17**	B	196.7(9)	42.5	[51]
$[(Cy_3P)_2RhCl(H)(BCat)]$ **18**	B	196.5(5)	37.0	[51]
$[(Me_3P)_3Rh(BCat)_3]$ **19**	C	205.3(4), 205.5(4), 206.1(4)	46.8	[48]
cis-$[(Ph_3P)_2Pt(BCat)_2]$ **20a**	C	204.9(6)	47.0	[52, 53]
cis-$[(Ph_3P)_2Pt(BPin)_2]$ **20b**	C	207.6(6), 207.8(7)	46.3	[53, 59, 60]
cis-$[(Ph_2P(CH_2)_2PPh_2)Pt(BCat)_2]$ **21a**	C	204.8(8), 205.8(8)	48.9	[53]
$[(Me_3P)_3IrCl(H)(BCat)]$ **22**	B	202.3(10)	32.8	[54]
$[(Cy_3P)_2IrCl(H)(BCat)]$ **23**	B	200.0(7)	–[d]	[51]
$[(C_6H_5Me)Ir(BCat)_3]$ **24a**	B	201.8(5), 202.4(5), 203.6(4)	37.7	[55]
$[(1,3,5\text{-}C_6H_3Me_3)Ir(BCat)_3]$ **24b**	B	201.6(3)	37.8	[55]
$[\{HB(1,2\text{-}N_2\text{-}3,5\text{-}Me_2C_3H)_3\}(CO)_2W\{BEt(CH_2\text{-}4\text{-}MeC_6H_4\}]$ **25**	D	207(1)	78	[57]
$[(C_5H_5)(CO)_2Fe(BPh_2)]$ **26**	A	203.4(3)	121.0	[46]
fac-$[(Me_3P)_3IrH_2(BC_8H_{14})]$ **27**	A	209.3(7)	106.2	[58]
$[(Me_2PCH_2CH_2PMe_2Pd(SnMe_3)\{B(MeNCH_2CH_2NMe)\}]$ **28**	D	207.7(6)	46.9	[61]
$[(C_5H_5)(CO)_2Fe\{B(NMe_2)BCl(NMe_2)\}]$ **29a**	A	209.0(3)	69.5	[62]
$[(C_5H_5)(CO)_3W\{B(NMe_2)BCl(NMe_2)\}]$ **29b**	A	237.0(8)	62.7	[62]
$[\{(C_5Me_5)(CO)_2Fe\}Cl_2B_3N_3H_3]$ **30a**	A	–[b]	59.0	[63]
$[\{(C_5H_4Me)(CO)_2Fe\}_2ClB_3N_3H_3]$ **30b**	A	204.5(1)	53.1	[63]
$[\{(C_5H_5)(CO)_2Fe\}_3B_3N_3H_3]$ **30c**	A	–[b]	49.7	[63]
$[(CO)_4Co\{BH_2(OC_4H_8)\}]$ **31**	D	–[b]	7.9	[64]
$[(\eta^1\text{-}Ph_2PCH_2PPh_2)(CO)_2Co(\mu\text{-}Ph_2PCH_2PPh_2)(BH_2)]$ **32**	D	222.7(6)	–25.9	[65]

[a] A = salt elimination, B = oxidative addition of B–H, C = oxidative addition of B–B, D = other method. [b] No details of the structure in the crystal are available. [c] Paramagnetic. [d] No details for $\delta(^{11}B)$.

type of regioisomerism has been long known for corresponding metallocene derivatives of niobium and tantalum,[43] this was the first time that the isomers could be separated and structurally characterized in the crystal.

$[(C_5H_5)_2NbH_2(BCat)]$ **6a**

endo-$[(C_5H_5)_2TaH_2(BCat)]$ **7a**

exo-$[(C_5H_5)_2TaH_2(BCat)]$ **7b**

$[(C_5H_5)_2WH(BCat)]$ **8**

$[(C_5H_5)_2W\{B(1,2\text{-}O_2\text{-}4\text{-}t\text{Bu}C_6H_3)\}_2]$ **9**

The elements of Groups 7 and 8 form phenylene-1,2-dioxyboryl complexes both with and without carbonyl ligands. The first group is made up of the manganese compound **10a**;[44] its rhenium analogue **10b**, whose crystal structure is not known, however;[44] and the iron complexes **11a**[45] and **12**.[46] Transition metals of Groups 9 and 10 form phosphane

$[(CO)_5Mn(BCat)]$ **10a**

$[(CO)_5Re(BCat)]$ **10b**

$[(CO)_4Fe\{B(1,2\text{-}O_2\text{-}4\text{-}t\text{Bu}C_6H_3)\}_2]$ **11a**

$Li[(CO)_4Fe\{B(1,2\text{-}O_2\text{-}4\text{-}t\text{Bu}C_6H_3)\}]$ **11b**

$[(C_5H_5)(CO)_2Fe(BCat)]$ **12**

$[(Me_3P)_3Co(BCat)_2]$ **13**

$[(Me_3P)_4Rh(BCat)]$ **14**

$[(i\text{Pr}_3P)_2RhCl(H)(BCat)]$ **15**

$[(Ph_3P)_2RhCl(BCat)_2]$ **16**

$[(Me_3P)_3RhCl(H)(BCat)]$ **17**

$[(Cy_3P)_2RhCl(H)(BCat)]$ **18**

$[(Me_3P)_3Rh(BCat)_3]$ **19**

cis-$[(Ph_3P)_2Pt(BCat)_2]$ **20a**

cis-$[(Ph_2P(CH_2)_2PPh_2)Pt(BCat)_2]$ **21a**

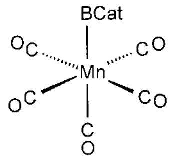
cis-$[(Ph_2P(CH_2)_3PPh_2)Pt(BCat)_2]$ **21b**

$[(Me_3P)_3IrCl(H)(BCat)]$ **22**

$[(Cy_3P)_2IrCl(H)(BCat)]$ **23**

$[(C_6H_5Me)Ir(BCat)_3]$ **24a**

$[(1,3,5\text{-}Me_3C_6H_3)Ir(BCat)_3]$ **24b** complexes such as the paramagnetic cobalt compound **13**,[47] whose crystal structure shows a short B–B distance; the rhodium complexes **14**,[48] **15**,[49] **16**,[50] **17**,[51] **18** (Cy = cyclohexyl),[51] and **19**;[48] and the platinum compounds **20a**[52, 53] and **21a**, **b**.[53] Compounds **15**, **16**, **18**, and **19** were the first electron-deficient boryl complexes with 16 valence electrons to be characterized. In the case of iridium, the two arene complexes **24a**, **b**[55] are known in addition to the phosphane complexes **22**[54] and **23**.[51]



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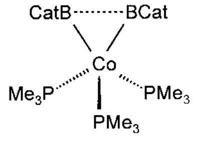

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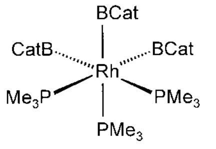

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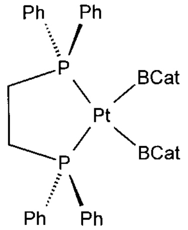


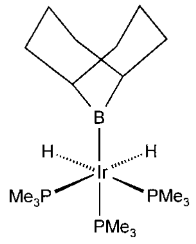
21a

The catecholboryl complexes mentioned are crystalline and sensitive to both air and moisture; their thermal stability can differ widely and depends on the nature of the metal fragment. The tungsten complex **8**, for example, is stable in boiling toluene for days, whereas the iron compound **11a** decomposes at room temperature even in the solid state.

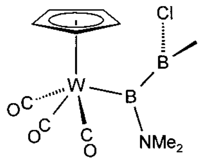
3.2. Boryl Complexes with Other Substituents on Boron

In contrast to the catecholboryl complexes, corresponding compounds with other substituents on boron are rather rare. Unambiguous knowledge of these compounds on the basis of complete spectroscopic characterization is limited to a few complexes of tungsten, iron, rhodium, palladium, and platinum. Although there is no suitable data available to make a comparison of the effect that the substituents on boron have on the strength of the metal–boron bonds, it can be assumed that the phenylene-1,2-dioxy group stabilizes the corresponding products in a special manner. To date there is no other ligand known with a comparably wide range of application. The other boryl complexes are therefore often unique cases.

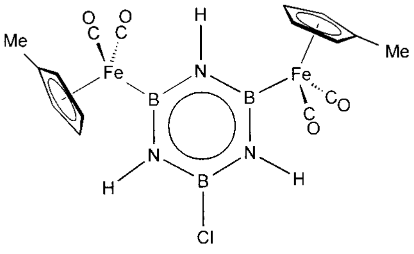
The crystal structures of just three boryl complexes with alkyl or aryl groups on boron have been described:[56] the tungsten complex **25**,[57] which shows an agostic interaction of a C–H unit of the methylene group on boron, the iron complex **26**,[46] and the iridium complex **27**.[58] The first X-ray structure analysis of a boryl–transition metal complex was performed on **27**. Although the tetramethylethylene-1,2-dioxy or pinacol group (Pin = $OCMe_2CMe_2O$) resembles the catechol group, only one corresponding boryl–platinum complex is known (**20b**).[53, 59, 60] The palladium complex **28** is the only structurally confirmed example of a compound with a comparable nitrogen-containing substituent on boron.[61]



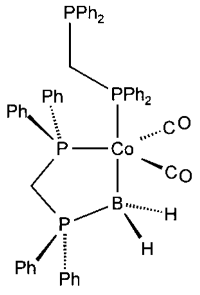
27



29b



30b



32

cis-$[(Ph_3P)_2Pt(BPin)_2]$ **20b**

$[\{HB(1,2\text{-}N_2\text{-}3,5\text{-}Me_2C_3H)_3\}(CO)_2W\{BEt(CH_2\text{-}4\text{-}MeC_6H_4\}]$ **25**

$[(C_5H_5)(CO)_2Fe(BPh_2)]$ **26**

fac-$[(Me_3P)_3IrH_2(BC_8H_{14})]$ **27**

$[(Me_2PCH_2CH_2PMe_2)Pd(SnMe_3)\{B(MeNCH_2CH_2NMe)\}]$ **28**

Recently it proved possible to synthesize boryl complexes containing ligands with more than one boron atom. Examples include **29a**, **b**, in which none of the previously mentioned boryl ligands but rather a diboran(4)-1-yl ligand is bonded to the metal atom.[62] A new coordination mode was found for the borazine ligand, which has been known for a long time in organometallic chemistry, in complexes **30a**–**c**.[63] In contrast to the above-mentioned compounds **B**,[20, 21] **30a**–**c** contain η^1-coordinated borazine ligands with σ bonds between the metal and boron atoms.

$[(C_5H_5)(CO)_2Fe\{B(NMe_2)BCl(NMe_2)\}]$ **29a**

$[(C_5H_5)(CO)_3W\{B(NMe_2)BCl(NMe_2)\}]$ **29b**

$[\{(C_5Me_5)(CO)_2Fe\}Cl_2B_3N_3H_3]$ **30a**

$[\{(C_5H_4Me)(CO)_2Fe\}_2ClB_3N_3H_3]$ **30b**

$[\{(C_5H_5)(CO)_2Fe\}_3B_3N_3H_3]$ **30c**

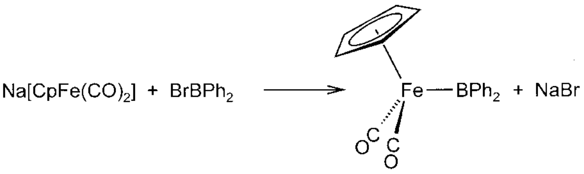
$[(CO)_4Co\{BH_2(OC_4H_8)\}]$ **31**

$[(\eta^1\text{-}Ph_2PCH_2PPh_2)(CO)_2Co(\mu\text{-}Ph_2PCH_2PPh_2)(BH_2)]$ **32**

In 1990 cobalt compounds **31**[64] and **32**[65] were characterized spectroscopically; the latter was also structurally characterized in the crystal. These compounds containing four-coordinate boron are the only known base adducts of boryl complexes.[66]

3.3. Synthesis of Boryl Complexes

Essentially two methods have proven to be successful for the preparation of the boryl complexes mentioned in Sections 3.1 and 3.2. Starting from an anionic transition metal complex and a haloborane, the metal–boron bond can be formed by nucleophilic substitution of the halide and salt elimination. This reaction was first successfully employed in the synthesis of the boryl-iron complexes **12**[46] and **26**[46] (Scheme 3).



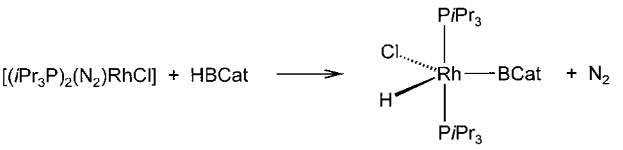
26

Scheme 3. Synthesis of **26**.

A large number of anionic complexes of the metals of Groups 5–7 are also available as starting materials. These can be prepared from metallocene or carbonyl derivatives and then converted into the corresponding boryl complexes (Table 1). The preparation of the bisboryl complex **11a**[45] from $Na_2[Fe(CO)_4]$ and $ClB(1,2\text{-}O_2\text{-}4\text{-}t\mathrm{Bu}C_6H_3)$ demonstrates that this method is not limited to monoanionic complexes.

It has been known for over forty years that B–H and B–B bonds in boranes and diboranes(4) oxidatively add to unsaturated compounds such as alkenes.[67–69] A comparable addition of boryl groups to transition metals was also used to prepare numerous boryl complexes.

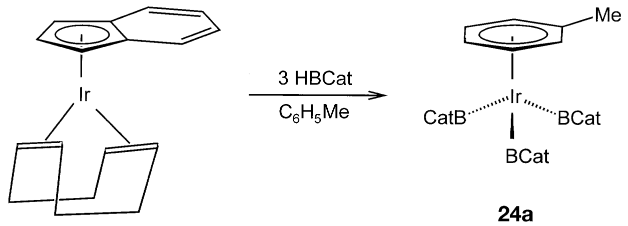
The synthesis of corresponding complexes of late transition metals with boranes usually occurs with elimination of neutral ligands such as N_2 or phosphanes, as in the formation of **15** (Scheme 4),[49] **16**,[50] and **27**.[58] In the case of the iridium compounds **22**[54] and **24a**, **b**,[55] however, alkenes are eliminated from the complexes. Depending on the stoichiometry, one or more boryl groups can be added, as in the reactions of $[(Ph_3P)_3RhCl]$ with HBCat.[70, 71]



15

Scheme 4. Synthesis of **15**.

The synthesis of the trisboryl complexes **24a**, **b** from $[(C_9H_7)Ir(C_8H_{12})]$ (C_9H_7 = indenyl, C_8H_{12} = cyclooctadiene) and excess HBCat in aromatic solvents such as toluene or mesitylene is particularly interesting (Scheme 5). Here, both



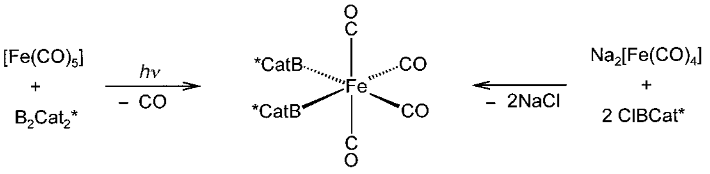
24a

Scheme 5. Synthesis of **24a**.

the ligands on the metal are eliminated, the iridium atom is oxidized, and a solvent molecule becomes coordinated in a η^6 fashion.

The rhodium and iridium complexes **18** and **23** can be synthesized by reaction of the highly reactive electron-deficient complexes $[(Cy_3P)_2MCl]$ (M = Rh, Ir; Cy = cyclohexyl) with HBCat; the elimination of phosphane ligands is not observed.[51] The formation of the niobium complex **6a**[39] from $[(C_5H_5)_2NbH_3]$ and HBCat does not occur with forced removal of neutral ligands, but rather elimination of H_2. Theoretical studies on the reaction of $[(C_5H_5)_2NbH_3]$ with BH_3 show that initial formation of an adduct with a Nb-H-B bridge is likely. This adduct would then react further with elimination of H_2 and subsequent oxidative addition of the B–H bond to the metal center. In the case of BH_3, addition to a central proton is energetically more favorable than to a lateral proton.[72]

The oxidative additions of diboranes(4) to metals proceed more uniformly, because bisboryl complexes are generally formed. For the synthesis of the tungsten complex **9**,[41, 42] the intermediate $[(C_5H_5)_2W]$ generated by irradiation of $[(C_5H_5)_2WH_2]$ may be used. In addition to the salt elimination mentioned above, an alternative photochemical method for preparing **11a** from $[Fe(CO)_5]$ is known (Scheme 6).[45] In contrast, the bisboryl complexes of cobalt and platinum are accessible by thermal elimination of PMe_3 or alkenes and alkynes.



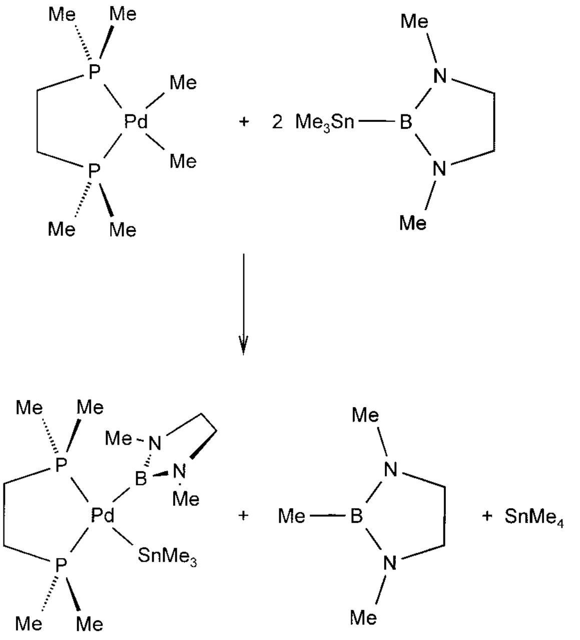
11a

Cat* = $1,2\text{-}O_2\text{-}4\text{-}t\mathrm{Bu}C_6H_3$

Scheme 6. Alternative syntheses of **11a**.

The only reaction that does not lead to the formation of a bisboryl complex is that of $[(Me_3P)_4RhMe]$ with B_2Cat_2. When one equivalent of B_2Cat_2 is used, the boryl complex **14** is initially formed with elimination of MeBCat. The complex then reacts further by oxidative addition of a further B_2Cat_2 molecule to give the trisboryl complex **19**.[48]

The synthesis of the palladium complex **28** (Scheme 7) is of particular relevance,[61] because this was the first time that a boryl complex was obtained by addition of another compound with a different boron–element bond. As the other reaction products $SnMe_4$ and $MeB(MeNCH_2CH_2NMe)$ show, the formation of **28** does not occur by oxidative addition, but rather by σ bond metathesis.



28

Scheme 7. Synthesis of **28**.

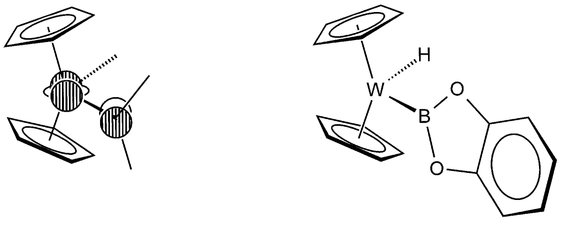
Both salt elimination and oxidative addition are synthetic methods with a wide range of application. In contrast, the reactions leading to the tungsten **25**[57] and cobalt complexes **32**[65] are not yet understood and are limited to the examples mentioned.[56]

3.4. Structures of Boryl Complexes

Owing to the sp^2 hybridization, boron atoms in boryl complexes have a trigonal-planar coordination. To compensate for the electronic deficiency, the formation of a π backbond from the metal to the boron atom is possible as long as occupied d orbitals of suitable symmetry on the metal are able to interact with the empty p_z orbital on boron. A similar situation is known for isoelectronic cationic carbene complexes.[73, 74]

Earlier work in this field[27] had to rely solely on IR and NMR spectroscopic data to describe the bonding in boryl complexes, as none of the products had been characterized by X-ray structure analysis. For example, ^{11}B NMR shifts between $\delta = -23$ and 45 were reported for diphenylboryl complexes of various metals, which are shifted strongly upfield in comparison to the value of $\delta \approx 60$ for BPh_3.[75] These results, together with IR spectroscopic data, served as proof for pronounced metal–boron backbonding. It is remarkable, however, that these findings do not concur with the spectroscopic properties of structurally characterized compounds. For example, a ^{11}B NMR shift of $\delta = 37$ for the iron compound **12**[76, 77] first reported in 1963 conflicts with the actual value of $\delta = 121$ reported for the fully characterized compound thirty years later.[46] The numerous structural and spectroscopic findings recently made together with ab initio studies in this field now allow a more detailed description of the bonding in boryl complexes. The evaluation of this data does not, however, result in a uniform picture which would fit all compounds. Hence, a detailed discussion of the individual types of compounds is necessary.

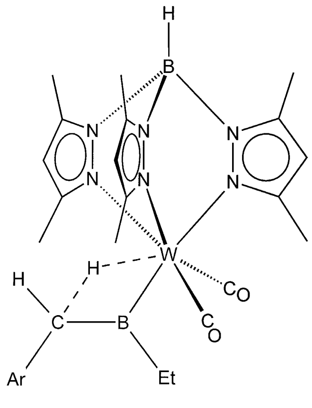
For the tantalum complexes **7a**, **b**[40] and the tungsten complexes **8**[39, 41] and **9**[41, 42] in the crystalline state the catechol ligands are arranged such that the oxygen atoms on boron point towards the cyclopentadienyl rings. Although this geometry is sterically unfavorable, it permits the formation of a π backbond from the metal to boron. Complexes of the type $[Cp_2ML_n]$ have an a_1-symmetrical metallike HOMO. If the boryl ligand is suitably arranged, this nonbonding orbital can interact with the free p orbital that is perpendicular to the bonding plane around the boron atom (**C**, Figure 1).[78]



C **8**

Figure 1. Arrangement of the orbitals in complexes of the type $[(C_5H_5)_2MX_2]$ with π backbonding (**C**); schematic representation of the structure of $[(C_5H_5)_2WH(BCat)]$ (**8**) in the crystal.

A corresponding geometry was also found for the tantalum–alkylidene complexes isoelectronic to **8** and **9**.[79, 80] In the case of the tungsten complexes **8** and **9**, this arrangement is achieved with a slight shortening of the W–B bond lengths (Table 1) with respect to the sum of their covalent radii. Hindered rotation around the W–B bond was not observed for any of the above-mentioned boryl complexes by NMR spectroscopy in solution down to −80 °C. This indicates that the π backbonds must be weak in nature.



25

The tungsten–boryl complex **25** (Ar = CH_2-4-MeC_6H_4) shows a stronger W–B backbond.[57] This compound has the shortest of all observed W–B bonds; with 207(1) pm this bond is about 5% shorter than the sum of the covalent radii of tungsten and boron. Furthermore, the ^{11}B NMR signal at $\delta = 77$ for the boron atom bound to tungsten is shifted strongly upfield in comparison to the resonances for other diaryl- and dialkylboryl complexes that have been characterized by X-ray structure analyses.

There are just two examples of complexes containing only carbonyl ligands in addition to the boryl ligand that have been structurally characterized: **10a**[44] and **11a**.[45] Although in both cases the metal–boron bond is longer than in complexes with mixed substituents, such as the iron complex **12**,[46] there are nevertheless indications of π-bonding contributions. The metal–carbon double bond is much shorter for carbonyl groups that are arranged *trans* to pure σ donors such as hydride or alkyl ligands than for two carbonyl ligands that are arranged *trans* to one another; this can be attributed to the higher electron density on the metal atom.[81, 82] This bond shortening does not occur in **10a** and **11a** because of the π-acceptor properties of the boryl group. IR spectroscopy of both boryl complexes also indicates metal–boron multiple bonding: The CO bands are shifted to significantly higher wave numbers compared to those for compounds such as $[(CO)_5MnMe]$[83] or *cis*-$[(CO)_4Fe\{GaR[(CH_2)_3NMe_2]\}_2]$ (R = *t*Bu, Ph),[84] for which π backbonding from the metal to the carbon or gallium atom can be ruled out.[85]

Boryl complexes of the type $[(C_5H_5)(CO)_2Fe(BRR')]$ are of particular interest, because they allow a comparison of the structural and spectroscopic properties of a catecholboryl complex with those of corresponding compounds with other substituents on boron. Complex **12**[46] has certain characteristics that were discussed above in some detail: 1) In the crystal the bonding plane around boron is almost coplanar with the symmetry plane of the $[(C_5H_5)(CO)_2Fe]$ fragment, which is defined by the atoms B and Fe and the center of the cyclopentadienyl ligand (dihedral angle 7.9°). The formation of a π backbond from the iron atom to the boron atom for this arrangement of the boryl ligand is made possible by the interaction of the metallike a″-symmetrical HOMO with the free p orbital on boron (**D**, Figure 2).[86] 2) In solution the IR bands for the carbonyl groups are shifted to higher wave numbers in comparison to those for $[(C_5H_5)(CO)_2FeMe]$.[87] In contrast to this, in the crystal the iron complexes **26**,[46] **29a**, and **30b**[63]—which show corresponding dihedral angles of between 75 and 90°—have a geometry which does not allow the formation of π backbonds (**E**, Figure 2). This is reflected in the considerably longer Fe–B distances of these compounds in comparison to those in **12**. The position of the CO bands at lower wavenumbers also indicates Fe–B bonds with predominantly σ character.

The structurally characterized bisborylplatinum complexes *cis*-$[(Ph_3P)_2Pt(BCat)_2]$ (**20a**),[52, 53] *cis*-$[(Ph_3P)_2Pt(BPin)_2]$ (**20b**),[53, 59, 60] and *cis*-$[(Ph_2P(CH_2)_nPPh_2)Pt(BCat)_2]$ (**21a** $n = 2$; **21b**, $n = 3$)[53] have Pt–B bond lengths that, under consideration of the difference in the covalent radii between sp^2-hybridized boron and carbon, are considerably shorter than the Pt–C distances of corresponding aryl complexes.[88] Furthermore, with values between 1500 and 1600 Hz the coupling constants $|^1J_{Pt,P}|$ observed in solution for the platinum–boryl complexes are about 200 Hz less than those of the platinum–aryl complexes. This can be attributed to a larger *trans* effect of the boryl ligands.[89] Both findings indicate π backbonding from platinum to boron.

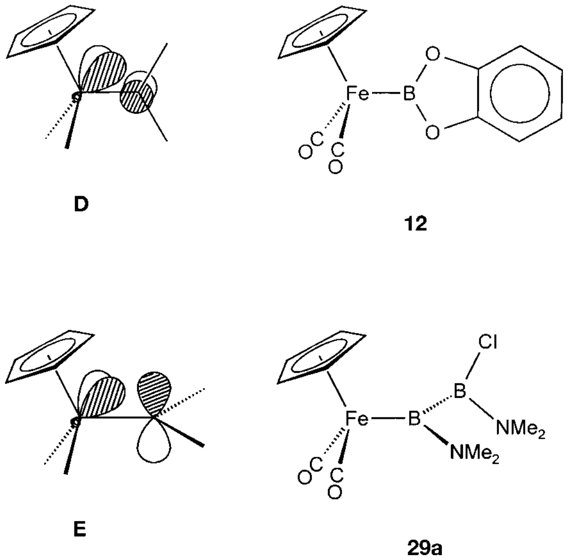
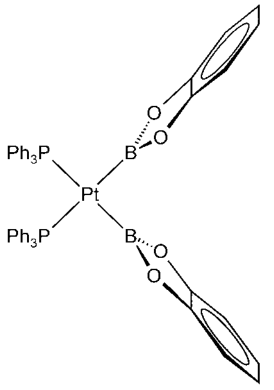
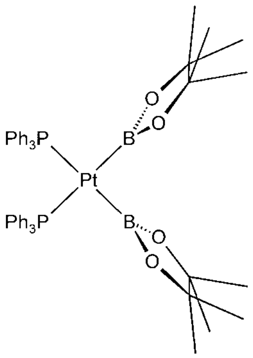


Figure 2. Arrangement of the orbitals in complexes of the type $[(C_5H_5)M(CO)_2X]$ with (**D**) and without π backbonding (**E**); schematic representation of the structure of $[(C_5H_5)(CO)_2Fe(BCat)]$ (**12**) and $[(C_5H_5)(CO)_2Fe\{B(NMe_2)BCl(NMe_2)\}]$ (**29a**) in the crystal.



20a

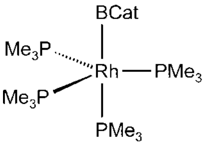


20b

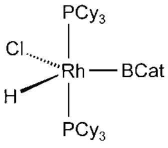
A comparison of the influence of substituents in catecholboryl and pinacolboryl complexes **20a** and **20b** does not demonstrate the same uniformity of the above-mentioned iron compounds of the type $[(C_5H_5)(CO)_2Fe(BRR')]$. Although **20a** and **21a,b** have shorter Pt–B bonds than **20b**, which could indicate a unique stabilization through the phenylene-1,2-dioxy substituents, the situation is reversed in solution. Here **20b** shows the smallest coupling constant $|^1J_{Pt,P}| = 1504$ Hz and thus the largest *trans* effect of these compounds.

In contrast to the phenylene-1,2-dioxyboryl complexes already mentioned, the corresponding iridium and rhodium compounds, barring two exceptions, show no indication of significant metal–boron backbonding, neither in solution nor in the crystalline state. The Ir–B bond lengths in **22**[54] and

24a, **b**[55] are comparable with that in *cis*, *trans*-[$(Me_3P)_2(CO)IrBr_2(\sigma$-2-$B_5H_8)$], which has predominantly σ character,[90] and are not shortened with respect to the sum of the covalent radii of the elements. Corresponding observations have also been made for metal–boron bonds in the rhodium complexes **14**, **15**,[49] **16**,[50] and **19**.[48]



14

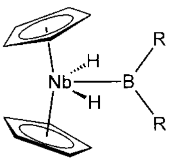


18

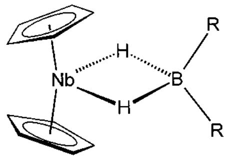
In the case of **14** in the crystalline state, the boryl ligand occupies an axial position; in such trigonal-bipyramidal rhodium complexes this site is usually preferred by ligands with strong σ-donor and only weak π-acceptor properties. To enable the formation of backbonding from rhodium to boron, the boryl ligand must be in an equatorial position.[91] In solution at room temperature **14** shows fluctional behavior; however, at $-80\,^{\circ}C$ the ^{31}P NMR spectra confirm the axial arrangement of the boryl ligand.

In contrast, the boryl ligands in the rhodium and iridium complexes **18** and **23** take up equatorial positions in the crystal, and the metal–boron bond lengths are shortened with respect to the sum of the covalent radii.[51] In **18** the Rh–B distance is about 8 pm smaller than in **14**. This indicates the presence of π backbonding in both cases.

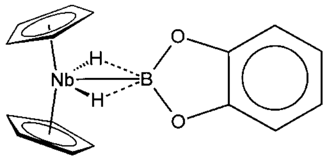
Two complexes deserve special treatment here owing to their interesting structural characteristics. For compounds of the type [$(C_5H_5)_2NbH_2(BRR')$], variation of the substituents on boron leads to a transition between two structural extremes: the boryl-niobium complex **F** and the dihydridoborate-niobium complex **G**.



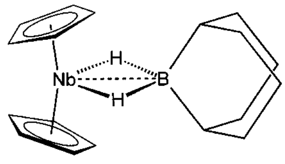
F



G



6a



6b

The phenylene-1,2-dioxyboryl complex **6a**[39] has B–H distances of 169(4) and 162(5) pm and an H-Nb-H angle of 92(2)°; therefore, **6a** lies in an intermediate region between **F** and **G**. However, owing to the large B–H distances, the large bond angle on niobium, and the small Nb–B bond length of 229.2(5) pm, **6a** can be better described as a boryl complex. The metallocene hydride derivatives **7a**, **b**[40] and **8**[39, 41] related to **6a** do not demonstrate any recognizable interaction between the boron atom and the hydrogen atoms bonded to the metal. If [$(C_5H_5)_2NbH_3$] is allowed to react with HBC_8H_{14} instead of HBCat, [$(C_5H_5)_2Nb(H_2BC_8H_{14})$] (**6b**) is obtained in an analogous manner.[39] In the crystal **6b** has a large Nb–B distance of 240(1) pm, a H-Nb-H angle of 70(3)°, and small B–H distances of 138(7) and 139(6) pm. Because of the good agreement of these values with those of other compounds of the type [$(C_5H_5)_2M(BH_4)$],[92–94] **6b** can also be described as a dihydridoborate complex. The structural data of **6b** mentioned essentially correspond with the results of the ab initio studies on [$(C_5H_5)_2Nb(BH_4)$].[72]

The discussion of ^{11}B NMR spectroscopic data has for the most part been avoided until now, because they are not particularly suitable for describing the precise structure of boryl complexes in solution. The chemical shifts observed for these products cover a wide range from about $\delta = 35$ to 121 (Table 1), and are shifted downfield with respect to the values for the borane and diborane(4) derivatives used. This would indicate only low or no π electron density on boron. The spectroscopic and structural results discussed above show, however, that the bonding situation cannot be meaningfully described solely on the basis of ^{11}B NMR spectroscopy.

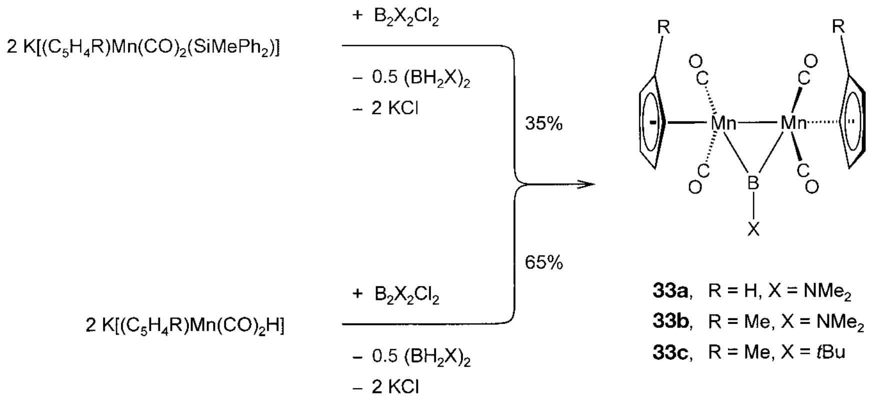
An initial estimation of the strength of the Ir–B bond in [$(Ph_3P)_2(CO)Ir(Cl)(H)(BCat)$] was provided by the measurement of the reaction enthalpy for the reaction of *trans*-[$(Ph_3P)_2(CO)IrCl$] with CatBH. Under consideration of the B–X bond dissociation energies for CatBX (X = H, Me) calculated by ab initio methods, an Ir–B bond strength of 66 $kcal\,mol^{-1}$ was determined. This lies well above the values for Ir–H and Ir–C bonds in comparable complexes.[95] In addition to the numerous experimental findings, preliminary theoretical studies of the bonding in boryl complexes were also considered. Ab initio calculations on complexes of the type *cis*-[$(H_3P)_2M(BX_2)_2$] (M = Pd, Pt; X = H, OH) provided metal–boron bond strengths of 51.0 (M = Pd; X = OH), 64.8 (M = Pt; X = H), and 62.9 $kcal\,mol^{-1}$ (M = Pt; X = OH).[96] These values are also up to 25 $kcal\,mol^{-1}$ greater than the corresponding bond energies of M–C bonds. This can be explained by the additional stabilization of the M–B bonds by π interactions. This is also indicated by the good agreement between the calculated Pt–B bond lengths of 206.9 (X = H) and 205.6 pm (X = OH) and those determined for structurally characterized platinum-boryl complexes; for these π bonding may also be assumed on the basis of other spectroscopic data.

This more detailed discussion of experimental and theoretical findings shows that the question regarding the nature of the metal–boron bond in boryl-transition metal complexes cannot be answered uniformly. A tendency towards the formation of π backbonds is clearly dependent both on the substituents bonded to boron and on the metal itself. It is noticeable that, in contrast to other substituents on boron, the phenylene-1,2-dioxyboryl group in complexes of the type [$(C_5H_5)(CO)_2Fe(BRR')$] enables backbonding from iron to boron. This additional stabilization may be responsible for the broad applicability of catecholborane derivatives in the synthesis of boryl complexes.

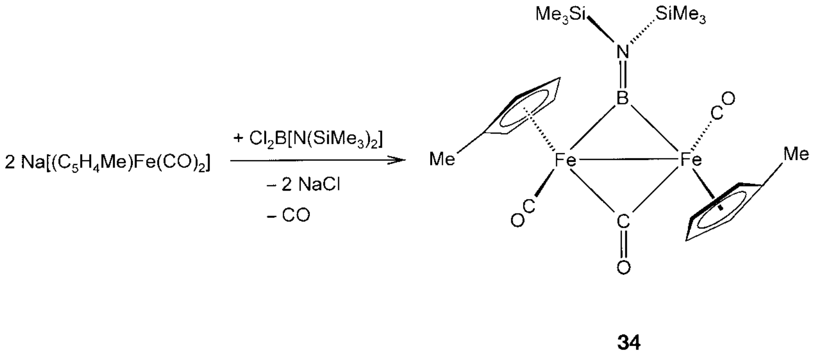
4. Borylene Complexes

Although there are numerous boryl complexes of metals of Groups 5–8, there are only a few structurally characterized examples of borylene complexes. These binuclear manganese and iron complexes each contain one bridging borylene ligand.

The reaction of K[$(C_5H_4R)Mn(CO)_2(SiMePh_2)$] with the diboranes(4) $B_2X_2Cl_2$ surprisingly leads to the diboranes(6) $(XBH_2)_2$ and the borylene complexes **33a–c** (ca. 35% yield, Scheme 8); the stoichiometry of the reaction, the origin of the proton bonded to boron in **33a**, and the fate of the silyl group are still unclear.[97] With the use of K[$(C_5H_4R)Mn(CO)_2H$] in place of the silyl complex, the borylene complexes can be obtained as products of stoichiometric reactions in considerably higher yields (ca. 65%, Scheme 8).[98] Further studies have shown that the unexpected formation of **33a–c** is dependent on the use of the diboranes(4), as no products with Mn–B bonds are formed when aminodichloroboranes are used.[98]



Scheme 8. Synthesis of borylene–manganese complexes.



Scheme 9. Synthesis of **34**.

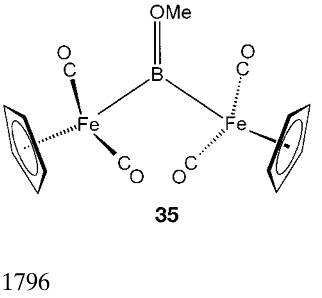
A more direct access to bridged borylene complexes is provided by the reaction of $Cl_2B[N(SiMe_3)_2]$ with Na[$(C_5H_4Me)Fe(CO)_2$] to form the iron compound **34** (Scheme 9).[99] As was the case with the salt eliminations discussed in Section 3.3, the Fe–B bonds are formed by nucleophilic substitution of the chloride ligands; in addition, a carbonyl group is eliminated.

Recent results show that this synthetic method has wider applicability. Starting from Na[$(C_5H_4Me)Fe(CO)_2$] and Na[$Mn(CO)_5$], **35** and **36** with bridging borylene ligands were obtained.[100] The iron complex **35** is formed without elimination of a carbonyl ligand; therefore, in contrast to the related **34**, it has four terminal carbonyl ligands.

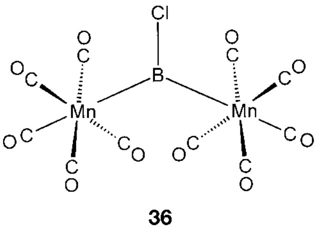
[μ-$BNMe_2\{(C_5H_5)Mn(CO)_2\}_2$] **33a**

[μ-$BNMe_2\{(C_5H_4Me)Mn(CO)_2\}_2$] **33b**

[μ-$BtBu\{(C_5H_4Me)Mn(CO)_2\}_2$] **33c**



35



36

[μ-$B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(C_5H_4Me)Fe(CO)\}_2$] **34**

[μ-$BOMe\{(C_5H_5)Fe(CO)_2\}_2$] **35**

[μ-$BCl\{Mn(CO)_5\}_2$] **36**

The structures of the borylene complexes **33** and **34** in solution and in the crystal are closely related with those of the isoelectronic dimanganese-[101] and diiron–vinylidene compounds.[102] The position of the CO bands in the IR spectra and the metal–boron bond lengths (Table 2) speak for σ-bonded borylene ligands. The metal–boron distances in **35** and **36** also give no indication of π bonding. On comparison of the ^{11}B NMR data of the borylene complexes (Table 2) with those of the boryl complexes, it is apparent that the formation of a second metal–boron bond leads to a considerable downfield shift of the signals. Whereas, for example, the resonances for alkyl-substituted boryl complexes lie in the region around $\delta = 107$, a value of $\delta = 170.0$ is found for **33c**.

Although **33a–c** and **34** show a very similar structure, they have very different chemical properties. Compounds **33c** and **34** are comparable with the above-mentioned boryl complexes, but the aminoborylene complexes **33a,b** are characterized by their remarkable inertness with respect to air and water.[103]

Table 2. Syntheses, M–B bond lengths, and $\delta(^{11}B)$ values of borylene complexes.

Compound	Synthesis[a]	d (M–B) [pm]	$\delta(^{11}B)$	Ref.
$[\mu\text{-BNMe}_2\{(C_5H_5)Mn(CO)_2\}_2]$ **33a**	C	203(1)	103.0	[97, 98]
$[\mu\text{-B}t\text{Bu}\{(C_5H_4Me)Mn(CO)_2\}_2]$ **33c**	C	–[b]	170.0	[97, 98]
$[\mu\text{-BCl}\{(C_5H_4Me)Mn(CO)_2\}_2]$ **33d**	B	–[b]	133.5	[102]
$[\mu\text{-B(NH}t\text{Bu)}\{(C_5H_4Me)Mn(CO)_2\}_2]$ **33e**	B	–[b]	102.4	[102]
$[\mu\text{-B(NHPh)}\{(C_5H_4Me)Mn(CO)_2\}_2]$ **33f**	B	–[b]	107.6	[102]
$[\mu\text{-BOMe}\{(C_5H_4Me)Mn(CO)_2\}_2]$ **33g**	B	–[b]	98.9	[102]
$[\mu\text{-BOEt}\{(C_5H_4Me)Mn(CO)_2\}_2]$ **33h**	B	198.8(2), 202.1(2)	97.6	[102]
$[\mu\text{-BOH}(C_5H_4Me)Mn(CO)_2\}_2]$ **33i**	B	–[b]	101.6	[102]
$[\mu\text{-B}\{N(SiMe_3)_2\}(\mu\text{-CO})\{(C_5H_4Me)Fe(CO)\}_2]$ **34**	A	200.7(3), 200.2(3)	119.1	[99]
$[\mu\text{-BOMe}\{(C_5H_5)Fe(CO)_2\}_2]$ **35**	A	206.8(9), 208.9(9)	96.7	[100]
$[\mu\text{-BCl}\{Mn(CO)_5\}_2]$ **36**	A	216.9(3), 217.0(3)	163.0	[100]

[a] A = salt elimination, B = substitution on boron, C = other method. [b] No details of the structure in the crystal are available.

5. Reactions

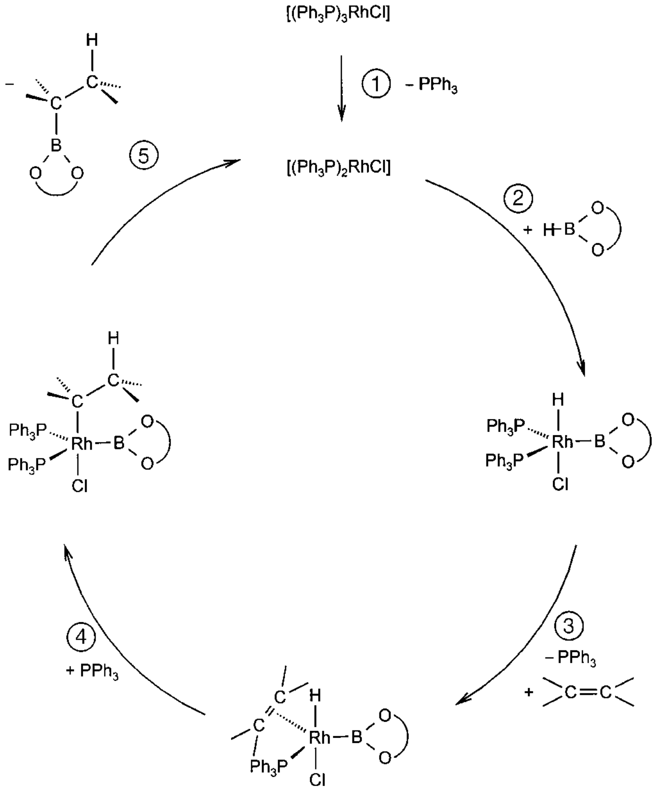
5.1. The Transition Metal Catalyzed Hydroboration and Related Reactions

Since its discovery about 40 years ago,[67] the hydroboration of unsaturated hydrocarbons has developed into one of the most useful methods for the functionalization of organic compounds.[104–106] In the last few years, in addition to the transition metal catalyzed hydrosilylation,[107–109] the influence of suitable complex compounds on the hydroboration reaction has been studied.[110] A large proportion of these results has already been reviewed.[111]

The current interest in boryl complexes is above all due to the fact that these compounds play a decisive role in the catalyzed hydroboration. Numerous investigations have been concerned with clarifying the mechanism of the reaction; boryl complexes synthesized since 1990 frequently serve as model substances. The longest known and beststudied is the catalytic efficacy of rhodium compounds such as the Wilkinson's catalyst $[(Ph_3P)_3RhCl]$. In 1985[110] a mechanism was suggested that is analogous to the Rh-catalyzed hydroboration of acrylic esters with carbaboranes.[112] Starting from $[(Ph_3P)_3RhCl]$, the mechanism involves the following steps (Scheme 10): 1) elimination of PPh_3, 2) oxidative addition with cleavage of the B–H bond, 3) elimination of PPh_3 and side-on coordination of the alkene, 4) addition of PPh_3 and insertion of the alkene into the Rh–H bond, and 5) reductive elimination of the alkylborane. This mechanism is in agreement with a current theoretical[113] and numerous experimental studies.[54, 111, 114] As discussed in Section 3.3, the reaction of $[(Ph_3P)_3RhCl]$ with CatBH does not proceed so uniformly. Side reactions such as the isomerization of the alkene or the catalytic decomposition of the catecholborane to BH_3 can occur.[70, 71, 115] Moreover, a corresponding insertion into the Rh–B bond has been suggested as an alternative to the insertion of the alkene into the Rh–H bond.[50, 70, 116]

The use of suitable transition metal complexes provides several advantages over the noncatalyzed hydroboration.[70, 110, 111, 117–120] For example, less reactive or thermally sensitive boranes can be induced to react under mild conditions. Furthermore, in many cases the chemo-, regio-, and stereoselectivity may be reversed, which greatly increases the applicability of this reaction. It is thus possible to carry out the hydroboration of C=C double bonds even in the presence of keto functional groups, or to functionalize cyclohexenone derivatives in the 3-position; in the case of the latter, noncatalyzed reactions lead to the attack of boron at the 2-position. The use of chiral complexes makes it possible to carry out stereoselective reactions even with achiral boranes, and the use of optically active material can be limited to the relatively small amount of catalyst required.

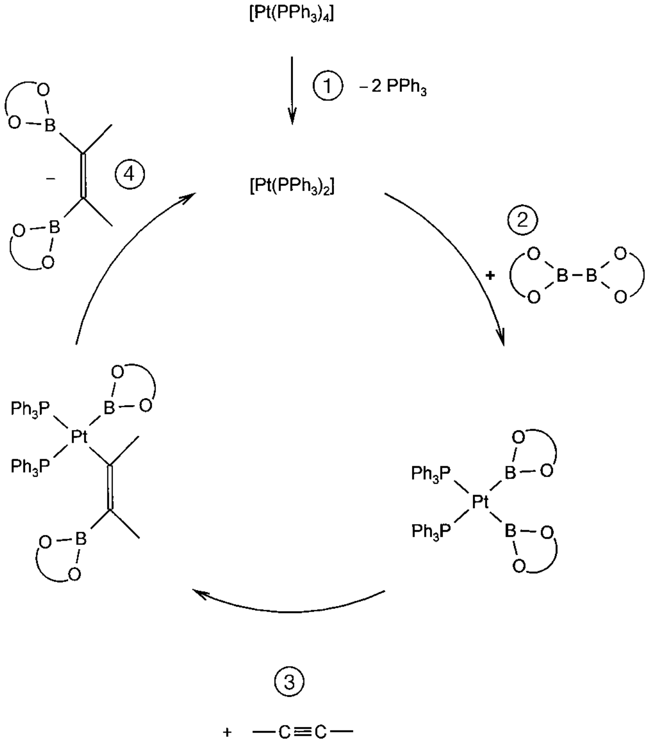
In addition to rhodium compounds, complexes of other transition metals have also been studied with regard to their catalytic activity, albeit to a lesser extent. For reactions with complexes of iridium,[54] palladium,[121] and nickel[122] in low oxidation states, a mechanism similar to that postulated for the rhodium-catalyzed reaction has been suggested. However, it has only been possible to fully characterize the intermediately formed boryl complex in the case of iridium.



Scheme 10. Mechanism of the rhodium-catalyzed hydroboration of alkenes.

Unlike the reactions mentioned, the transition metal catalyzed hydroboration can also take place by a different route without formation of metal–boron bonds. Lanthanum,[123] titanium,[124–126] and zirconium[127, 128] complexes have proven to be suitable catalysts. In contrast to the above-mentioned mechanism, the initial reaction in this case is that of an alkene or alkyne with the catalyst. Then, in a second step, the borane attacks this ligand now coordinated to the metal. Both mechanisms are discussed for the hydroboration of imines in the presence of copper, silver, or gold complexes, but the actual mechanism has still not been clarified.[129]

Closely related to the transition metal catalyzed hydroboration are corresponding additions of compounds with B–B, B–Si, B–Sn, and B–S bonds to unsaturated hydrocarbons. On the basis of numerous experimental findings, a similar mechanism can be assumed for the platinum-catalyzed boroboration of alkenes[130] and alkynes[53, 59] with B_2Cat_2 and B_2Pin_2 (Scheme 11). As described in Section 3.3, the addition of the diborane(4) to platinum takes place with formation of a bisboryl complex (step 2), which undergoes insertion of the C–C unit into a metal–boron bond (step 3) and subsequent reductive elimination of the doubly borylated product (step 4). A corresponding mechanism has been suggested for the boroboration of vinyl arenes with B_2Cat_2 in the presence of rhodium or gold complexes. The most effective catalyst system for the preparation of the difunctionalized products proved to be $[(Et_3P)AuCl]$ in the presence of two equivalents of $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$. The use of various rhodium complexes invariably involves a β-H elimination as a competing reaction, which leads to monoborated alkanes or alkenes.[131] Whereas noncatalyzed boroboration reactions for the synthesis of difunctionalized organic molecules are limited to the use of highly reactive tetrahalodiboranes(4),[67, 68] the catalysts mentioned make possible the use of less reactive and thus easy-to-handle tetraalkoxydiboranes(4) and tetraaryloxydiboranes(4). A similar activation of the boron–element bond in silyl-,[132] stannyl-,[133] and sulfanylboranes[134] with regard to the oxidative addition to alkynes can be achieved with palladium and platinum complexes.



Scheme 11. Mechanism of the platinum-catalyzed boroboration of alkynes.

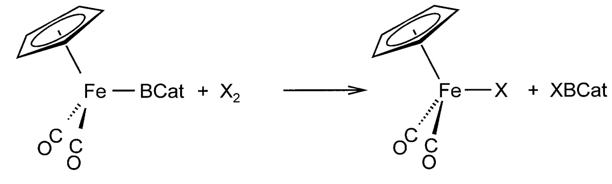
5.2. Further Reactions of Boryl Complexes

As discussed in Section 3.4, certain metal–boron bonds are stronger than corresponding metal–carbon bonds.[95, 96] However, the catalyzed hydroboration and related reactions are based on the facile cleavage of the metal–boron bond; this is an indication of the kinetic lability of boryl complexes.[45] Whereas reactions with unsaturated compounds have been the subject of extensive studies, comparatively little is known about the further reactivity of these complexes. For instance, the reaction of the tungsten complex **8** with $HNEt_2$ to give $[(C_5H_5)_2WH_2]$ and Et_2NBCat[41] takes place with cleavage of metal–boron bonds under the influence of protic compounds such as alcohols or amines to form the corresponding metal hydride complexes.[41, 42, 45, 46]

An interesting synthesis is that of the anionic boryl complex **11b** from **11a** and $LiN(SiMe_3)_2$, in which an amino(phenylene-1,2-dioxy)borane is also formed (Scheme 12).[45] Metal–boron bonds can also be cleaved by unpolar reagents, as is demonstrated by the reactions of the iron–boryl complex **12** with Br_2 or H_2 (Scheme 13).[46] The corresponding addition of the B–B bond of a diborane(4) derivative to a metal–boron bond leads to an exchange of boryl ligands by σ-bond metathesis, as observed in the case of the rhodium complex **16**[134] and the platinum compound **20a**.[53]

$$\underset{\mathbf{11a}}{[(CO)_4Fe(BCat^*)_2]} + LiN(SiMe_3)_2 \longrightarrow \underset{\mathbf{11b}}{Li[(CO)_4FeBCat^*]} + [(Me_3Si)_2N]BCat^*$$

Scheme 12. Synthesis of **11b**.



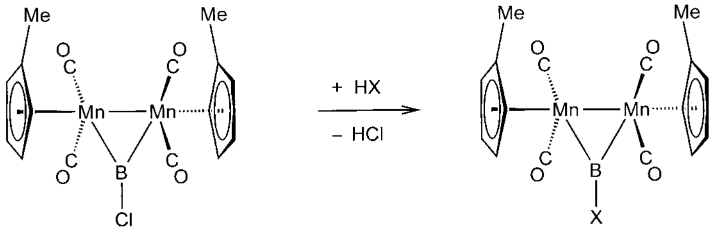
12

Scheme 13. Reaction of **12** with X_2 (X = H, Br).

An interesting possibility for the functionalization of organic compounds is provided by the photolysis of boryl complexes such as **10a**, **b** or **12** in the presence of arenes or alkenes.[44] Activation of C–H bonds leads to the formation of aryl- and vinylboranes in high yields. At present, only a few complex compounds are known that can simultaneously activate and functionalize unreactive hydrocarbons.[135, 136] The recently introduced functionalization of alkanes deserves special attention. Alkyl esters of boronic acids are formed by selective addition of the catecholboryl group to terminal carbon atoms upon photolysis of phenylene-1,2-dioxyboryl complexes in aliphatic solvents. The functionalized alkanes thus formed can be isolated in yields of up to 85%.[137]

5.3. Reactions With Retention of the Metal–Boron Bond

All of the reactions of boryl complexes mentioned so far take place with cleavage of the metal–boron bonds. In contrast, substitution reactions of boryl ligands coordinated to metals are unknown. The aminoborylene complex **33a** displays a fundamentally different chemical behavior.[103] The reaction with HCl leads, for instance, to the substitution of the amino group with formation of the chloroborylene complex **33d**; cleavage of the Mn–B bond is not observed. In agreement with the known properties of amino- and chloroboranes, **33d** is significantly more reactive than the amino derivative **33a**, which is stable to both air and moisture, and serves as the starting material for further substitution reactions on boron. With protic compounds such as primary amines, alcohols, or water, it is possible to obtain the corresponding substituted borylene complexes **33e**–**i** in good yield with elimination of HCl (Scheme 14). The spectroscopic and structural properties of these derivatives (Table 2) show no great differences to those of **33a**–**c**.[97]



33d

33e, X = NH*t*Bu
33f, X = NHPh
33g, X = OMe
33h, X = OEt
33i, X = OH

Scheme 14. Reaction of **33d** with protic compounds.

[μ-BCl{(C_5H_4Me)Mn$(CO)_2$}$_2$] **33d**

[μ-B(NH*t*Bu){(C_5H_4Me)Mn$(CO)_2$}$_2$] **33e**

[μ-B(NHPh){(C_5H_4Me)Mn$(CO)_2$}$_2$] **33f**

[μ-BOMe{(C_5H_4Me)Mn$(CO)_2$}$_2$] **33g**

[μ-BOEt{(C_5H_4Me)Mn$(CO)_2$}$_2$] **33h**

[μ-BOH{(C_5H_4Me)Mn$(CO)_2$}$_2$] **33i**

6. Summary and Outlook

The results presented here demonstrate that the fundamental difficulties involved with the synthesis of crystalline transition metal complexes of boron can be overcome. The salt elimination and the oxidative addition of compounds with boron–element bonds are two methods for preparing boryl complexes, and the use of phenylene-1,2-dioxyborane derivatives has proved to be extremely useful. Knowledge of the stability of the complexes as a function of the substituents on boron would greatly assist in the search for other boranes with a similar wide range of use.

Whereas the boryl complexes have been extensively studied, in particular because of their interesting application possibilities in the functionalization of organic compounds, there is only little confirmed information on borane and borylene complexes. In the case of the borane complexes only one compound could be spectroscopically characterized in solution. Access to complexes with bridging borylene ligands was initially limited to one very special and unexpected reaction; most recent results show, however, the salt elimination could find a wider scope of applicability here. Complexes containing terminal borylene ligands with a metal–boron double bond are not known as yet, and the synthesis of such compounds is certainly one of the greatest challenges in this field.

The transition metal catalyzed hydroboration has long proven to be a valuable method in the functionalization of organic compounds. Recently further interesting application possibilities for boryl complexes in organic synthesis have presented themselves. Examples include the preparation of difunctionalized hydrocarbons starting from silylboranes, stannylboranes, sulfanylboranes, and diboranes(4), and, most importantly, the selective synthesis of terminal alkyl esters of boronic acids by the photochemically induced C–H activation of alkanes.

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