The Chemistry of Borylene Complexes

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Over the past seven years, complexes of various transition metals with bridged or terminal borylene ligands BR have for the first time been reported and fully characterised. Being closely related to important organometallic compounds, such as carbene, vinylidene, and carbonyl complexes, they have already attracted considerable interest both from experimental and computational points of view. Those studies have provided some detailed information about the nature of the metal–boron bond and about the nature of metal and borylene moieties required for the formation of stable complexes. Various methods for their preparation have been developed and the first studies on their reactivity have demonstrated an interesting chemistry.

1. Introduction

Transition metal complexes with electron-precise, two-centre, two-electron (2c-2e) bonds linking the metal centre to a main group element have now been well established for decades, and for almost any main group element from group 13 to 17. Corresponding complexes with metal−boron bonds, however, became known only much later, indicating the difficulties associated with the synthesis and characterisation of these compounds. Despite very early investigations in this area (vide infra),[1] the first structurally authenticated transition metal complexes of boron date back only to 1990.[2,3] Until then, confirmed knowledge of compounds with direct transition metal−boron bonds was restricted to borides,[4−6] metallaboranes[7−9] and complexes with π-bonded boron-containing ligands such as borole,[10−12] diborolene,[13] borabenzene,[14,15] borazine,[16,17] and diazadiboretidine.[17] The natures of the metal−boron interactions in these classes of compounds are diverse, but none of them is characterised by classical 2c-2e bonds.

Thanks to the vigorous research into transition metal complexes of boron since 1990,[18−21] a variety of different coordination modes for boron-centred ligands have been obtained, allowing for a systematic classification of those compounds (Figure 1). According to the coordination number of boron and the number of metal−boron bonds, one can distinguish between borane (**I**), boryl (**II**), bridged (**III**) and terminal borylene (**IV**) complexes. Borane complexes can be understood as Lewis acid−base adducts of basic metal centres and acidic boranes BR_3, giving rise to fourfold coordination of the boron atom. Boryl complexes, however, show boron in coordination number three, achieved by the linking of a BR_2 group to a metal centre. The borylene ligand BR can adopt two different coordination modes: either bridging between two metal centres − also showing boron in coordination number three − or terminal to one metal centre with formation of a formal

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double bond and a decrease in the coordination number to two. Provided that the boron atom in **II−IV** is still Lewis acidic, there is the possibility to add a suitable base L, which results in the formation of the corresponding adducts of boryl (**IIa**) and both bridged (**IIIa**) and terminal (**IVa**) borylene complexes. Examples of all types of compounds **I−IV** had already been described in earlier literature between 1963 and 1970, but without structural confirmation.[1] The spectroscopic data reported for these compounds are in disagreement with more recent findings and the proposed constitutions of those complexes have to some extent been disproved.

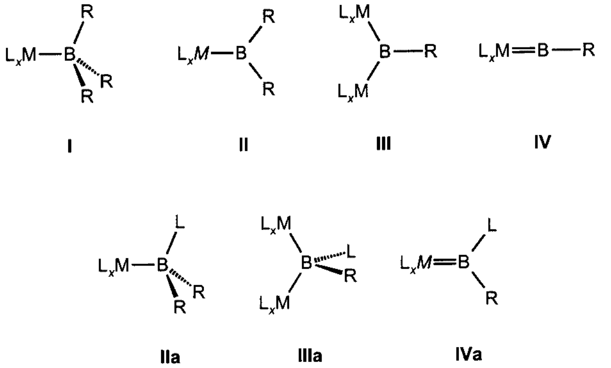


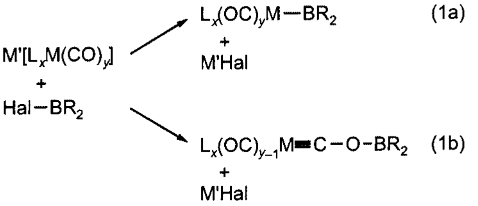
Figure 1. Different types of transition metal complexes of boron

The production of borylene complexes with either bridging or terminal BR ligands is one of the most recent achievements in the field of transition metal complexes of boron, and these compounds are still exceptionally rare in comparison with boryl and other group 13 "elementdiyl" complexes.[22] Thanks to their close relationship to pivotal organometallic compounds such as carbene, vinylidene and especially carbonyl complexes, borylene complexes have already attracted considerable interest.[23−25] This is also reflected by the numerous theoretical studies[26−32] (vide infra), which greatly outnumber the experimental reports. Furthermore, borylene complexes allow for the stabilisation of the hypovalent borylene **:**BR in the coordination sphere of a transition metal centre. In contrast to related subvalent main group element species such as carbenes, silylenes, or alanediyls, no free borylenes are known at ambient temperature and in condensed phase.

2. Terminal Borylene Complexes

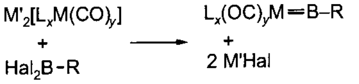
2.1. Synthesis

The salt elimination reaction between mononuclear anionic transition metal carbonyl complexes $M'[L_xM(CO)_y]$ and main group element halides $HalER_z$ is a fundamental reaction in transition metal chemistry, and has had a pivotal role in establishing complexes of the type $[L_x(OC)_yM-ER_z]$ with transition metal−element bonds.[33,34] Over the past decade, salt elimination reactions have also become a very facile method for the synthesis of boryl complexes $[L_x(OC)_yM-BR_2]$ [Equation (1a)]. We have reported, however, that the formation of (boryloxy)-carbyne complexes $[L_x(OC)_{y-1}M{\equiv}C-O-BR_2]$ [Equation (1b)] with nucleophilic attack of the CO oxygen atom represents an alternative reaction pathway to the expected synthesis of boryl complexes in certain cases.[35−37]



(1)

Extension of this synthetic approach to dianionic carbonylates and suitable dihaloboranes [Equation (2)] gave access to the first structurally authenticated terminal borylene complexes $[(OC)_4Fe-B(\eta^5\text{-}C_5Me_5)]$ (**1**)[38] and $[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**2**),[39] reported by Cowley and by us in 1998 (Figure 2). By applying the corresponding precursors $K_2[Fe(CO)_4]$ and $Na_2[Cr(CO)_5]$ we also obtained the related aminoborylene complexes $[(OC)_4Fe{=}B{=}N(SiMe_3)_2]$ (**3**)[39] and $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**4**)[39] (Figure 2), the latter of which was subsequently characterised by X-ray structure analysis.[40] The formation of **1−4** implies that the boron centre in such terminal borylene complexes requires stabilisation by a sterically demanding and electron-releasing ligand. Evidently, both the η^5-C_5Me_5 and the $N(SiMe_3)_2$ ligands provide sufficient steric shielding and π-electron stabilisation. In the case of the former, an alternative point of view may be applied, namely that the electron deficiency of the boron centre is relieved by its incorporation into a non-classical pentacarba-*nido*-hexaborane cage. From our experience with the formation of transition metal−boron bonds by salt elimination reactions, the aminoborane $Br_2B{=}N(SiMe_3)_2$ appeared to be the most promising borane precursor for the synthesis of terminal aminoborylene complexes because of the increased electrophilicity of the boron centre in relation to (dialkylamino)boranes, and consequent facilitation of the nucleophilic substitution of the halides by transition metals.[41,42]



$$\begin{matrix} M'_2[L_xM(CO)_y] \\ + \\ Hal_2B-R \end{matrix} \longrightarrow \begin{matrix} L_x(OC)_yM{=}B{-}R \\ + \\ 2\ M'Hal \end{matrix} \qquad (2)$$

Despite significant efforts[43−45] and the vast amount of various borane precursors at hand, all attempts to obtain corresponding $[(OC)_xM{=}B{=}NR_2]$ complexes from any other aminoborane $Hal_2B{=}NR_2$ have so far failed, thus emphasising the particular significance of $Br_2B{=}N(SiMe_3)_2$ for the production of terminal borylene complexes. The failure to undergo salt elimination reactions with dianionic metal carbonylates according to Equation (2) appears to extend to common alkyl- and aryl(dihalo)boranes Hal_2B-R,[43−45] thus hampering the synthesis of terminal borylene complexes of the type $[(OC)_xM{=}B{-}R]$. These compounds are of particular interest, however, since the boron centre is both coordinatively and electronically unsaturated and thus represents a very unusual bonding situation in boron chemistry, known only in a very few methyl-

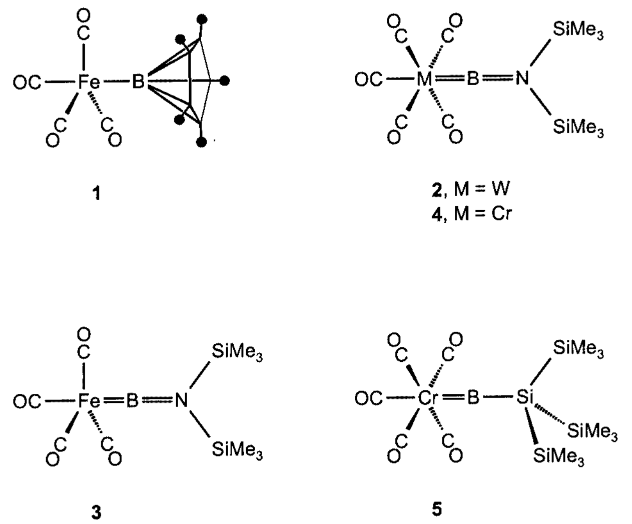


Figure 2. Selected terminal borylene complexes

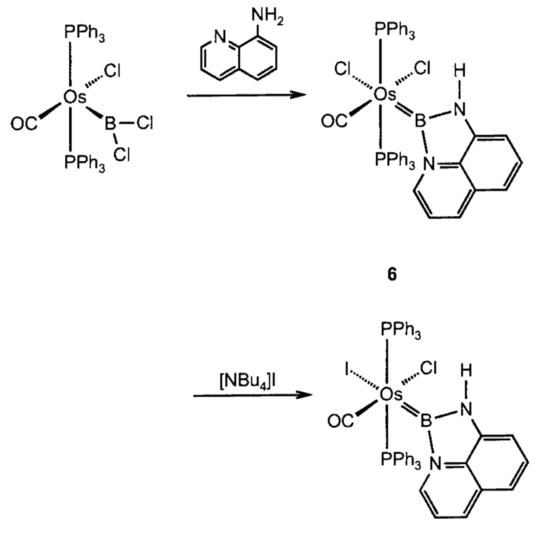


Figure 3. Synthesis of **7**

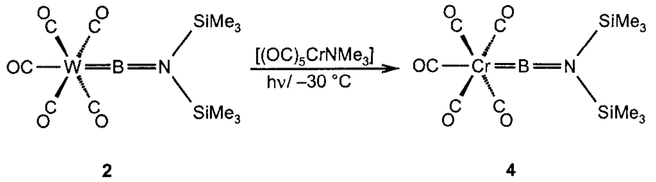
eneboranes of the $(Me_3Si)_2C=B-R$ type (R = Me, *t*Bu, 2,3,5,6-tetramethylphenyl, 2,4,6-trimethylphenyl).[46–50] Because of their obvious significance[23] for the understanding of metal–boron bonding, alkyl- and arylborylene complexes $[(OC)_xM=B-R]$ had already been the subjects of several theoretical studies[28–31] before we succeeded in providing the first experimental evidence for such a compound. The use of the sterically demanding silylborane $Cl_2B-Si(SiMe_3)_3$ finally allowed for the synthesis and full characterisation of $[(OC)_5Cr=B-Si(SiMe_3)_3]$ (**5**) as the first terminal borylene complex with a both coordinatively and electronically unsaturated boron atom[51] (Figure 2). This silylborylene complex proved to be extremely sensitive, in contrast to its rather stable amino analogue $[(OC)_5Cr=B=N(SiMe_3)_2]$ (**4**), and shows significant decomposition in solution and even in the solid state after several hours at ambient temperature. The enhanced sensitivity of **5** is obviously due to the lack of ligand-to-boron π-interaction, as its steric shielding must be considered equal to or even larger than that in **4**.

As mentioned above, a low-coordinated boron centre displays some potential Lewis acidic character, which in the case of terminal borylene complexes might provide access to corresponding base-stabilised species of the type $[L_xM=B(L)-R]$ (**IVa**, Figure 1). The only example so far was reported in 2000 by Roper, who obtained $[Os(=BNHC_9H_6N)Cl_2(CO)(PPh_3)_2]$[52] (**6**) by treatment of the borylosmium complex $[Cl_2BOsCl(CO)(PPh_3)_2]$ with 8-aminoquinoline as shown in Figure 3.

Subsequent treatment of **6** with $[Bu_4N]I$ yielded the corresponding borylene complex $[Os(=BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**7**), in which the chloro ligand *trans* to the boron atom was replaced by iodine, thus providing evidence for the *trans* influence of the borylene ligand.[52]

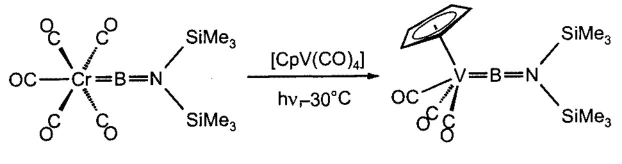
Obviously, this synthesis of **6** is very specific, but even the salt elimination reaction as in Equation (2) suffers from a certain lack of wider applicability in borylene chemistry. The restriction to a rather narrow range of dihaloboranes has already been discussed, but the same also appears to be true for the dianionic transition metal precursor. Over the past few years we have employed a wide variety of such dianionic complexes or corresponding synthetic equivalents[53,54] in combination with various dihaloboranes, but without much success.[43–45]

The need for alternative synthetic methods in this chemistry initiated our studies on the potential use of complexes of the type $[(OC)_5M=B=N(SiMe_3)_2]$ (**2**: M = W; **4**: M = Cr) as a source of the aminoborylene $B=N(SiMe_3)_2$. The generation of such hypovalent borylenes B–R – the boron analogues of carbenes CR_2 – usually requires drastic conditions: Timms' classical method involves the reduction of boron trihalides at temperatures above 2000 °C,[55,56] while alternatively, West obtained the silylborylene $B-SiPh_3$ photochemically from $RB(SiPh_3)_2$ (R = Me, Mes) in hydrocarbon matrices at −196 °C.[57] The reductive[58,59] or photochemical[60] generation of species B–R in condensed phase might be assumed from the nature of the corresponding trapping products. There is, however, no direct proof for the intermediacy of borylenes – the system $MeBBr_2/2{\cdot}C_8K$ as a source for B–Me in particular has been reported to be questionable.[61] As early as 1973 Timms recognised borylene complexes as a potentially useful source of borylenes in cases in which gaseous species cannot be used.[56] We have recently reported on the first photochemically induced intermetal borylene transfer, as shown in Equation (3), thus proving that terminal borylene complexes may indeed act as a unique source of hypovalent borylenes in condensed phase and close to ambient temperature.[62]



(3)

The formation of **4** as in Equation (3) merely represents an alternative synthesis of an already known compound. However, the generation of $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ (**8**), similarly obtained from **4** and $[(\eta^5\text{-}C_5H_5)V(CO)_4]$ as shown in Equation (4),[63] emphasises the significance of photochemically induced intermetal borylene transfer, since all attempts to obtain the vanadium complex **8** by salt elimination reactions from $Na_2[(\eta^5\text{-}C_5H_5)V(CO)_3]$ and $Hal_2B{=}N(SiMe_3)_2$ failed.[43−45]



4 **8** (4)

2.2. Structure

In solution, the common and most characteristic spectroscopic feature of all terminal borylene complexes with coordinatively unsaturated (i.e., two-coordinate) boron atoms are the ^{11}B NMR resonances, which are significantly deshielded with respect to those of corresponding amino- and silylboryl complexes of the types $[L_xM{-}B(X)NR_2]$[18−21] and $[L_xM{-}B(X)SiR_3]$.[64] The aminoborylene complexes **2**−**4**, and **8** exhibit ^{11}B NMR shifts in the range from $\delta = 87$ to 93 ppm (Table 1), thus resembling those of corresponding bridged borylene complexes with π-donating ligands at the boron atom (vide infra). The silylborylene complex $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**5**) is characterised by a strikingly deshielded ^{11}B NMR resonance at $\delta = 204.3$ ppm, and so greatly extends the known dispersion of the ^{11}B nucleus for classical boranes. Similarly low-field-shifted resonances have been reported only for metal clusters containing interstitial boron atoms, such as *cis*- and *trans*-$[Fe_4Rh_2(CO)_{16}B]^-$ ($\delta = 211$ and 205 ppm).[65,66] The observed significant difference between **2** and **5** could be expected for terminal borylene complexes in which the boron centre was not part of a boron−ligand π-system,[23] if one compares the bridged amino- and alkylborylene complexes of the type $[(\mu\text{-}BR)\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ ($R = NMe_2$: $\delta^{11}B = 103$ ppm; $R = t$Bu: $\delta^{11}B = 170$ ppm).[67−69] Because of the higher coordination numbers of the boron centres, $[(OC)_4Fe{-}B(\eta^5\text{-}C_5Me_5)]$ (**1**)[70] and $[Os({=}BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**7**)[52] display much more shielded ^{11}B NMR resonances − at $\delta = -35.3$ and 51.7 ppm, respectively − with the former being characteristic for apical boron atoms in such *nido*-carboranes.

Crystal structure data are available for the following terminal borylene complexes: $[(OC)_4Fe{-}B(\eta^5\text{-}C_5Me_5)]$ (**1**),[38] $[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**2**),[39] $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$

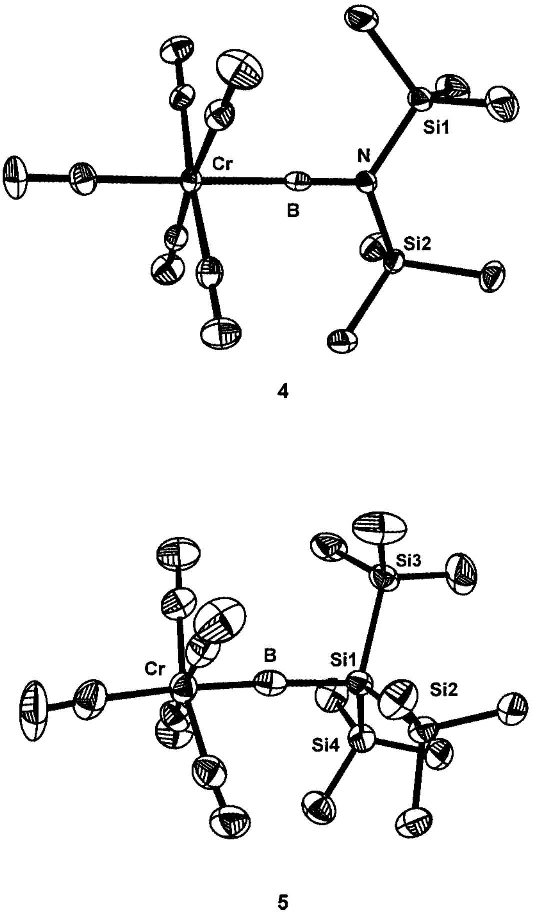
Table 1. Metal−boron distances and ^{11}B NMR shifts

Compound	Synthesis	*d*(M−B) [pm]	$\delta^{11}B$ [ppm]	Ref.
$[(OC)_4Fe{-}B(\eta^5\text{-}C_5Me_5)]$ (**1**)	a[a]	201.0(3)	−35.3	[38]
$[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**2**)	a	215.1(7)	86.6	[39]
$[(OC)_4Fe{=}B{=}N(SiMe_3)_2]$ (**3**)	a	X	88.2	[39]
$[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**4**)	a, c	199.6(6)	92.3	[39][40]
$[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**5**)	a	187.8(10)	204.3	[51]
$[Os({=}BNHC_9H_6N)Cl_2(CO)(PPh_3)_2]$ (**6**)	c	X	y	[52]
$[Os({=}BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**7**)	c	205.5(8)	51.7	[52]
$[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ (**8**)	c	197.1(8)	98.3	[63]
$[(OC)_5W{=}B{=}N(SiH_3)_2\}]$ (**9**)	−	215.2*	y	[29][30]
$[(OC)_4Fe{-}B(\eta^5\text{-}C_5H_5)]$ (**10**)	−	196.2*	y	[29][30]
$[\mu\text{-}B(NMe_2)\{\eta^5\text{-}(C_5H_5)Mn(CO)_2\}_2]$ (**12**)	b	203(1)	103.0	[90][91]
$[\mu\text{-}B(NMe_2)\{\eta^5\text{-}(C_5H_5)Mn(CO)_2\}_2]$ (**12**)	−	204.9*	y	[26]
$[\mu\text{-}B(NMe_2)\{\eta^5\text{-}(C_5H_4Me)Mn(CO)_2\}_2]$ (**13**)	b	X	102.8	[90][91]
$[\mu\text{-}BtBu\{\eta^5\text{-}(C_5H_4Me)Mn(CO)_2\}_2]$ (**14**)	b	X	170.0	[90][91]
$[\mu\text{-}B\{N(C_4H_8)\}\{\eta^5\text{-}(C_5H_4Me)Mn(CO)_2\}_2]$ (**15**)	b	X	100.3	[88]
$[\mu\text{-}B\{N(C_5H_{10})\}\{\eta^5\text{-}(C_5H_4Me)Mn(CO)_2\}_2]$ (**16**)	b	X	101.1	[88]
$[\mu\text{-}BH(PMe_3)(\mu\text{-}CO)\{Co(CO)_3\}_2]$ (**17**)	b	211.2(9), 210.8(11)	17.5	[92]
$[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Fe(CO)\}_2]$ (**18**)	a	X	118.4	[93]
$[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_4Me)Fe(CO)\}_2]$ (**19**)	a	200.7(3), 200.2(3)	119.1	[93]
$[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2]$ (**20**)	a	X	105.9	[94]
$[\mu\text{-}B\{N(SiMe_3)_2\}\{(\eta^5\text{-}C_5H_5)Re(CO)_2\}$ (**21**)	c	X	100.4	[40]
$[\mu\text{-}BCl\{(C_5H_4Me)Mn(CO)_2\}_2]$ (**22**)	c	203.9(11), 197.6(9)	133.5	[103]
$[\mu\text{-}B(NHtBu)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2]$ (**23**)	c	X	102.4	[102]
$[\mu\text{-}B(NHPh)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2]$ (**24**)	c	X	107.6	[102]
$[\mu\text{-}B(OMe)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2]$ (**25**)	c	X	98.8	[102]
$[\mu\text{-}B(OEt)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2]$ (**26**)	c	198.8(2), 202.1(2)	97.6	[102]
$[\mu\text{-}B(OiPr)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2]$ (**27**)	c	X	96.5	[44]
$[\mu\text{-}B(OH)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2]$ (**28**)	c	X	101.6	[102]

[a] a: From monoboranes; b: from diboranes(4); c: other method; X: no X-ray data available; y: no ^{11}B NMR spectroscopic data available; * geometry from ab initio calculation.

(**4**),[40] $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**5**),[51] $[Os({=}BNHC_9H_6N)Cl(I)(CO)(PPh_3)_2]$ (**7**),[52] and $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ (**8**)[63] (Table 1). The metal−boron distances in the aminoborylene complexes **2**, **4**, and **8** range from 197.1 to 215.1 pm, which, together with further spectroscopic and structural data, suggests strong boron-to-metal σ-donation and weaker metal-to-boron π-backbonding. For aminoborylene complexes of first row transition metal complexes this situation was predicted on the basis of ab initio calculations.[26] For **1**, which features a six-coordinate borylene ligand in an axial position, an iron−boron distance of 201.0 pm was reported, indicating a corresponding single bond. The base-stabilised borylene complex **7** is characterised by an osmium−boron distance of 205.5 pm, and so is longer than expected for a double bond. Corresponding findings have been made for related base-stabilised silylene complexes.[71−73]

The decisive influence of the boron-bound ligand R on the metal−boron linkage in terminal borylene complexes $[L_xM{=}B{-}R]$ has already to some extent been demonstrated by the mentioned differences in the ^{11}B NMR shifts. In the solid state, this influence becomes even more evident if one compares the results of the X-ray structure analyses of $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**4**)[40] and $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (**5**)[51] (Figure 4).



4

5

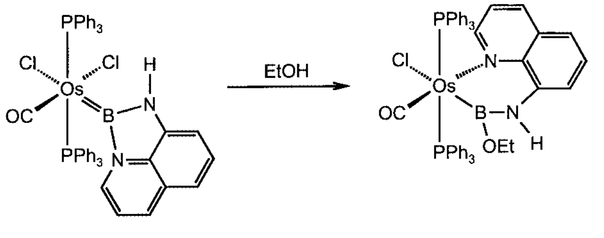
Figure 4. Structures of **4** and **5** in the crystal

The $Cr(CO)_4$ moieties in both molecules exhibit approximate C_{4v} symmetry, and the central Cr−B−E fragment (E = N, Si) adopts a linear arrangement. The Cr−B distance in **5** was found to be 187.8 pm, and thus 12 pm shorter than in the amino counterpart **4**. Obviously, the electron deficiency of the boron centre in the silylborylene complex demands enhanced Cr−B π-backbonding. Further evidence for increased backbonding in **5** stems from the umbrella effect detected for the equatorial CO ligands and the pronounced *trans* effect the $B{-}Si(SiMe_3)_3$ ligand has on the axial CO ligand.[51] Unlike in the previously mentioned methyleneboranes $(Me_3Si)_2C{=}B{-}R$, there is no spectroscopic, structural, or computational evidence for the presence of nonclassical B−Si−Si three-centre, two-electron bonds (hyperconjugation) − well known to relieve electron deficiency at such coordinatively and electronically unsaturated boron centres − in the case of **5**.[46−50]

The question of the nature of the metal−boron bond in terminal borlyene complexes has been addressed in many theoretical studies in the recent past,[26−32] and the selected examples $[(OC)_5W{=}B{=}N(SiH_3)_2\}]$ (**9**) and $[(OC)_4Fe{-}B(\eta^5\text{-}C_5H_5)]$ (**10**) in particular have been investigated as model compounds for complexes **1** and **2**. It was concluded that borylene ligands BR in general have both good σ-donor and π-acceptor properties, but because of the electrophilicity of the boron centre, terminal borylene complexes should only be stable with sterically protecting and electron-releasing substituents such as $N(SiMe_3)_2$ or $\eta^5\text{-}C_5Me_5$ on the boron atom.[26] The nature of the transition metal−boron bond in $[L_xM{=}B{-}R]$ is obviously strongly influenced by the boron-bonded ligand R. Descriptions based on calculations range from an almost purely RB→TM σ-bonded model (TM = transition metal), for R being a good π-donor, up to a strong TM→BR π-back-donation model when R is a weaker π-donor.[28−30] Recent studies, however, have made the point that the sum of the covalent interactions does not even give a bond order of 1, but the nature of the TM−BR bond is mainly ionic.[29−31]

2.3. Reactivity

In addition to the photochemically induced borylene transfer discussed in Sect. 2.2, knowledge about the reactivity of terminal borylene complexes is restricted to only one recent report by Roper.[52] The base-stabilised borylene complex $[Os({=}BNHC_9H_6N)Cl_2(CO)(PPh_3)_2]$ (**6**) undergoes a reaction with ethanol to yield the amino(ethoxy)boryl complex $[Os\{B(OEt)NHC_9H_6N\}Cl(CO)(PPh_3)_2]$ (**11**) as shown in Equation (5), with a 1,2-shift of the quinoline nitrogen atom from the boron to the osmium centre. This alcoholysis of **6** indicated that even the boron atom in base-stabilised borylene complexes displays some electrophilic character − a fact already predicted by a theoretical study.[26]



6 **11** (5)

3. Bridged Borylene Complexes

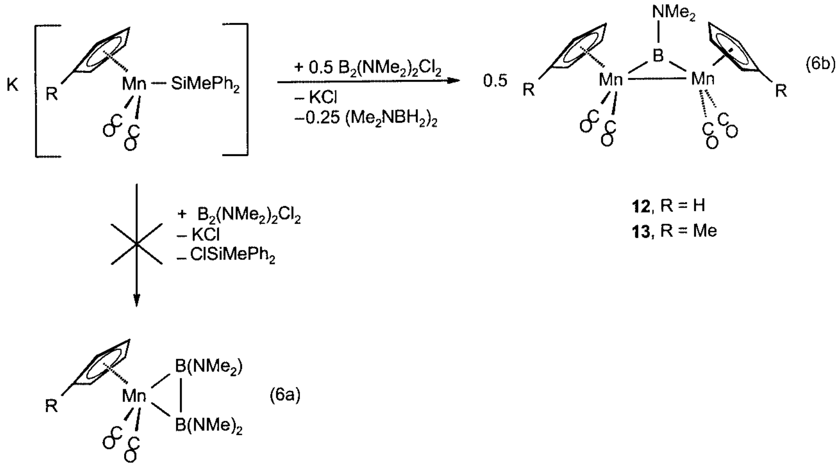
Although bridged borylene complexes $[\mu\text{-BR(ML}_x)_2]$ (**III**) and corresponding base adducts $[\{\mu\text{-BR(L)}\}(\text{ML}_x)_2]$ (**IIIa**) are still rare, they have been known for slightly longer than their terminal counterparts, and their chemistry, briefly summarised in 2000,[24] has developed to a somewhat greater extent. There is now some knowledge about their reactivity, and three different methods for their synthesis have been developed.

3.1. Synthesis

3.1.1. From Diboranes(4)

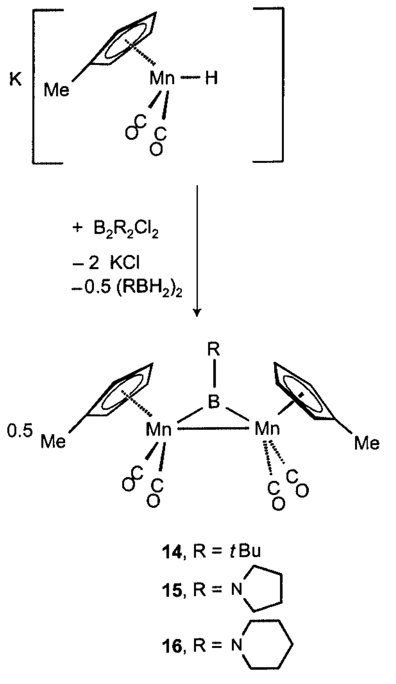
From 1994 onwards, Hartwig, Marder, Norman, and others have been reporting that certain diboranes(4) of the general formula X_2B-BX_2 (X = OR, F) may undergo oxidative additions to suitable transition metal centres, with cleavage of the boron−boron bond and formation of mono-, bis-, or trisboryl complexes $[L_xM(BX_2)_n]$ (n = 1−3).[74−85] Subsequently, we have been able to show that salt elimination reactions between 1,2-dihalodiboranes(4) and anionic transition metal complexes proceed without cleavage of the diborane and hence can provide access to novel complexes of the type $[L_xM\{B(R)-B(R)X\}]$ (X = Cl, Br, I), featuring η^1-coordinated diborane(4)yl ligands.[35,37][86−89] Our attempts to achieve an η^2- or side-on coordination mode for the diborane(4) moiety as in Equation (6a), by treatment of $ClB(NMe_2)-B(NMe_2)Cl$ with $K[\eta^5\text{-}(C_5H_4R)Mn(CO)_2(SiMePh_2)]$ as a synthetic equivalent for a dianionic transition metal complex,[53] resulted in the unexpected formation [Equation (6b)] of the first borylene complexes $[\mu\text{-}B(NMe_2)\{\eta^5\text{-}(C_5H_4R)Mn(CO)_2\}_2]$ (**12**: R = H; **13**: R = Me).[90] The dinuclear borylene complexes **12** and **13** are the products of a nonstoichiometric and obviously complex reaction, accompanied by cleavage of the boron−boron bond and the formation of a corresponding diborane(6) derivative $(Me_2N-BH_2)_2$ − the origin of the hydrogen atoms and the fate of the metal-bound silyl group, however, remained unclear.[90] A significant improvement in this synthesis was achieved by employing the related hydride complex $K[(\eta^5\text{-}(C_5H_4R)MnH(CO)_2]$ as a precursor, giving the complexes **12** and **13** in higher yields as products of a stoichiometric reaction, as shown in Equation (7). In this case, a hydrogen transfer from the manganese to the boron centre occurred and resulted in the formation of $(Me_2N-BH_2)_2$. Our further studies have shown that the cleavage of the boron−boron bond in the starting diboranes(4) decisively contributes to the formation of the bridged borylene complexes, since no products with B−Mn bonds were formed from related monoboranes $RBCl_2$.[91] In addition to complexes **12** and **13** we were able to obtain further bridged borylene complexes of the type $[\mu\text{-BR}\{\eta^5\text{-}(C_5H_4Me)Mn(CO)_2\}_2]$ {**14**: R = *t*Bu; **15**: R = $N(C_4H_8)$; **16**: $N(C_5H_{10})$}[88,90,91] by treatment of $K[\eta^5\text{-}(C_5H_4Me)MnR(CO)_2]$ (R = H, $SiMePh_2$) with corresponding diboranes(4).

In 1998 Shimoi succeeded in another approach to bridged borylene complexes.[92] By starting from $[Co_2(CO)_8]$ and $B_2H_4{\cdot}2PMe_3$ it was possible to produce the cobalt borylene complex $[\mu\text{-BH}(PMe_3)(\mu\text{-CO})\{Co(CO)_3\}_2]$ (**17**) in a cleavage reaction similar to that of a diborane(4). Fragmentation of the 1,2-bis(trimethylphosphane)diborane(4) into $BH_3{\cdot}PMe_3$ and $BH{\cdot}PMe_3$ and the liberation of one CO group afforded **17** [Equation (8)], which represents the only example of a donor-stabilised bridged borylene complex.

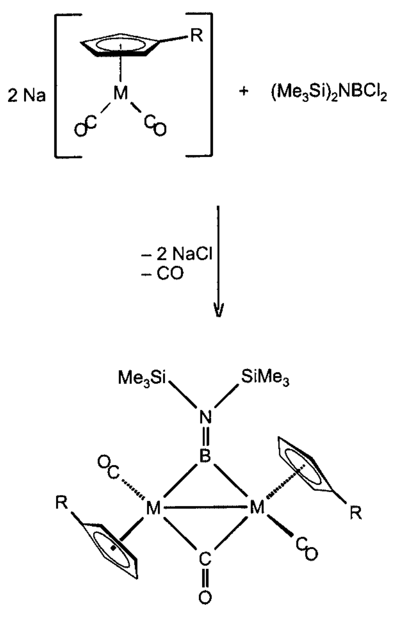


12, R = H
13, R = Me

(6)

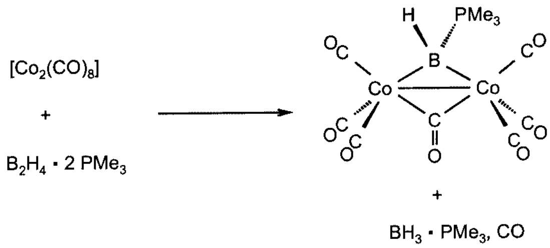


(7)



18, R = H, M = Fe
19, R = Me, M = Fe
20, R = H; M = Ru

(9)



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(8)

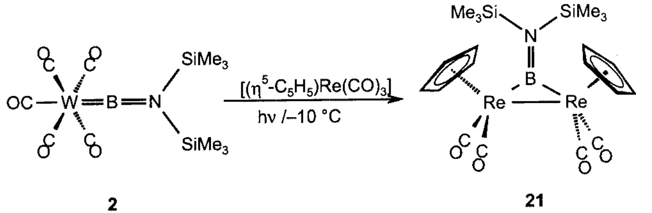
3.1.2. From Monoboranes

The previously mentioned syntheses of dinuclear borylene complexes are very specific, and are restricted to the two systems discussed. In order to provide a more general route to bridged borylene complexes, we investigated reactions between aminodihaloboranes and anionic transitionmetal compounds in a 1:2 ratio. The bridged borylene complexes [μ-B{$N(SiMe_3)_2$}(μ-CO){(η^5-C_5H_4R)Fe(CO)}$_2$] (**18**: R = H; **19**: R = Me)[93] and [μ-B{$N(SiMe_3)_2$}(μ-CO){(η^5-C_5H_5)Ru(CO)}$_2$] (**20**)[94] were obtained from $(Me_3Si)_2NBCl_2$ and Na[(η^5-C_5H_4R)M$(CO)_2$] (M = Fe, R = H, Me; M = Ru, R = H) as shown in Equation (9), with salt elimination and cleavage of one carbonyl ligand.

The formation of the boryleneiron complexes **18** and **19** was observed under all conditions, while the formation of the corresponding ruthenium complex **20** depended on the reaction conditions and stoichiometry employed. Only an excess of Na[(η^5-C_5H_5)Ru$(CO)_2$] and slow addition of the borane, for example, provided **20** as the sole product. Interestingly, sterically less demanding aminodichloroboranes such as Me_2NBCl_2 reacted in both cases with substitution of only one boron-bonded chloride ion and formation of the corresponding boryl complexes. This result was attributed to the electron-withdrawing effect of the silyl groups, which in the case of $(Me_3Si)_2NBCl_2$ make the boron centre more electrophilic and hence more reactive.[93,94]

3.1.3. By Borylene Transfer

Photochemically induced borylene transfer has already been discussed as a valuable synthetic method for the generation of terminal borylene complexes not accessible through conventional salt elimination reactions. At least in one case, we have recently been able to demonstrate that this method also has similar potential for the synthesis of bridged borylene complexes. While K[(η^5-C_5H_5)MnR$(CO)_2$] (R = H, $SiMePh_2$) proved to be a versatile precursor for the generation of bridged borylene complexes (vide supra), all of our attempts to extend this to the rhenium analogues by treatment of K[(η^5-C_5H_5)ReR$(CO)_2$] (R = H, $SiMePh_2$) with mono- or diboranes(4) disappointingly failed.[43−45] Photolysis of [$(OC)_5W{=}B{=}N(SiMe_3)_2$] (**2**) in the presence of [(η^5-C_5H_5)Re$(CO)_3$], however, yielded the bridged borylene complex [μ-B{$N(SiMe_3)_2$}{(η^5-C_5H_5)Re$(CO)_2$} (**21**) as the only boron-containing species, as in Equation (10).[40]



2

21

(10)

3.2. Structure

Because of the formation of two metal−boron bonds, all bridged borylene complexes show characteristically deshielded ^{11}B NMR resonances, ranging from $\delta = 100$ to 120 ppm in the cases of the (amino)borylene complexes **12**, **13**, **15**, **16**, and **18−21**, in which B−N π-bonding components are present, (Table 1). For the (*tert*-butyl)borylene complex **14**, which is free of boron−ligand π-interaction, an even more deshielded signal is observed at $\delta = 170.0$ ppm. As in the case of terminal borylene complexes, the base-stabilised complex [μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**17**) is characterised by a significantly shielded ^{11}B NMR resonance at $\delta = 17.5$ ppm, due to the increased coordination number of the boron centre.

X-ray structural data are available for [μ-B(NMe$_2$){(η^5-C$_5$H$_5$)Mn(CO)$_2$}$_2$] (**12**), [μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**17**), [μ-B{N(SiMe$_3$)$_2$}(μ-CO){(η^5-C$_5$H$_4$Me)Fe(CO)}$_2$] (**19**), and two further derivatives of the type [μ-BX{(η^5-C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (vide infra). The metal and boron atoms in both aminoborylene complexes form isosceles triangles, with metal−metal and metal−boron distances in the range expected for corresponding single bonds (Table 1). The overall molecular structure data resemble those of the isoelectronic vinylidene[95,96] or the corresponding bridged methylene complexes,[97−99] which can be viewed as dimetallacyclopropane derivatives. The tetrahedrally coordinated boron centre in the base-stabilised complex **17** shows the expected increase in the metal−boron distances, which thus range between those in borylcobalt complexes[76,100] and those in cobaltaboranes.[101]

Recently, complex **12** was subject to theoretical investigations, and the theoretically predicted and the experimentally derived structural parameters were found to be in very good agreement (Table 1).[26] From density functional theoretical studies it was found that borylenes BX can be viable ligands in the design of transition metal complexes, which are thermodynamically stable with respect to a homolytic metal−boron bond dissociation. On the one hand, the high thermodynamic stability is traceable to the good σ-donor and π-acceptor properties of BX ligands, owing to the σ- and π-orbital energies. On the other hand, the high polarity and the small HOMO−LUMO gap of the uncoordinated BX ligand suggest low kinetic stability. Increasing the HOMO−LUMO gap by complexation also increases the kinetic stability to a certain extent, but the imbalance between σ-donation and π-acceptance produces a positive charge on BX and promotes nucleophilic attack. In complex **12**, the kinetic stability is enhanced by steric protection of the reactive frontier orbitals of the BNMe$_2$ ligand by complexation at a bridging site and additionally by the bulky methyl substituents. The dinuclear Mn$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$ fragment also reduces the build-up of positive charge at BNMe$_2$, since it is an excellent π-donor with just the right frontier orbitals to restore the M−BNMe$_2$ σ-donation and π-back-donation balance.

3.3. Reactivity

In agreement with the previously mentioned computational studies, we found that the (amino)borylene complexes **12** and **13** displayed extremely low reactivity towards nucleophilic substitution at the bridging boron centre. Stability to both air and moisture is the consequence, and these compounds can even be obtained in high yields by aqueous workup.[69] Treatment of **13** with an excess of gaseous HCl, however, provided the (chloro)borylene complex [μ-BCl{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**22**), which, because of its

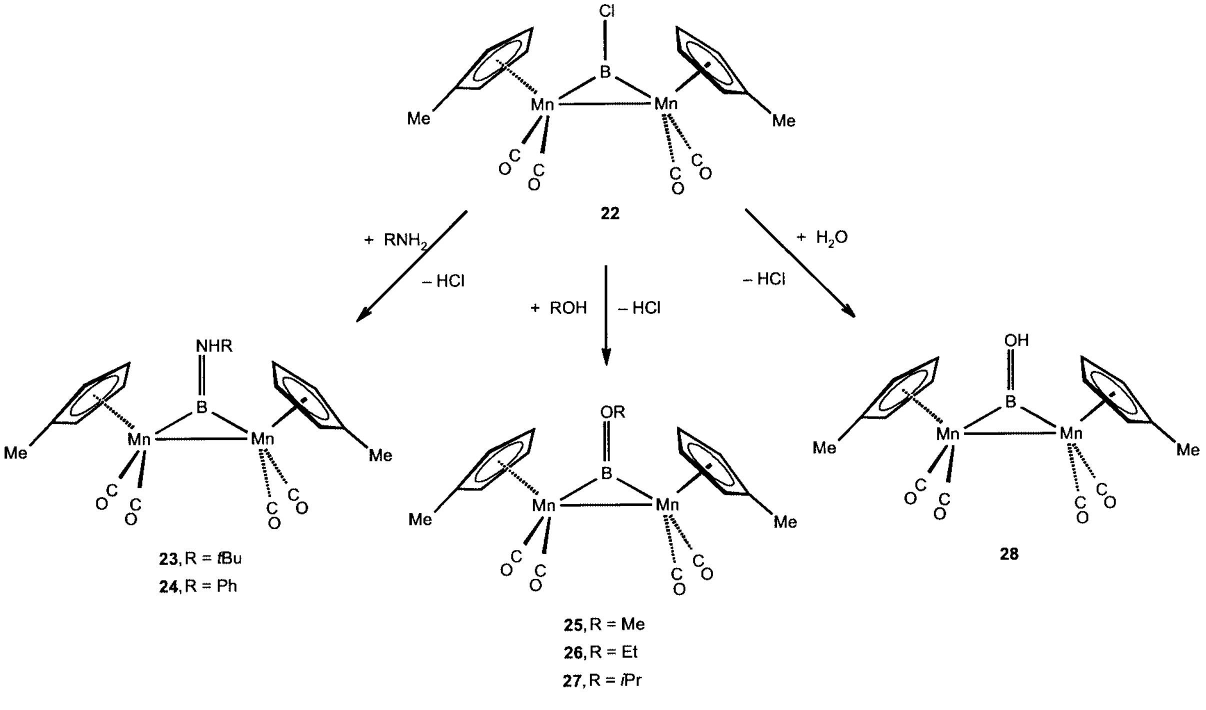
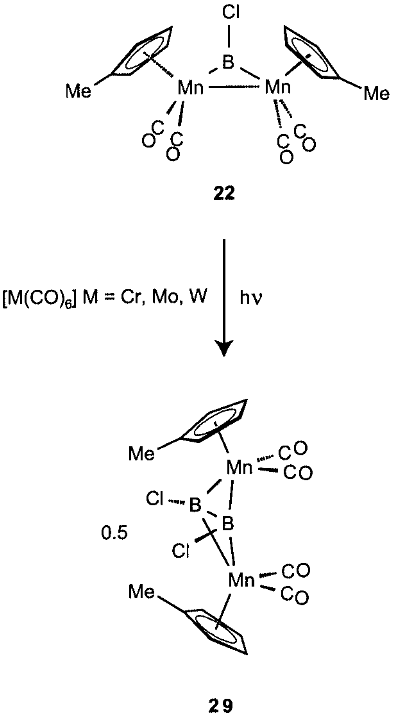


Figure 5. Substitution reactions at the metal-coordinated boryelene ligand

increased reactivity, served as starting material for further substitution reactions at the borylene centre. Treatment with protic reagents such as primary amines, alcohols and water afforded the corresponding substituted borylene complexes [μ-BX{(C_5H_4Me)Mn(CO)$_2$}$_2$] (**23**: X = NH*t*Bu; **24**: X = NHPh; **25**: X = OMe; **26**: X = OEt; **27**: X = O*i*Pr; **28**: X = OH) in high yields (Figure 5).[44,102] Structural data are available for complexes **22**[103] and **26**[44] (Table 1), and match those of the corresponding amino derivative **12**. It should be noted that such reactions at the boron centre with retention of the M−B linkage are very rare for both boryl and borylene complexes, due to the kinetic lability of the metal−boron bond, and have subsequently been observed (by Roper) only in the case of one boryl complex.[104]

Our very recent studies have shown that the photochemistry of bridged borylene complexes differs significantly from that of their terminal counterparts. Irradiation of the bridged (chloro)borylene complex **22** in the presence of [M(CO)$_6$] (M = Cr, Mo, W) resulted not in the formation of an M=B−Cl species with borylene transfer, but in the novel dimetalla-*nido*-tetraborane [B_2Cl_2{(η^5-$C_5H_4CH_3$)Mn(CO)$_2$}$_2$] (**29**) as shown in Equation (11), thus establishing the first synthetic link between electron-precise borylene complexes and electron-deficient metallaboranes.[103]



(11)

Conclusion

Since the first report on a structurally authenticated borylene complex in 1995, the chemistry of these compounds has developed considerably, due to the ambitious experimental and computational effort of several research groups worldwide. As a consequence, there is now a more detailed understanding of the bonding situation in borylene complexes, and some of the reasons why these compounds eluded researchers for such a long time have probably become clearer. Several methods for the preparation of both bridged and terminal species are now at hand, and so future studies can focus now more on the reactivity of theses complexes − the chemistry of terminal borylene complexes especially is as yet virtually unexplored. In view of their close relationship to important organometallics such as carbene or carbonyl complexes, one might even envisage similar applications in stoichiometric or catalytic reactions.

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[105] Note added during revision (August 15, 2002): Very recently Aldridge reported the synthesis and structure of the bridged borylene complex [μ-BMes$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2$], obtained from $MesBBr_2$ by salt elimination (Mes = 2,4,6-Me_3-C_6H_2): S. Aldridge, D. L. Coombs, C. Jones, *Chem. Commun.* **2002**, 856−857.

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