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Transition metal complexes of boron — synthesis, structure and reactivity

Holger Braunschweig [a],*, Miriam Colling [b]

[a] *Department of Chemistry, Imperial College of Science, Technology, and Medicine, South Kensington,*
London SW 7 2AY, UK
[b] *Institut für Anorganische Chemie der Technischen Hochschule, Templergraben 55,*
D-52056 Aachen, Germany

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* Corresponding author.
E-mail address: h.braunschweig@ic.ac.uk (H. Braunschweig).

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Abstract

Over the past decade, transition metal complexes of boron have become established as the fourth class of compounds involving direct metal–boron interactions. In contrast to the other three major groups in this field, i.e. borides, metallaboranes, and π-complexes with boron-containing ligands, transition metal complexes of boron are characterised by electron-precise two-centre two-electron bonds between boron and the metal centre. According to this pattern of metal–boron interaction, a variety of different co-ordination modes for boron-containing ligands have been realised, allowing for a systematic classification of those compounds into borane, boryl, and borylene complexes. Research in this area is stimulated by the interesting applications boryl complexes have, for the functionalisation of hydrocarbons by metal-catalysed hydroboration and C–H activation. By now, a variety of synthetic methods are at hand for the preparation of those compounds and the spectroscopic and structural data available provide some insight into the nature of the metal–boron linkage of those compounds. More recently, theoretical studies have become another valuable source of information in this respect. The present review introduces the three compound types (borane, boryl, and borylene complexes), which at the moment constitute the class of transition metal complexes of boron, addressing their synthesis, structure and reactivity.

1. Introduction

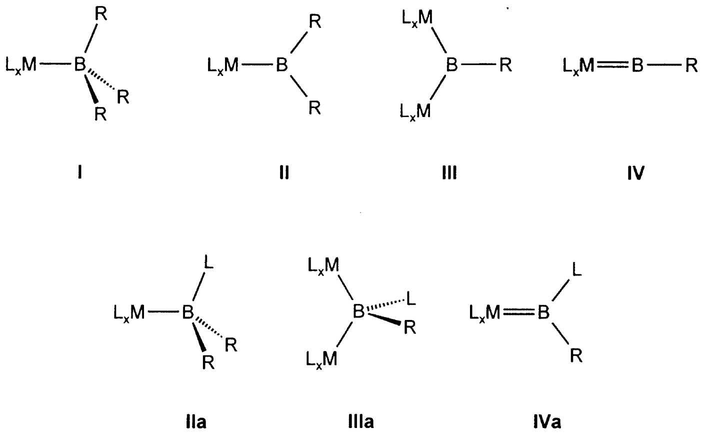
Boron, the only non-metal of Group 13, displays a unique structural diversity in its combinations with transition metals. For example, borides have been known for almost 60 years and about a 1000 examples have been identified in more than 130 different structural types [1–3]. The constitution of these phases ranges from boron-deficient compounds such as $Y_2Co_{14}B$ [4], with isolated boron atoms, to boron-rich phases like YB_{66}, showing a three-dimensional network of linked boron clusters [5]. Metallaboranes [6–8] and metallaheteroboranes [9–11], which have also been known for more than four decades, constitute another class of boron–transition metal compounds comprising several hundreds of examples. The last long-known class of compounds in this series are transition metal complexes with boron-containing ligands derived from conjugated boron heterocycles such as borole [12–14], borabenzene [15,16], borazine [17,18] and diazadiboretidine [19].

The nature of the chemical bond between boron and the transition metal in these compounds is diverse: borides show contributions of all three principle bond types, i.e. ionic, covalent and metallic bonding. The metallaboranes, as close relatives of the parent boranes, are characterised by an atomic skeleton being linked by three-centre two-electron bonds. Finally, the interaction of a boron heterocycle with the central metal in the corresponding complexes is due to π-bonding.

In addition to these three well-established classes of boron–transition metal compounds there is a fourth one, which is characterised by a different type of boron–metal interaction, namely, electron-precise two-centre two-electron bonds. This is already known for decades in transition metal complexes of many other main Group elements, especially of Groups 14 and 15, leading to classes of compounds such as alkyl- [20,21], alkylidene- [22,23], silyl- [24,25], and silylene [26,27] complexes, respectively. The corresponding transition metal complexes of boron [28–30] and its higher homologues [31], however, were not fully characterised until 1990, but have attracted considerable interest ever since.

Over the past ten years, transition metal complexes of boron were established as a novel class of compounds by the ambitious efforts of several research groups worldwide. Compounds that have been reported so far can be systematically classified according to the co-ordination number of boron and the number of boron–transition metal bonds as borane- (**I**), boryl- (**II**), and bridged (**III**) as well as terminal borylene complexes (**IV**) (Scheme 1).

Borane complexes (**I**) can be understood as Lewis acid–base adducts of acidic boranes, BR_3, with basic metal centres resulting in a fourfold co-ordination of the boron atom. Boryl complexes, however, show boron in co-ordination number three, which is achieved by linking a $-BR_2$ group to a metal centre. The borylene ligand $=BR$ can adopt two different co-ordination modes: either bridging between two



Scheme 1. Classification of transition metal complexes of boron; borane- (**I**), boryl- (**II**), bridged borylene- (**III**), terminal borylene (**IV**) complexes. **IIa**, **IIIa**, **IVa** are the corresponding Lewis base adducts.

metal centres and showing boron in co-ordination number three (**III**), or terminal to one metal centre with the formation of a formal double bond and a decrease of the co-ordination number to two (**IV**). Provided the boron atom in **II**–**IV** is still Lewis-acidic, there is the possibility of adding 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 for all types of compounds **I**–**IV** have been already described in the earlier literature between 1963 and 1970, however, without structural confirmation [32]. The spectroscopic data reported for these compounds are in contrast to more recent findings, and the proposed constitution of those complexes was disproved to some extent.

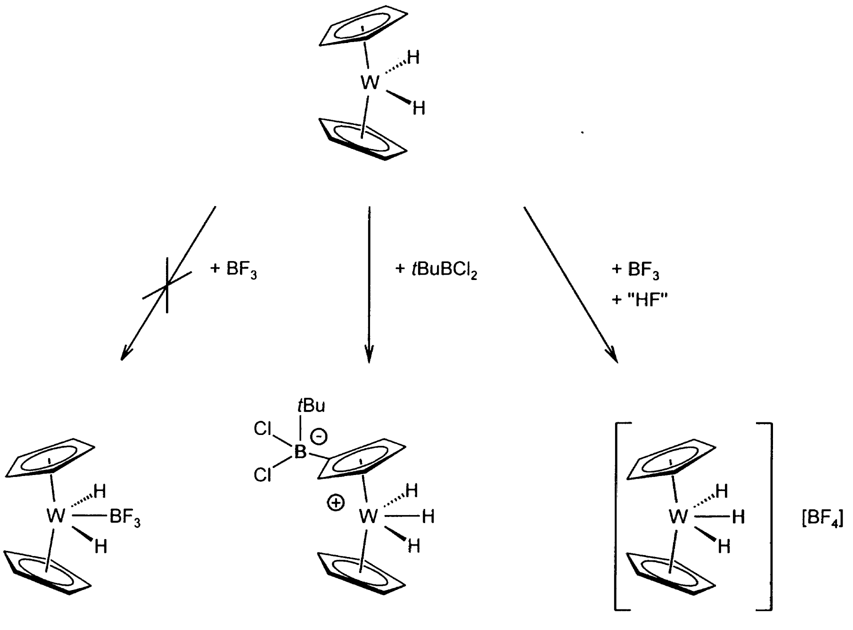
The recent interest in transition metal complexes of boron is not restricted only to synthesis and characterisation. Possible applications obviously make these compounds rewarding targets. Boryl complexes, for example, play an important role as intermediates in the transition metal-catalysed hydroboration and also give access to functionalised alkanes by photochemical-induced C–H activation. Synthetic work on these compounds is increasingly paralleled by theoretical investigations providing additional insight into the electronic structure and the nature of the boron–metal linkage.

2. Borane complexes

The chemistry of boron-containing compounds is, in many ways, defined by the fact that boron has only three valence electrons, but four valence orbitals available for bonding. This results in a tendency of many boranes to form multi-centre 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.

The history of borane complexes dates back to the early 1960s. Investigations of the reaction between bis(cyclopentadienyl)hydride complexes such as [Cp_2WH_2] — containing a basic metal centre which can be protonated — and various boranes led in 1966 to a report of the first borane complex [$(C_5H_5)_2WH_2(BF_3)$] (**1**), the constitution of which was deduced from IR spectroscopic data and elemental analysis [33,34]. Recent studies have shown, however, that instead of compounds containing a tungsten–boron bond, either zwitterionic complexes **2** [35] or salt-like compounds **3** [36] were obtained from the reactions of [Cp_2WH_2] with various boranes (Scheme 2). Alkyldichloroboranes such as *t*-$BuBCl_2$ afforded compounds like **2** by substitution of a Cp-bonded hydrogen atom by the neutral borane and protonation of the tungsten centre, whereas the latter compounds were yielded by trihaloboranes such as BF_3 and BCl_3 or dialkylchloroboranes.

The formation of [Cp_2WH_3][BF_4] and related species is due to a non-stoichiometric reaction since one equivalent of HX ($X = F$, Cl) is required. Further investigations proved the WH_2 moiety to be the source of the proton [37]. The identification of **2** and **3** by spectroscopy in solution and X-ray structure analysis disproved the formerly postulated borane complex.



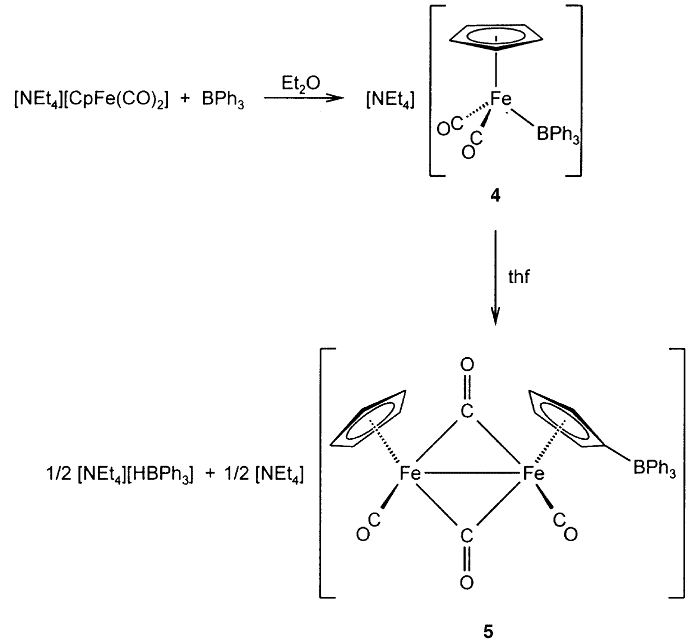
1 **2** **3**

Scheme 2. Proposed (**1**) and authentic (**2**, **3**) products from the reactions of [Cp_2WH_2] with various boranes.

Besides uncharged transition metal complexes, the use of anionic complexes may also lead to the requested adducts with acidic boranes. [NEt_4][$CpFe(CO)_2$] for example, gave the anionic borane iron complex **4** as an amorphous solid from reaction with BPh_3 in diethyl ether (Scheme 3) [38], which is characterised in solution by a high-field shifted ^{11}B-NMR signal at $\delta = -28.8$ characteristic of fourfold co-ordinated boron.

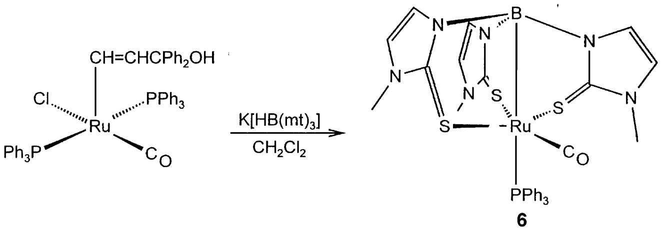
The CO stretching frequencies in the IR spectrum resemble those of the corresponding alkane complex, which is structurally authentic. Dissolution of **4** in THF, however, is followed by a spontaneous migration of the BPh_3 group from the iron centre to the Cp-ligand, affording [NEt_4][$HBPh_3$] and the anionic dinuclear complex **5** (Scheme 3), which was subsequently characterised by X-ray structure analysis [39].

Several other ionic and neutral transition metal borane complexes such as Na[$H_3BRe(CO)_4$], Na[$H_3BMn(CO)_3PPh_3$], Na[$H_3BCo(CO)_4$] [40], [$X_3BRh(PPh_3)_2$-(CO)X] (X = Cl, Br) [41], and [$(Me_2PC_2Me_2BMe_2)_2Rh(CO)Cl$] [42] have been reported since 1963, however without structural proof. The presence of transition metal–boron bonds in these compounds is still open to question. Even very recently, ruthenium borane complexes were reported from the reactions of [$Cp^*RuCl(PPh_3)_2$] and [$Cp^*RuCl(dppe)$] (dppe = $Ph_2PCH_2CH_2PPh_2$) with BF_3, but again their constitutions were without full spectroscopic and structural proof [43].



Scheme 3. In situ formation and subsequent rearrangement of the anionic borane iron complex **4**.

Later, in 1999, investigations of poly(azolyl)borate ligands led to the first structurally authentic borane complex [Ru{B(mt)$_3$}(CO)(PPh$_3$)] (**6**) (mt = 2-sulfanyl-1-methylimidazol). This can be described as a metallaboratrane derivative and was obtained from the reaction of [Ru(CH=CHCPh$_2$OH)Cl(CO)(PPh$_3$)$_2$] with K[HB(mt)$_3$] in high yields according to Eq. (1) [44].

 (1)

From the pattern of the reactions of [Ru(C$_6$H$_5$)Cl(CO)(PPh$_3$)$_2$] with boranes R$_2$BH (vide infra) via the postulated mechanism, one can conclude that an abstraction of one mt-arm, agostic B–H co-ordination and following oxidative addition should give a *cis*-hydridovinylcomplex, which leads to **6** via reductive elimination of the alkene. The metallaboratrane complex **6** shows an ^{11}B-NMR signal at $\delta = 17.1$ for the bridging boron atom, which is expected for boron with co-ordination number four. The X-ray structure analysis of **6** shows a tetrahedral co-ordinated boron with angles between 105.5(4) and 113.9(4)° and a distorted octahedral co-ordinated ruthenium atom. The ruthenium–boron distance of 216.1(5) pm resembles that in the ruthenium diboran(4)yl complex $[Ru\{B(NMe_2)BBr(NMe_2)\}Cp(CO)_2]$ (**108**) (217.3(3) pm) (vide infra), suggesting a comparably strong metal–boron bond. This and the *trans*-arrangement of the boron atom to the stronger donor ligand, lead to the assumption that the description of zerovalent ruthenium does not reflect the real bonding situation entirely.

3. Boryl complexes

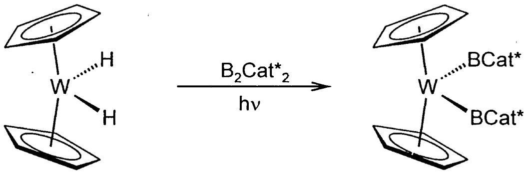
Among transition metal complexes of boron, the group of boryl compounds $L_xM–BR_2$ (**II**) is the largest one, comprising some 70 structurally authentic examples. The phenylene-1,2-dioxo- or catechol group (Cat) as a ligand to boron had a pivotal role in establishing these compounds. Within a short period of time, the use of catecholborane and its derivatives gave access to a large number of boryl complexes, and to date there is no other ligand available with a comparably wide range of applications. More recently, it was shown that boranes with boron–nitrogen bonds might also serve as versatile starting compounds for these products, whereas boryl complexes with $–BR_2$ groups (R = alkyl, aryl) deriving from diorganylboranes are still very rare. For the preparation of boryl complexes, there are now a number of various synthetic methods at hand, which will be described subsequently. Most of them, such as salt elimination reactions and oxidative additions to low-valent transition metal centres, date back to the 1960s, when a substantial number of boryl complexes were reported for the first time. None of these compounds, however, was structurally characterised, and spectroscopic data, such as the ^{11}B-NMR shifts, are in sharp contrast to recent findings. Until 1970, ^{11}B-NMR signals for boryl complexes were reported to be in the range from $\delta = 15$ to $\delta = 43$, thus being always high-field shifted with respect to the signals of the starting boranes. The structurally authentic boryl complexes being described over the past decade, however, are characterised by ^{11}B-NMR shifts ranging from $\delta = 24$ to $\delta = 141$ which are low-field shifted with respect to the signals of the starting boranes. Furthermore, the strong metal-to-boron π-interaction, which was suggested as an explanation for the significant shielding found for the formerly proposed boryl complexes [32], applies only to few of those compounds being characterised in recent times. The distinct interest in transition metal boryl complexes is due to the fact that these compounds exhibit a strong potential for the functionalisation of hydrocarbons: on the one hand, they are known to be key intermediates in the transition metal-catalysed hydroboration of olefins, and on the other hand, they gave access to a photochemically induced selective α-borylation of alkanes by C–H-activation.

3.1. Synthesis

3.1.1. Oxidative addition

The oxidative addition of a suitable substrate to a transition metal centre represents a fundamental reaction in organometallic chemistry and is essential to both stoichiometric and catalytic applications [45–51]. In general, the formation of transition metal–element bonds by oxidative addition is achieved by reacting a low-valent, co-ordinatively unsaturated metal centre with either non-polar homo-diatomic molecules $R_xE–ER_x$ or with polar hetero-diatomic species $R_xE–E'R_y$. In the case of transition metal boryl complexes, both routes were very successfully applied giving access to a large number of complexes with one, two or three boryl groups. Among the boron–element bonds which undergo such oxidative additions, the non-polar B–B bond in diboranes(4) $R_2B–BR_2$ and the polar B–H bond in diorganylboranes $R_2B–H$ are the most prominent ones. Besides, there are also some examples for the addition of boron–halide and boron–tin bonds. In certain cases, the formation of metal–boron bonds proceeds via σ-bond metathesis rather than oxidative addition. Also, these examples will be discussed subsequently.

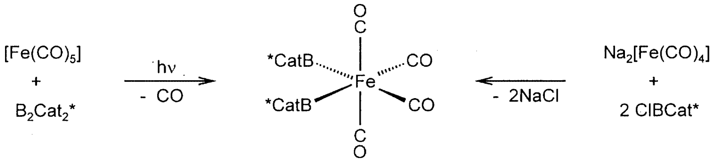
3.1.1.1. Oxidative addition of diboranes(4) $R_2B–BR_2$. The reaction of a diborane(4) with a suitable transition metal complex generally proceeds with formation of the corresponding bisboryl complex. As for all other oxidative additions, the metal centre has to provide a vacant site, thus allowing for the reaction with the B–B bond. Hence, either complexes with readily dissociating ligands are used, or alternatively, a highly reactive intermediate has to be generated, for example, by irradiation of a less reactive precursor complex. The latter was realised by the photochemical-induced addition of $B_2Cat^*_2$ (Cat* = 1,2-O_2-4-*t*-BuC_6H_3) to $[Cp_2WH_2]$ via the intermediate $[Cp_2W]$, yielding the bisboryl complex $[Cp_2W(BCat^*)_2]$ (**7**) according to Eq. (2) [52,53].



7

(2)

Similarly, $B_2Cat^*_2$ adds to $[Fe(CO)_4]$ being obtained upon irradiation of $[Fe(CO)_5]$ with the formation of *cis*-$[(Cat^*B)_2Fe(CO)_4]$ (**8**) (Eq. (3); **8** may be alternatively obtained by salt elimination, see Section 3.1.2) [54].



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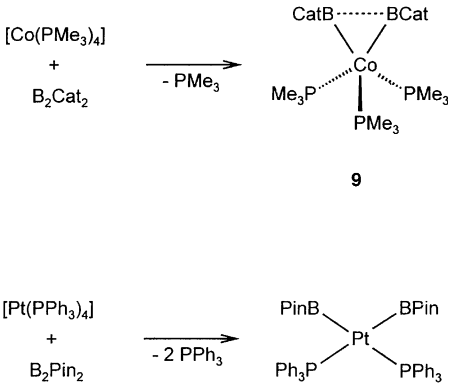
(3)

A variety of bisboryl complexes of the late transition metals Co, Rh, Ir, and Pt were obtained from reactions of diboranes(4) with the displacement of more labile ligands such as alkenes or phosphanes. As far as homoleptic phosphane complexes are concerned, reactions of $[Co(PMe_3)_4]$ and $[Pt(PPh_3)_4]$ resulted in the formation $[(CatB)_2Co(PMe_3)_3]$ (**9**) [55] and *cis*-$[(PinB)_2Pt(PPh_3)_2]$ (**10**; Pin = tetramethylethylene-1,2-dioxo) [56,57] with the cleavage of one and two phosphane ligands, respectively, according to Eq. (4a and b).



9

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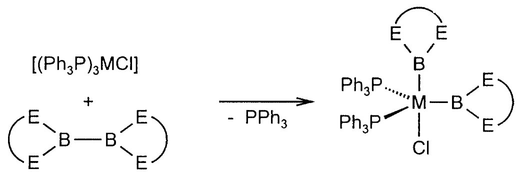
(4)

The paramagnetic cobalt complex **9** is characterised in the crystal by a relatively short boron–boron distance [55]. An entire series of bisboryl complexes of Rh and Ir was obtained from the reactions of $[MCl(PR_3)_3]$ (M = Rh, Ir; R = alkyl, aryl) (Eq. (5)) with the cleavage of one phosphane ligand.



11-19

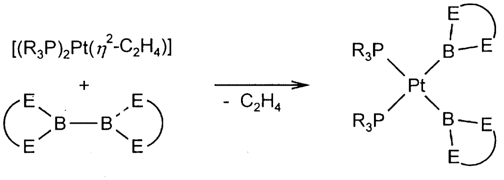
(5)

M = Rh, Ir

E E = various ligands, see text

Wilkinson's catalyst $[RhCl(PPh_3)_3]$ gave the bis(catecholboryl)complex $[(CatB)_2RhCl(PPh_3)_2]$ (**11**) and the closely related derivatives $[\{B(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)\}_2RhCl(PPh_3)_2]$ (**12**), $[\{B(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)\}_2RhCl(PPh_3)_2]$ (**13**), $[\{B(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)\}_2RhCl(PPh_3)_2]$ (**14**), $[(Cat^*B)_2RhCl(PPh_3)_2]$ (**15**), $[\{B(1,2\text{-}O_2\text{-}3,5\text{-}t\text{-}Bu_2C_6H_3)\}_2RhCl(PPh_3)_2]$ (**16**), $[\{B(1,2\text{-}S_2C_6H_4)\}_2RhCl(PPh_3)_2]$ (**17**), $[\{B(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)\}_2RhCl(PPh_3)_2]$ (**18**), and $[(TartB)_2RhCl(PPh_3)_2]$ (**19**) (Tart = *R*,*R*-1,2-$O_2CH(CO_2Me)CH(CO_2Me)$) [58–61]. Alternatively, most of these compounds may also be obtained from the interaction of $[\{Rh(\mu\text{-}Cl)(PPh_3)_2\}_2]$ with the corresponding diboranes(4) without PPh_3-cleavage [60]. Additional formations of bisboryl complexes according to the general Eq. (5) were reported for the bis(triethylphosphane) complexes $[(CatB)_2RhCl(PEt_3)_2]$ (**20**) [60] and $[(CatB)_2IrCl(PEt_3)_2]$ (**21**) [62].

The methylrhodium complex $[RhMe(PMe_3)_4]$ shows a different reactivity towards B_2Cat_2: the first equivalent B_2Cat_2 forms the Rh(I)-species $[CatBRh(PMe_3)_4]$ (**22**) with cleavage of CatBMe, presumably via the bisboryl–Rh(III) complex $[(CatB)_2RhMe(PMe_3)_3]$. Further reaction of **22** with a second equivalent B_2Cat_2 gives the trisboryl complex $[(CatB)_3Rh(PMe_3)_3]$ (**23**) with cleavage of one trimethylphosphane ligand; both **22** and **23** were characterised by X-ray structure analyses [61]. Besides phosphane complexes, a number of olefin complexes were similarly successfully employed. According to Eq. (6), especially $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ gave rise to the following *cis*-bisboryl complexes: *cis*-$[(CatB)_2Pt(PPh_3)_2]$ (**24**), *cis*-$[\{B(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)\}_2Pt(PPh_3)_2]$ (**25**), *cis*-$[\{B(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)\}_2Pt(PPh_3)_2]$ (**26**), *cis*-$[\{B(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)\}_2Pt(PPh_3)_2]$ (**27**), *cis*-$[(Cat^*B)_2Pt(PPh_3)_2]$ (**28**), *cis*-$[\{B(1,2\text{-}O_2\text{-}3,5\text{-}t\text{-}Bu_2C_6H_3)\}_2Pt(PPh_3)_2]$ (**29**), *cis*-$[\{B(1,2\text{-}S_2C_6H_4)\}_2Pt(PPh_3)_2]$ (**30**), *cis*-$[\{B(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)\}_2Pt(PPh_3)_2]$ (**31**), *cis*-$[\{B(1,2\text{-}O_2C_6Cl_4)\}_2Pt(PPh_3)_2]$ (**32**), *cis*-$[\{B(1,2\text{-}O_2C_6Br_4)\}_2Pt(PPh_3)_2]$ (**33**), *cis*-$[(TartB)_2Pt(PPh_3)_2]$ (**34**), *cis*-$[\{B\{R,R\text{-}O_2CHPhCHPh\}\}_2Pt(PPh_3)_2]$ (**35**), *cis*-$[\{B(S\text{-}O_2CH_2CHPh)\}_2Pt(PPh_3)_2]$ (**36**) and *cis*-$[(PinB)_2Pt(PPh_3)_2]$ (**10**), the latter being obtained alternatively to the synthesis already described above [29,63–66].



10, 24 - 36

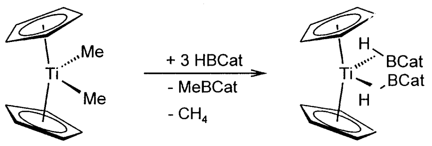
(6)

E⌒E = various ligands, see text

A further example for the oxidative addition of a boron–boron bond to a metal centre with cleavage of an olefin, is the reaction of $[IrCl(PMe_3)_3cod]$ with B_2Cat_2 giving the Ir(III) complex $[(CatB)_2IrCl(PMe_3)_3]$ (**37**) [62]. Particularly noteworthy in this chapter are the syntheses of *cis*-$[(F_2B)_2Pt(PPh_3)_2]$ (**38**) and *cis*-$[\{Cl(Me_2N)B\}_2Pt(PPh_3)_2]$ (**39**) which were obtained according to the general Eq. (6) from $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ and the corresponding diboranes(4) B_2F_4 and $B_2(NMe_2)_2Cl_2$, respectively [67,68]. These compounds represent rare examples for the formation of bisboryl complexes from diboranes(4) not showing $-E-(CR_x)_y-E-$ ($E = O, S$) ligands at boron. Despite being structurally characterised, the fact that compound **39** was obtained together with a mixture of further products, preventing purification, underlines the synthetic difficulties which are associated with many diboranes(4) not deriving from catechol or related species.

3.1.1.2. Oxidative addition of boranes R_2B–H and related syntheses. In 1990, the first structurally authentic boryl complexes were obtained by the reactions of different boranes R_2BH with Ir(I) complexes, and ever since, the addition of a boron–hydrogen bond to metal centres has become an increasingly important synthetic method for the preparation of boryl complexes [69,70]. As a matter of fact, the addition of a borane, R_2B–H, proceeds along the lines already discussed in the previous section for diboranes(4) and makes the same demands on the complex precursors such as the presence of readily dissociating ligands. As far as the mechanism for the formation of a boryl complex from a borane (R_2B–H) is concerned, there are some cases where the spectroscopic data available do not yet allow to exclusively distinguish between oxidative addition and further possibilities such as σ-bond metathesis or a concerted reaction. Hence, these related syntheses are also discussed in this section.

Although transition metals from Groups 5 to 8 form the corresponding boryl complexes, no such products have been reported yet for titanium and its higher homologues. Interestingly, the reaction of [Cp_2TiMe_2] with three equivalents of HBCat according to Eq. (7) yields [$Cp_2Ti(HBCat)_2$] (**40**) in which the boron–hydrogen bonds of two catecholborane molecules are co-ordinated to the titanium. The structural details as well as the stoichiometric and catalytic reactions of these σ-complexes were extensively studied [71–74].



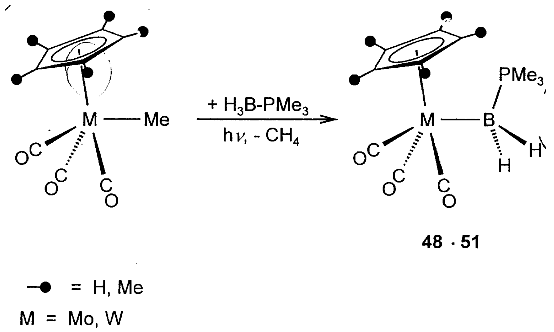
(7)

40

From niobium and tantalum, the metallocene boryl complexes *endo*-[$Cp_2NbH_2(BCat)$] (**41**), *endo*-[$Cp_2NbH_2(BC_8H_{14})$] (**42**), *endo*-[$Cp^*_2NbH_2(BCat)$] (**43**), *endo*-[$Cp^*_2NbH_2\{B(1,2\text{-}O_2\text{-}3\text{-}t\text{-}BuC_6H_3)\}$] (**44**), *endo*-[$Cp_2TaH_2(BCat)$] (**45**), *endo*-[$Cp^*_2TaH_2(BCat)$] (**46**), and *endo*-[$Cp^*_2TaH_2(BCat^*)_2$)] (**47**) were obtained from the corresponding boranes R_2B–H and either [Cp_2NbH_3] or [$(\eta^5\text{-}C_5R_5)_2MH(CH_2{=}CHR')$] ($R = H$, Me; $M = Nb$, Ta; $R' = H$, Me) [75–77]. The syntheses of **41** and **42** from [Cp_2NbH_3] occur with elimination of H_2, and theoretical investigations on the corresponding reaction of [Cp_2NbH_3] with BH_3 show that initial formation of an adduct with a Nb–H–B bridge is likely. This adduct would then further react with elimination of dihydrogen and subsequent oxidative addition of the B–H bond to the niobium centre [78]. For the formation of the latter compounds **43**–**47**, a mechanism is discussed involving addition of the B–H bond to the 16-electron intermediate alkyl complex [$(\eta^5\text{-}C_5R_5)_2M\text{–}CH_2\text{–}CH_2R'$] which results from the ground state olefin complex [$(\eta^5\text{-}C_5R_5)_2MH(CH_2{=}CHR')$] by insertion of the olefin into the M–H bond. The aforementioned niobium boryl complexes show remarkable structural features due to interactions between the boron atom and the two hydrogen co-ligands. Spectroscopic and crystallographic studies reveal that these compounds cover a structural continuum being defined by three extremes: a d^0 boryl complex (**A**), a d^2 dihydroborate complex (**B**) and a d^2 σ-borane complex (**C**) similar to the titanium complex **40** (Scheme 4, Table 1).

endo-$[Cp_2NbH_2(BCat)]$ (**41**), for example, shows in the solid state, major contributions of **A** and might be considered as a Nb(V) boryl complex, while *endo*-$[Cp_2NbH_2(BC_8H_{14})]$ (**42**) and *endo*-$[Cp^*_2NbH_2(BCat)]$ (**43**) should be better described as Nb(III) borate complexes **B**. In some cases, at lower temperatures, niobium σ-borane complexes of type **C** were spectroscopically identified as intermediates, which subsequently rearranged to the final products.

Some rare examples of base adducts of boryl complexes were obtained upon irradiation of $[(\eta^5\text{-}C_5R_5)_2M(CO)_3Me]$ (M = Mo, W; R = H, Me) in the presence of $H_3B\text{–}PMe_3$ (Eq. (8)), affording the Group 6 boryl complex PMe_3 adducts $[Cp^*_2W(BH_2PMe_3)]$ (**48**), $[Cp^*_2Mo(BH_2PMe_3)]$ (**49**), $[Cp_2W(BH_2PMe_3)]$ (**50**), and $[Cp_2Mo(BH_2PMe_3)]$ (**51**), the latter being only spectroscopically identified due to rapid decomposition [79].



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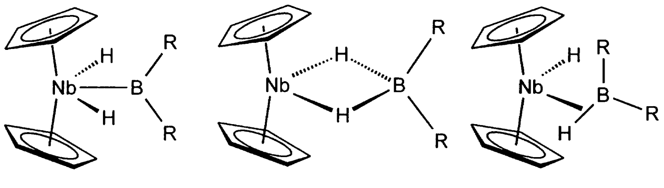
(8)

Besides, there is only one further structurally authentic compound of the type $[L_xM\text{–}BR_2L]$ (**IIa**) known (vide infra), and interestingly, all these products were obtained by direct syntheses and not by subsequent addition of a base to an isolated boryl complex. In the present case, spectroscopic studies could not yet



A **B** **C**

Scheme 4. Possible structures for compounds $[Cp_2NbH_2(BR_2)]$; d^0 boryl complex (**A**), d^2 dihydroborate complex (**B**), and d^2 σ-borane complex (**C**).

Table 1
Boryl-, σ-borane complexes, and base adducts of boryl complexes

Compound	Synthesis	*d*(M–B) (pm)	δ ^{11}B [a]	Ref.
Group 4				
Titanium				
$[Cp_2Ti(HBCat)_2]$ (**40**)	b	233.5(5)	45.0	74
Group 5				
Niobium				
endo-$[Cp_2NbH_2(BCat)]$ (**41**)	b	229.2(5)	59.0	75
endo-$[Cp_2NbH_2(BC_8H_{14})]$ (**42**)	b	240(1)	57.0	75
endo-$[Cp^*_2NbH_2(BCat)]$ (**43**)	b	x	60.2	76
endo-$[Cp^*_2NbH_2\{B(1,2\text{-}O_2\text{-}3\text{-}t\text{-}BuC_6H_3)\}]$ (**44**)	b	234.8(4)	60.0	76
Tantalum				
endo-$[Cp_2TaH_2(BCat)]$ (**45**)	b, d	226.3(6)	72.7	77, 96
endo-$[Cp^*_2TaH_2(BCat)]$ (**46**)	b	x	73.5	76
endo-$[Cp^*_2TaH_2(BCat^*)_2]$ (**47**)	b	x	72.7	76
exo-$[Cp_2TaH_2(BCat)]$ (**86**)	d	229.5(11)	64.7	96
Group 6				
Molybdenum				
$[Cp^*_2Mo(BH_2PMe_3)]$ (**49**)	b	249.7(5)	−24.6	79
$[Cp_2Mo(BH_2PMe_3)]$ (**51**)	b	x	−27.8	79
$[CpMo\{B(NMe_2)B(NMe_2)Br\}(CO)_3]$ (**89**)	d	236.5(5)	69.5	100
$[Cp(CO)_2Mo{\equiv}COB(NMe_2)B(NMe_2)Mo(CO)_3Cp]$ (**116**)	d	234.8(4)	65.2	115
Tungsten				
$[Cp_2W(BCat^*)_2]$ (**7**)	a	219(1) 223(1)	59.3	52, 53
$[Cp^*_2W(BH_2PMe_3)]$ (**48**)	b	247.6(7)	−27.6	79
$[Cp_2W(BH_2PMe_3)]$ (**50**)	b	x	−31.7	79
$[Cp_2WH(BCat)]$ (**87**)	d	219.0(7)	57.0	98, 52
$[CpW\{B(NMe_2)B(NMe_2)Cl\}(CO)_3]$ (**88**)	d	237.0(8)	62.7	99
$[Cp^*W\{B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_3\}(CO)_3]$ (**90**)	d	x	53.0	101
$[Cp(CO)_2W{\equiv}COB(NMe_2)B(NMe_2)W(CO)_3Cp]$ (**117**)	d	x	62.7	115
$[\{HB(1,2\text{-}N_2\text{-}3,5\text{-}Me_2C_3H)_3\}(CO)_2W\text{-}\{BEt(CH_2\text{-}4\text{-}MeC_6H_4\}]$ (**122**)	e	207(1)	77.0	121
$[Cp_2WH(BPh_2)]$ (**123**)	d	x	114.0	75
Group 7				
Manganese				
$[CatBMn(CO)_5]$ (**91**)	d	210.8(6)	42.8	103
Rhenium				
$[CatBRe(CO)_5]$ (**92**)	d	x	44.0	102
Group 8				
Iron				
cis-$[(Cat^*B)_2Fe(CO)_4]$ (**8**)	a, d	202.8(7)	45.0	54
$[CpFe(BCat)(CO)_2]$ (**93**)	d	195.9(6)	51.8	104
$[CpFe(BPh_2)(CO)_2]$ (**94**)	d	203.4(3)	121.0	104
$[CpFe\{B(NMe_2)Cl\}(CO)_2]$ (**95**)	d	x	56.9	105
$[CpFe\{B\{Si(SiMe_3)_3\}Cl\}(CO)_2]$ (**96**)	d	199.3(7)	141.2	179
$[(C_5H_4Me)Fe\{B(NMe_2)Cl\}(CO)_2]$ (**97**)	d	x	56.4	105
$[Cp^*Fe\{B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_3\}(CO)_2]$ (**98**)	d	x	54.0	52

Table 1 (*Continued*)

Compound	Synthesis	*d*(M–B) (pm)	δ ^{11}B ^{a}	Ref.
[Cp*Fe{B(NMe$_2$)Cl}(CO)$_2$] (**99**)	d	202.7(5)	59.1	105
[Cp*Fe{B(NMe$_2$)Br}(CO)$_2$] (**100**)	d	x	57.2	106
[CpFe{B(NMe$_2$)B(NMe$_2$)Cl}(CO)$_2$] (**105**)	d	209.0(3)	69.5	99
[CpFe{B(NC$_4$H$_8$)B(NC$_4$H$_8$)Cl}(CO)$_2$] (**106**)	d	x	66.5	107
[CpFe{B(NC$_5$H$_{10}$)B(NC$_5$H$_{10}$)Cl}(CO)$_2$] (**107**)	d	x	68.0	107
[Cp*Fe(B$_3$N$_3$H$_3$Cl$_2$)(CO)$_2$] (**109**)	d	x	59.0	108
[{(C$_5$H$_4$Me)Fe(CO)$_2$}$_2$(B$_3$N$_3$H$_3$Cl)] (**110**)	d	204.5(1)	53.1	108
[{Cp*Fe(CO)$_2$}$_3$(B$_3$N$_3$H$_3$)] (**111**)	d	x	49.7	108
Li[Cat*BFe(CO)$_4$] (**124**)	e	x	55.0	54
Ruthenium				
[CatBRuCl(CO)(PPh$_3$)$_2$] (**52**)	b	x	y	80
[CatBRuCl(CS)(PPh$_3$)$_2$] (**53**)	b	x	y	80
[{B(1,2-O$_2$C$_{10}$H$_6$)}RuCl(CO)(PPh$_3$)$_2$] (**54**)	b	x	y	80
[{B(1,2-O$_2$-3-MeC$_6$H$_3$)}RuCl(CO)(PPh$_3$)$_2$] (**55**)	b	x	y	80
[{B{1,2-(NH)$_2$C$_6$H$_4$}}RuCl(CO)(PPh$_3$)$_2$] (**56**)	b	x	y	80
[{B{1-S-2-NHC$_6$H$_4$}}RuCl(CO)(PPh$_3$)$_2$] (**57**)	b	x	y	80
[{B{1-S-2-(NH)C$_6$H$_4$}}RuCl(CS)(PPh$_3$)$_2$] (**58**)	b	x	y	80
[CpRu{B(NMe$_2$)Cl}(CO)$_2$] (**101**)	d	x	50.3	106
[CpRu{B(NMe$_2$)Br}(CO)$_2$] (**102**)	d	x	48.1	106
[Cp*Ru{B-1,2-O$_2$-3,5-Me$_2$C$_6$H$_3$}(CO)$_2$] (**103**)	d	x	48.0	101
[CpRu{B(Cl)N(SiMe$_3$)B(Cl)N(SiMe$_3$)$_2$(CO)$_2$] (**104**)	d	211.5(2)	60.3	106
[CpRu{B(NMe$_2$)B(NMe$_2$)Br}(CO)$_2$] (**108**)	d	217.3(3)	63.3	100
[CatBRu(CO)(MeCN)$_2$(PPh$_3$)$_2$] [SbF$_6$] (**130**)	e	x	y	29
Osmium				
[CatBOsCl(CO)(PPh$_3$)$_2$] (**59**)	b	217.7(14)	y	29, 80
[CatBOsCl(CS)(PPh$_3$)$_2$] (**60**)	b	x	y	80
[{B(1,2-O$_2$-3-MeC$_6$H$_3$)}OsCl(CO)(PPh$_3$)$_2$] (**61**)	b	x	y	80
[{B{1,2-(NH)$_2$C$_6$H$_4$}}OsCl(CO)(PPh$_3$)$_2$] (**62**)	b	220.1(9)	y	29, 80
[{B{1-S-2-NHC$_6$H$_4$}}OsCl(CO)(PPh$_3$)$_2$] (**63**)	b	220.0(22)	y	29, 80
[Cl$_2$BOsCl(CO)(PPh$_3$)$_2$] (**64**)	b	x	y	29, 132
[{(EtO)$_2$B}OsCl(CO)(PPh$_3$)$_2$] (**125**)	e	207.6(3)	y	132
[{B{1,2-(NMe)$_2$C$_6$H$_4$}}OsCl(CO)(PPh$_3$)$_2$] (**126**)	e	208.2(10)	y	132
[CatBOsI(CO)$_2$(PPh$_3$)$_2$] (**127a**) (CO *trans* to B)	e	214.5(5)	y	132
[CatBOsI(CO)$_2$(PPh$_3$)$_2$] (**127b**) (I *trans* to B)	e	209.0(3)	y	132
[CatBOs(CO)(MeCN)$_2$(PPh$_3$)$_2$] (**131**)	e	209.4(5)	y	131
[{B(OEt)NHC$_9$H$_6$N}OsCl(CO)(PPh$_3$)$_2$] (**142**)	e	207.2(3)	y	202
Cobalt				
[(CatB)$_2$Co(PMe$_3$)$_3$] (**9**)	a	194.5(11) 197.0(11)	z	55
[(CO)$_4$CoBH$_2$ · thf] (**118**)	e	x	7.9	117
[(CO)$_4$CoBH$_2$ · SMe$_2$] (**119**)	e	x	−10.0	118
[(η^1-Ph$_2$PCH$_2$PPh$_2$)(CO)$_2$Co(μ-Ph$_2$PCH$_2$PPh$_2$)(BH$_2$)] (**120**)	e	222.7(6)	−25.9	119
Rhodium				
[(CatB)$_2$RhCl(PPh$_3$)$_2$] (**11**)	a, b	195.6(8) 200.8(7)	35.9	58, 60, 84, 157
[{B(1,2-O$_2$-3-MeC$_6$H$_3$)}$_2$RhCl(PPh$_3$)$_2$] (**12**)	a	190.6(13) 203.4(12)	40.3	60

Table 1 (*Continued*)

Compound	Synthesis	*d*(M–B) (pm)	δ ^{11}B [a]	Ref.
[{B(1,2-O$_2$-3-MeOC$_6$H$_3$)}$_2$RhCl(PPh$_3$)$_2$] (**13**)	a	x	y	60
[{B(1,2-O$_2$-4-MeC$_6$H$_3$)}$_2$RhCl(PPh$_3$)$_2$] (**14**)	a	x	37.0	60
[(BCat*)$_2$RhCl(PPh$_3$)$_2$] (**15**)	a	x	38.9	58, 60
[{B(1,2-O$_2$-3,5-*t*-Bu$_2$C$_6$H$_3$)}$_2$RhCl(PPh$_3$)$_2$] (**16**)	a	x	42.6	58
[{B(1,2-S$_2$C$_6$H$_4$)}$_2$RhCl(PPh$_3$)$_2$] (**17**)	a	x	56.1	60
[{B(1,2-S$_2$-4-MeC$_6$H$_3$)}$_2$RhCl(PPh$_3$)$_2$] (**18**)	a	x	y	60
[(TartB)$_2$RhCl(PPh$_3$)$_2$] (**19**)	a	x	36.2	60
[(CatB)$_2$RhCl(PEt$_3$)$_2$] (**20**)	a	197.3(2) 199.4(2)	39.7	60, 157
[CatBRh(PMe$_3$)$_4$] (**22**)	a	204.7(2)	49.0	61
[(CatB)$_3$Rh(PMe$_3$)$_3$] (**23**)	a	205.5(4) 205.3(4) 206.1(4)	46.8	61
[CatBRhHCl(PPh$_3$)$_2$] (**65**)	b	x	35.8	85
trans-[CatBRhHCl(P*i*Pr$_3$)$_2$] (**66**)	b	196.1(7)	37.7	87
mer-[CatBRhHCl(PMe$_3$)$_3$] (**67**)	b	x	42.8	86
Iridium				
[(CatB)$_2$IrCl(PEt$_3$)$_2$] (**21**)	a	199.1(6) 200.4(6)	41.7	62
[(CatB)$_2$IrCl(PMe$_3$)$_3$] (**37**)	a	199.1(6) 200.4(6)	41.7	62
fac-[(Me$_2$HCMe$_2$CBH)IrH$_2$(PMe$_3$)$_3$] (**68**)	b	x	107.8	70
fac-[(H$_{14}$C$_8$B)IrH$_2$(PMe$_3$)$_3$] (**69**)	b	209.3(7)	106.2	70
mer-[CatBIrHCl(PMe$_3$)$_3$] (**70**)	b	202.3(10)	32.8	69
trans-[CatBIrHCl(P*i*Pr$_3$)$_2$] (**71**)	b	x	40.1	88
trans-[CatBIrHCl(CO)(PPh$_3$)$_2$] (**72**)	b	204.5(5)	30.8	88
trans-[CatBIrHBr(CO)(dppe)] (**73**)	b	x	y	89
trans-[CatBIrHI(CO)(dppe)] (**74**)	b	x	y	89
trans-[CatBIrHBr(CO){Ph$_2$PCH(Me)CH(Me)PPh$_2$}] (**75**)	b	x	y	89
[(CatB)$_3$Ir(η^6-C$_6$H$_6$)] (**76**)	b	x	37.7	90
[(CatB)$_3$Ir(η^6-C$_6$D$_6$)] (**77**)	b	x	37.9	90
[(CatB)$_3$Ir(η^6-C$_6$H$_5$Me)] (**78**)	b	203.6(4) 201.8(5) 202.4(5)	37.7	90
[(CatB)$_3$Ir(η^6-1,3,5-Me$_3$C$_6$H$_3$)] (**79**)	b	x	37.8	90
[(CatB)$_2$IrH(CO)(dppe)] (**80**)	b	x	y	89
[Cp*IrH(BPin)(CO)] (**81**)	b	x	33.0	91
[Cp*IrH(BCat)(CO)] (**82**)	b	x	y	91
[Cp*IrH(BF$_2$)(PMe$_3$)] (**112**)	d	x	23.9	109
[Cp*IrH(BPh$_2$)(PMe$_3$)] (**113**)	d	x	93.0	109
[(C$_{12}$H$_8$BF)IrCl(PMe$_3$)$_3$][BPh$_4$] (**121**)	e	200(1)	z	120
Palladium				
[{B-1,2-(NMe)$_2$C$_2$H$_4$}PdSnMe$_3$(dmpe)] (**83**)	c	207.7(6)	46.9	93
Platinum				
cis-[(PinB)$_2$Pt(PPh$_3$)$_2$] (**10**)	a	207.6(6) 207.8(7)	46.3	56, 57, 64, 175
cis-[(CatB)$_2$Pt(PPh$_3$)$_2$] (**24**)	a	207.6(6) 207.8(6)	47.0	63, 64

Table 1 (*Continued*)

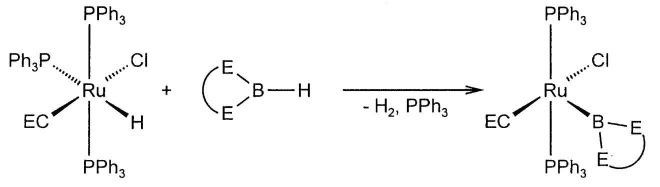
Compound	Synthesis	*d*(M–B) (pm)	δ ^{11}B [a]	Ref.
cis-[{B(1,2-O$_2$-3-MeC$_6$H$_3$)}$_2$Pt(PPh$_3$)$_2$] (**25**)	a	x	y	29
cis-[{B(1,2-O$_2$-3-MeOC$_6$H$_3$)}$_2$Pt(PPh$_3$)$_2$] (**26**)	a	x	y	29
cis-[{B(1,2-O$_2$-4-MeC$_6$H$_3$)}$_2$Pt(PPh$_3$)$_2$] (**27**)	a	x	y	29
cis-[(Cat*B)$_2$Pt(PPh$_3$)$_2$] (**28**)	a	204.5(11) 204.6(13)	50.1	64
cis-[{B(1,2-O$_2$-3,5-*t*-Bu$_2$C$_6$H$_3$)}$_2$Pt(PPh$_3$)$_2$] (**29**)	a	x	y	29
cis-[{B(1,2-S$_2$C$_6$H$_4$)}$_2$Pt(PPh$_3$)$_2$] (**30**)	a	205.6(4) 207.5(4)	72.0	65
cis-[{B(1,2-S$_2$-4-MeC$_6$H$_3$)}$_2$Pt(PPh$_3$)$_2$] (**31**)	a	x	y	29
cis-[{B(1,2-O$_2$C$_6$Cl$_4$)}$_2$Pt(PPh$_3$)$_2$] (**32**)	a	x	51.5	65
cis-[{B(1,2-O$_2$C$_6$Br$_4$)}$_2$Pt(PPh$_3$)$_2$] (**33**)	a	x	48.0	65
cis-[(TartB)$_2$Pt(PPh$_3$)$_2$] (**34**)	a	205.4(7) 206.5(5)	48.1	66
cis-[{B{*R*,*R*-O$_2$CHPhCHPh}}$_2$Pt(PPh$_3$)$_2$] (**35**)	a	x	47.3	66
cis-[{B(*S*-O$_2$CH$_2$CHPh)}$_2$Pt(PPh$_3$)$_2$] (**36**)	a	207.0(3) 205.4(4)	48.2	66
cis-[(F$_2$B)$_2$Pt(PPh$_3$)$_2$] (**38**)	a	205.8(6) 204.7(5)	42.3	67
cis-[{Cl(Me$_2$N)B}$_2$Pt(PPh$_3$)$_2$] (**39**)	a	208.4(3) 207.6(4)	50.8	68
trans-[CatBPtCl(PPh$_3$)$_2$] (**84**)	c	200.8(8)	28.7	65
trans-[CatBPtBr(PPh$_3$)$_2$] (**85**)	c	x	30.9	65
cis-[(CatB)$_2$Pt(dppe)] (**128**)	e	205.8(8) 204.8(8)	48.9	64
cis-[(CatB)$_2$Pt(Ph$_2$PC$_3$H$_6$PPh$_2$)] (**129**)	e	203.1(8)	48.9	64

a: Oxidative addition of B–B; b: oxidative addition of B–H; c: oxidative addition of B–E; d: salt elimination; e: other method; x: no X-ray data available; y: no ^{11}B-NMR data available; z: paramagnetic; dppe: Ph$_2$PC$_2$H$_4$PPh$_2$; dmpe: Me$_2$PC$_2$H$_4$PMe$_2$; Cat*: 1,2-O$_2$-4-*t*-BuC$_6$H$_3$.

[a] Only metal-linked boron atoms considered.

reveal if the reaction after initial loss of CO proceeds by oxidative addition of the boron–hydrogen bond or rather by a concerted mechanism.

The reactions of either [RuHCl(CE)PPh$_3$)$_3$] or [OsCl(CE)(Ph$_3$)$_2$] (E = O, S) with a series of benzannelated heteroborolenes gave access to fivefold co-ordinated and hence co-ordinatively unsaturated Ru(II) and Os(II) boryl complexes. According to Eq. (9), [CatBRuCl(CO)(PPh$_3$)$_2$] (**52**), [CatBRuCl(CS)(PPh$_3$)$_2$] (**53**), [{B(1,2-O$_2$C$_{10}$H$_6$)}RuCl(CO)(PPh$_3$)$_2$] (**54**), [{B(1,2-O$_2$-3-MeC$_6$H$_3$)}RuCl(CO)(PPh$_3$)$_2$] (**55**), [{B{1,2-(NH)$_2$C$_6$H$_4$}}RuCl(CO)(PPh$_3$)$_2$] (**56**), [{B{1-S-2-NHC$_6$H$_4$}}RuCl(CO)-(PPh$_3$)$_2$] (**57**), and [{B{1-S-2-(NH)C$_6$H$_4$}}RuCl(CS)(PPh$_3$)$_2$] (**58**) were obtained with the elimination of PPh$_3$ and H$_2$.



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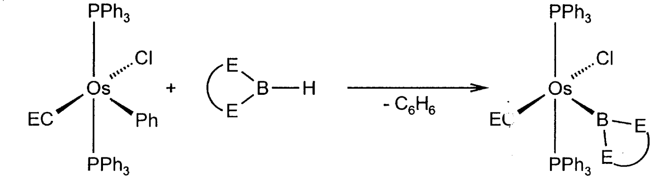
E E = various ligands, see text
E = O, S

(9)

Similarly, but now with elimination of benzene, the related osmium boryl complexes [CatBOsCl(CO)(PPh$_3$)$_2$] (**59**), [CatBOsCl(CS)(PPh$_3$)$_2$] (**60**), [{B(1,2-O$_2$-3-MeC$_6$H$_3$)}OsCl(CO)(PPh$_3$)$_2$] (**61**), [{B{1,2-(NH)$_2$C$_6$H$_4$}}OsCl(CO)(PPh$_3$)$_2$] (**62**), and [{B{1-S-2-NHC$_6$H$_4$}}OsCl(CO)(PPh$_3$)$_2$] (**63**) were obtained according to Eq. (10).



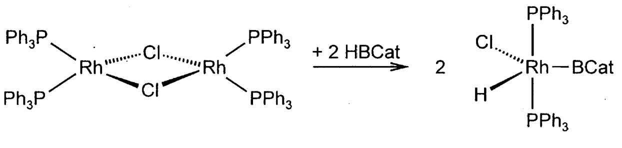
59 - 64

E E = various ligands, see text
E = O, S

(10)

The use of $HBCl_2 \cdot OEt_2$ instead of the aforementioned benzannelated heteroborolenes yielded the osmium dichloroboryl complex [Cl$_2$BOsCl(CO)(PPh$_3$)$_2$] (**64**). The ruthenium complex **52** could be alternatively obtained from the reaction of CatBH with [RuCl(CO)(PPh$_3$)$_2${CH=CHPh}] [29,80,81]. So far, there is no evidence for the mechanism of the formation of these Ru–B and Os–B bonds, respectively. Either an oxidative addition of the B–H bond or a σ-bond metathesis may apply.

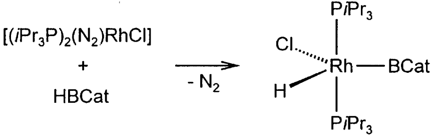
The reaction of Wilkinson's catalyst [RhCl(PPh$_3$)$_3$] with boranes R$_2$B–H is the most thoroughly investigated oxidative addition of a B–H bond to a metal centre. This is certainly due to the importance this rhodium complex has, in metal-mediated additions of element hydrogen bonds to hydrocarbons. In 1975, the first reaction of [RhCl(PPh$_3$)$_3$] with CatBH was reported, and ten years later it was shown that this rhodium complex is indeed a highly selective catalyst for the hydroboration of alkenes and alkynes [82–84]. The stoichiometric reaction of Wilkinson's catalyst with CatBH affords [CatBRhHCl(PPh$_3$)$_2$] (**65**) with elimination of PPh$_3$. Detailed investigations, however, proved this reaction to be far more complex and affording, besides **65**, a range of boron and ruthenium compounds alongside such as H$_3$B–PPh$_3$, B$_2$Cat$_3$, [RhCl(PPh$_3$)$_3$], and [RhH$_2$Cl(PPh$_3$)$_3$]. These species originate from degradation products of the starting catechol borane, the latter being due to reactions of the liberated PPh$_3$ with CatBH [85,86]. Dimeric [{Rh(PPh$_3$)$_2$(μ-Cl)}$_2$] provides another access to [CatBRhHCl(PPh$_3$)$_2$] (**65**) free of side products (Eq. (11)) since no PPh$_3$ is released.



65

(11)

The related bisboryl complex $[(CatB)_2RhCl(PPh_3)_2]$ (**11**), which was alternatively yielded by B_2Cat_2 (Eq. (5)), is obtained from **65** and another equivalent of CatBH [85]. Further oxidative additions to Rh(I) complexes were reported for the reactions of $[RhCl(N_2)(P\textit{i}Pr_3)_2]$ (Eq. (12)) and $[RhCl(PMe_3)_3]$ with CatBH, yielding *trans*-$[CatBRhHCl(P\textit{i}Pr_3)_2]$ (**66**) and *mer*-$[CatBRhHCl(PMe_3)_3]$ (**67**), respectively.

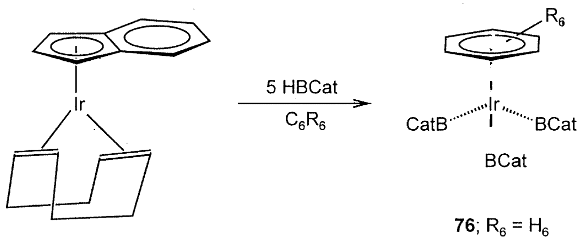


66

(12)

The formation of **66** is accompanied by cleavage of N_2, while the six co-ordinate Rh(III) complex **67** is yielded without loss of any labile ligand [86,87].

Related iridium boryl complexes were obtained similarly by oxidative addition of B–H bonds to low-valent Ir complexes. $[IrH(PMe_3)_4]$, for example, reacts with two equivalents of $H_2BCMe_2CHMe_2$ (thexylborane) or $(HBC_8H_{14})_2$ (dimeric 9-BBN), yielding *fac*-$[(Me_2HCMe_2CBH)IrH_2(PMe_3)_3]$ (**68**) and *fac*-$[(H_{14}C_8B)IrH_2(PMe_3)_3]$ (**69**), respectively. The liberated phosphane forms the corresponding adducts with excessive borane [70]. Cleavage of labile olefin ligands such as cyclooctene (coe) afforded *mer*-$[CatBIrHCl(PMe_3)_3]$ (**70**) from $[IrHCl(PMe_3)_3(coe)]$ and the related dimeric iridum complex $[\{Ir(coe)_2(\mu\text{-}Cl)\}_2]$ gave *trans*-$[CatBIrHCl(P\textit{i}Pr_3)_2]$ (**71**) in the presence of $P\textit{i}Pr_3$ [69,88]. Oxidative addition of CatBH to Ir(I) complexes without accompanying ligand dissociation was reported for the reactions of some diphosphane complexes of the type $[IrX(CO)(PR_3)_2]$ (X = various halides, $(PR_3)_2$ = mono- or bidentate phosphanes), yielding *trans*-$[CatBIrHCl(CO)(PPh_3)_2]$ (**72**) [88], *trans*-[CatBIrHBr(CO)(dppe)] (**73**), *trans*-[CatBIrHI(CO)(dppe)] (**74**) (dppe = $Ph_2PC_2H_4PPh_2$), and *trans*-$[CatBIrHBr(CO)\{Ph_2PCH(Me)CH(Me)PPh_2\}]$ (**75**), respectively [89]. Particularly interesting, is the formation of iridium trisboryl complexes according to Eq. (13). The treatment of $[(\eta^5\text{-}C_9H_7)Ir(cod)]$ (C_9H_7 = indenyl, cod = cyclooctadiene) with a fivefold excess of CatBH in aromatic solvents such as benzene, toluene or mesitylene leads to substitution of both former ligands, oxidation of the iridium centre and addition of a solvent molecule, yielding $[(CatB)_3Ir(\eta^6\text{-}C_6H_6)]$ (**76**), $[(CatB)_3Ir(\eta^6\text{-}C_6D_6)]$ (**77**), $[(CatB)_3Ir(\eta^6\text{-}C_6H_5Me)]$ (**78**), or $[(CatB)_3Ir(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]$ (**79**).



(13)

76; $R_6 = H_6$
77; $R_6 = D_6$
78; $R_6 = H_5Me$
79; $R_6 = H_3Me_3$

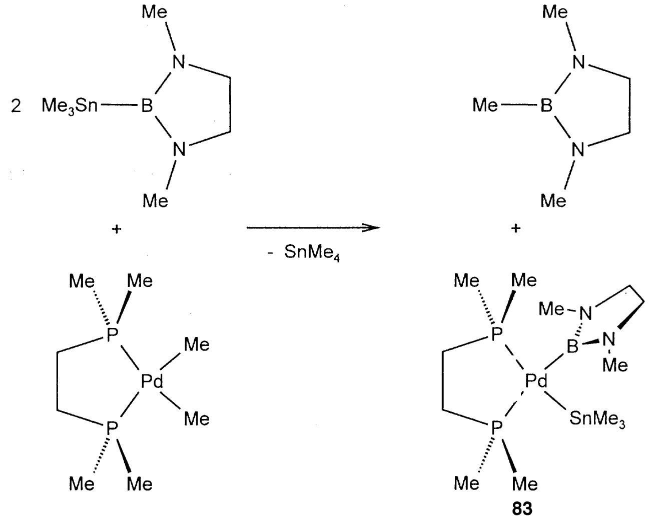
Presumably, the cleavage of both the indenyl and the cod ligand is initiated by hydroboration and/or hydrogenation [90]. When Ir(III) complexes are the starting materials, the addition of boranes R_2BH is more likely to proceed via either σ-bond metathesis or a sequence of reductive elimination/oxidative addition steps. $[IrH_3(CO)(dppe)]$ reacts with two equivalents of CatBH with formation of the bisboryl complex $[(CatB)_2IrH(CO)(dppe)]$ (**80**) and loss of H_2 [89]. Very recently, the first half-sandwich iridium boryl complexes [Cp*IrH(BPin)(CO)] (**81**) and [Cp*IrH(BCat)(CO)] (**82**) were obtained from [Cp*IrH(*cyclo*-C_6H_{11})(CO)] and the corresponding boranes [91].

3.1.1.3. Oxidative addition of heteroboranes R_2B–X and related syntheses. Some low-valent palladium and platinum complexes were reported to undergo additions of boron–heteroelement bonds with formation of the corresponding boryl complexes. For sila- and stannaboranes R_2B–ER_3 (E = Si, Sn), a number of metal-mediated additions to unsaturated hydrocarbons were reported [92], which most likely proceed via oxidative addition of the B–E bond to palladium and platinum centres, respectively. The corresponding stoichiometric additions, however, are far less numerous such as the formation of $[\{B\text{-}1,2\text{-}(NMe)_2C_2H_4\}PdSnMe_3(dmpe)]$ (**83**) (dmpe = $Me_2PC_2H_4PMe_2$) according to Eq. (14) [93].

In contrast to the general formation of *cis*-bisboryl complexes from $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ and B_2Cat_2 (Eq. (5)), the corresponding halocatecholboranes CatBX (X = Cl, Br) gave the *trans*-boryl complexes *trans*-$[CatBPtCl(PPh_3)_2]$ (**84**) and *trans*-$[CatBPtBr(PPh_3)_2]$ (**85**) after oxidative addition of the boron–halide bond and isomerisation [65].

3.1.2. Salt elimination

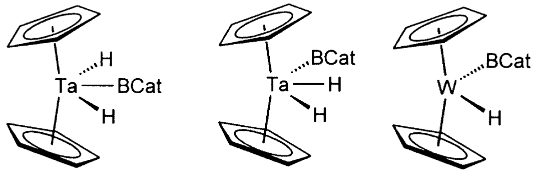
Just like the oxidative addition, the salt elimination reaction between an anionic transition metal complex and a suitable element halide represents another fundamental synthetic approach to organometallic compounds with metal–element bonds [94,95]. In the case of transition metal complexes of boron, this synthesis was successfully applied not only to boryl complexes, but also to diborane(4)yl, η^1-borazine, and bridged as well as terminal borylene complexes (vide infra) using nucleophilic anionic precursors mostly deriving from cyclopentadienyl and carbonyl complexes, respectively.



(14)

$[Cp_2TaH_2(BCat)]$, the *endo*-isomer of which being subsequently obtained by oxidative addition of CatBH (vide supra), was originally afforded from CatBCl and $\{Li[Cp_2TaH_2]\}_x$ [96]. In contrast to the addition of CatBH to $[Cp_2TaH_3]$, the latter salt elimination yielded *endo*-$[Cp_2TaH_2(BCat)]$ (**45**) together with its constitutional isomer *exo*-$[Cp_2TaH_2(BCat)]$ (**86**) (Fig. 1).

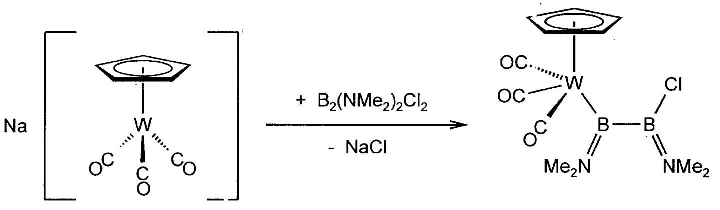
The *exo*-isomer is kinetically favoured and dominates slightly, however, it converts upon heating into the thermodynamically more stable *endo*-isomer. Although this regioisomerism is long known for corresponding niobocene and tantalocene derivatives [97], in the present case, both isomers could be separated and structurally characterised for the first time. Similarly, the related tungstenocene boryl complex $[Cp_2WH(BCat)]$ (**87**) (Fig. 1) was obtained from CatBCl and $\{Li[Cp_2WH]\}_4$ [98,52]. In general, reactions of diboranes(4) with suitable transition metal complexes proceed with cleavage of the boron–boron bond and formation of either bisboryl (see Section 3.1.1.1) or bridged borylene complexes (vide infra). In the case of $B_2(NMe_2)_2Cl_2$ and $Na[CpW(CO)_3]$, however, the boron–boron bond is retained with formation of the first diborane(4)yl complex $[CpW\{B(NMe_2)B(NMe_2)Cl\}(CO)_3]$ (**88**) (Eq. (15)), and the corresponding molybdenum complex



45 **86** **87**

Fig. 1. Some metallocene boryl complexes of Ta and W; *endo*-$[Cp_2TaH_2(BCat)]$ (**44**), *exo*-$[Cp_2TaH_2(BCat)]$ (**86**), and $[Cp_2WH(BCat)]$ (**87**).

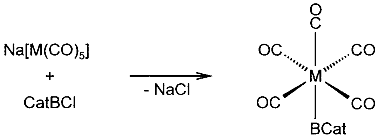
$[CpMo\{B(NMe_2)B(NMe_2)Br\}(CO)_3]$ (**89**) was subsequently obtained from the more reactive $B_2(NMe_2)_2Br_2$ [99,100].



(15)

88

Another half-sandwich complex of tungsten $[Cp^*W\{B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_3\}(CO)_3]$ (**90**) was also afforded by salt elimination [101]. As far as homoleptic transition metal carbonylates are concerned, $[CatBMn(CO)_5]$ (**91**) and $[CatBRe(CO)_5]$ (**92**) were obtained from the corresponding pentacarbonylates $Na[M(CO)_5]$ (M = Mn, Re) according to Eq. (16) [102,103].

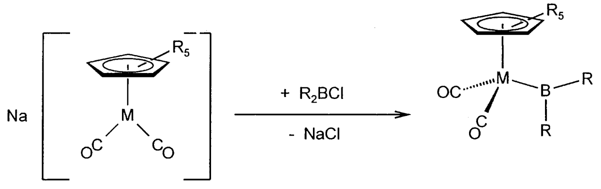


(16)

91, M = Mn

92, M = Re

The alternative preparation of $[(Cat^*B)_2Fe(CO)_4]$ (**8**) (see Eq. (3), Section 3.1.1.2) from $Na_2[Fe(CO)_4]$ and Cat^*BCl shows that salt elimination reactions are not limited to monoanionic species [52]. The strongly nucleophilic $Na[CpFe(CO)_2]$ and its ruthenium analogue $Na[CpRu(CO)_2]$ provided access to a large number of boryl complexes and related species. According to the general Eq. (17), the following compounds were obtained: $[CpFe(BCat)(CO)_2]$ (**93**), $[CpFe(BPh_2)(CO)_2]$ (**94**), $[CpFe\{B(NMe_2)Cl\}(CO)_2]$ (**95**), $[CpFe\{B\{Si(SiMe_3)_3\}Cl\}(CO)_2]$ (**96**), $[(C_5H_4Me)Fe\{B(NMe_2)Cl\}(CO)_2]$ (**97**), $[Cp^*Fe\{B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_3\}(CO)_2]$ (**98**), $[Cp^*Fe\{B(NMe_2)Cl\}(CO)_2]$ (**99**), $[Cp^*Fe\{B(NMe_2)Br\}(CO)_2]$ (**100**), $[CpRu\{B(NMe_2)Cl\}(CO)_2]$ (**101**), $[CpRu\{B(NMe_2)Br\}(CO)_2]$ (**102**), and $[Cp^*Ru\{B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_3\}(CO)_2]$ (**103**) [101,104–106].

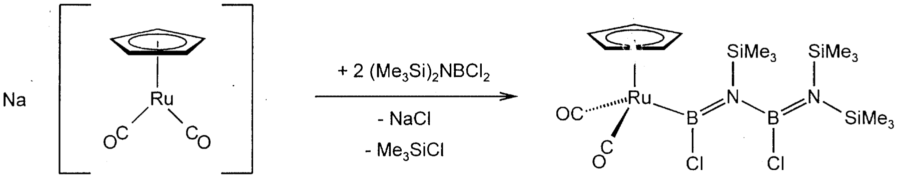


(17)

93 - 103, 105 - 108

R_2 = various ligands, see text
R_5 = H_5, H_4Me, Me_5
M = Fe, Ru

The reaction of Na[CpRu(CO)$_2$] with two equivalents of (Me$_3$Si)$_2$NBCl$_2$ affords the unusual ruthenium boryl complex [CpRu{B(Cl)N(SiMe$_3$)B(Cl)N(SiMe$_3$)$_2$(CO)$_2$] (**104**) (Eq. (18)) with intramolecular cleavage of Me$_3$SiCl [106]. Apart from the aforementioned boryl complexes, the diborane(4)yl complexes [CpFe{B(NMe$_2$)-B(NMe$_2$)Cl}(CO)$_2$] (**105**), [CpFe{B(NC$_4$H$_8$)B(NC$_4$H$_8$)Cl}(CO)$_2$] (**106**), [CpFe-{B(NC$_5$H$_{10}$)B(NC$_5$H$_{10}$)Cl}(CO)$_2$] (**107**), and [CpRu{B(NMe$_2$)B(NMe$_2$)Br}-(CO)$_2$] (**108**) were obtained similarly from the corresponding 1,2-dihalodiboranes(4) [99,100,107].



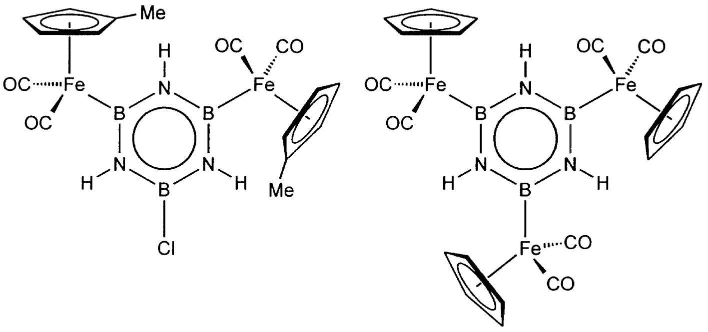
(18)

104

The first η^1-borazine complex, [Cp*Fe(B$_3$N$_3$H$_3$Cl$_2$)(CO)$_2$] (**109**), was also obtained by salt elimination from trichloroborazine and Na[Cp*Fe(CO)$_2$]; subsequent treatment of **109** with an excess of Na[(C$_5$R$_5$)Fe(CO)$_2$] yielded the di- and trisubstituted borazines [{(C$_5$H$_4$Me)Fe(CO)$_2$}$_2$(B$_3$N$_3$H$_3$Cl)] (**110**) and [{CpFe(CO)$_2$}$_3$-(B$_3$N$_3$H$_3$)] (**111**), respectively (Fig. 2) [108].

The only examples for iridium boryl complexes being obtained by salt eliminations so far are [Cp*IrH(BF$_2$)(PMe$_3$)] (**112**) and [Cp*IrH(BPh$_2$)(PMe$_3$)] (**113**) which are derived from the strongly basic lithium iridate Li[Cp*IrH(PMe$_3$)] and the corresponding haloboranes [109].

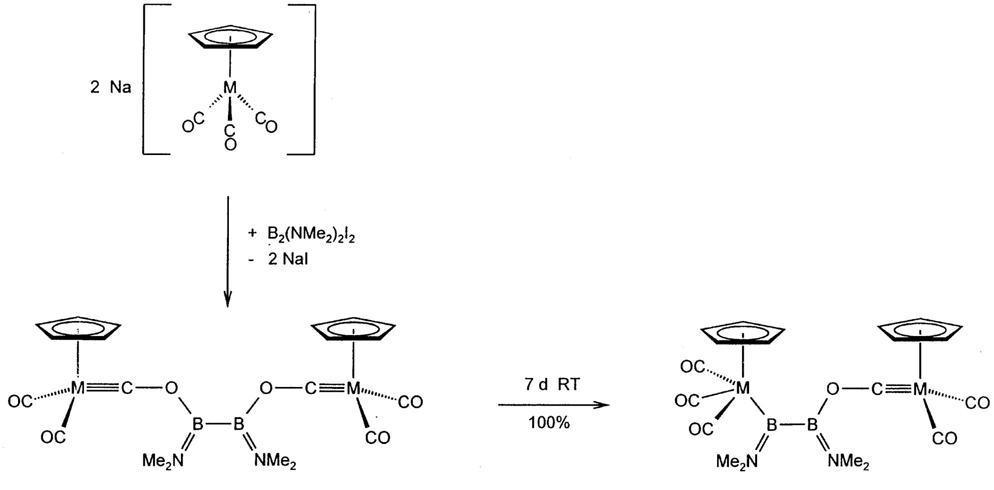
As far as anionic carbonyl complexes of the formula M′[L$_x$M(CO)$_y$] are concerned, in this chapter, the general formation of metal–boron linkages from reactions with haloboranes implies that the transition metal M in M′[L$_x$M(CO)$_y$] acts as the nucleophilic centre. As mentioned above, this reactivity pattern estab-



110 **111**

Fig. 2. η^1-Borazine complexes; [{(C$_5$H$_4$Me)Fe(CO)$_2$}$_2$(B$_3$N$_3$H$_3$Cl)] (**110**) and [{Cp*Fe(CO)$_2$}$_3$(B$_3$N$_3$H$_3$)] (**111**).

lished salt elimination as a pivotal method for the synthesis of compounds [$L_x(CO)_yM–ER_z$] with metal–element bonds. There is, however, spectroscopic and experimental evidence that the carbonyl oxygen atom in $M'[L_xM(CO)_y]$ also displays some nucleophilic character, especially towards hard and bulky Lewis acids [110–113]. In the case of an addition of the carbonyl oxygen atom to the element E, with salt elimination, one has to expect the formation of transition metal oxycarbyne complexes [$L_x(CO)_{y-1}M{\equiv}C–O–ER_z$]; this alternative pathway to the common formation of [$L_x(CO)_yM–ER_z$], was only observed in one single case [114]. More recently, however, there were some reports on reactions of transition metal carbonylates with haloboranes yielding boryloxycarbyne complexes, which may indicate that the aforementioned alternative is more common in boron chemistry. In contrast to the formation of [$CpMo\{B(NMe_2)B(NMe_2)Cl\}(CO)_3$] (**89**) and related diborane(4)yl complexes from $B_2(NMe_2)_2X_2$ (X = Cl, Br) according to Eq. (15), the corresponding diiododiborane(4) $B_2(NMe_2)_2I_2$ yields the dinuclear bis(boryloxycarbyne) complexes [$Cp(CO)_2M{\equiv}COB(NMe_2)B(NMe_2)OC{\equiv}M(CO)_2Cp$] (**114**, M = Mo; **115**, M = W) with nucleophilic addition of two CO-oxygen atoms to both boron atoms. Interestingly, **114** and **115** represent the kinetically favoured products of this reaction and undergo a quantitative rearrangement, yielding the thermodynamically more stable products [$Cp(CO)_2M{\equiv}COB(NMe_2)B(NMe_2)M(CO)_3Cp$] **116** and **117** (Eq. (19)) with a 1,3-shift of one boryl group from the carbyne oxygen atom to the metal centre and restoration of the former CO ligand [115].



114, M = Mo
115, M = W

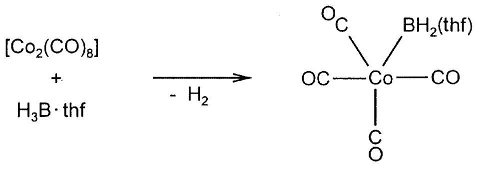
116, M = Mo
117, M = W

(19)

Similar boryloxycarbyne complexes, however, without subsequent rearrangement to boryl complexes, were reported for the reactions of $K_2[Fe_3(CO)_{11}]$ and $K[CpNi(CO)]$ with various aminohaloboranes and corresponding diboranes(4) [116].

3.1.3. Miscellaneous syntheses

Some boryl complexes were obtained by syntheses other than the addition of a reactive boron–element bond to a metal centre or salt elimination from haloboranes and anionic transition metal species. These syntheses represent mostly unique reactions without a broader range of application. In the case of $[Co_2(CO)_8]$, however, at least two reactions were reported yielding base adducts of boryl complexes. Treatment of the dicobalt octacarbonyl with $H_3B \cdot THF$ at −25 °C gave $[(CO)_4CoBH_2 \cdot THF]$ (**118**) together with H_2 according to Eq. (20).

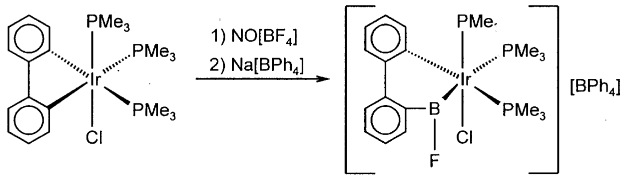


118

(20)

Due to the thermal instability of **118**, it was characterised spectroscopically in solutions at low temperatures [117]. The corresponding sulfane adduct $[(CO)_4CoBH_2 \cdot SMe_2]$ (**119**) was obtained similarly from $H_3B \cdot SMe_2$ [118]. More stable and structurally characterised, is the related phosphane adduct $[(\eta^1\text{-}Ph_2PCH_2PPh_2)(CO)_2Co(\mu\text{-}Ph_2PCH_2PPh_2)(BH_2)]$ (**120**), however, being obtained from the reduction of $CoCl_2$ with $Na[BH_4]$ in the presence of CO and dppm (dppm = $Ph_2PCH_2PPh_2$) (Fig. 3) [119].

$[(C_{12}H_8BF)IrCl(PMe_3)_3][BPh_4]$ (**121**) represents the only example of an Ir(IV) boryl complex. This cationic complex was obtained upon oxidation with $NO[BF_4]$ with insertion of a BF-moiety into an iridium–biphenyl bond of $[(C_{12}H_8)IrCl(PMe_3)_3]$ according to Eq. (21) [120].



121

(21)

Another unique formation of a boryl complex was reported from the reaction of the carbyne complex $[(tpz)W{\equiv}CC_7H_7(CO)_2]$ (tpz = trispyrazolyl borate) with Et_2BH. Most likely, the formation of the metal–boron linkage is initiated by hydroboration of the metal≡carbon triple bond, mechanistic details, however, are not known yet.

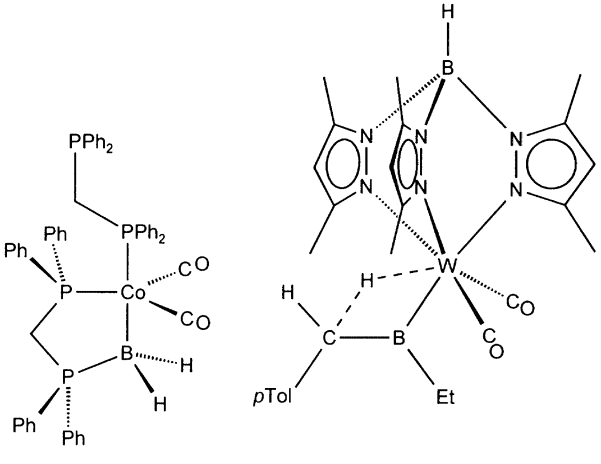
The crystal structure analysis of the obtained product [{HB(1,2-N_2-3,5-$Me_2C_3H)_3$}$(CO)_2W${BEt(CH_2-4-MeC_6H_4}] (**122**) revealed a short tungsten–boron bond and the presence of a β-agostic hydride (Fig. 3) [121].

3.2. Structure

The metal–boron bond in boryl complexes can be regarded as the structural key feature of these compounds. As a result of the successful experimental work of the past decade, there is now a substantial range of spectroscopic and structural data available providing some insight into the nature of this bond. More recently, theoretical investigations proved to be another source of information. Borylene complexes, however, which are still very rare, have been still subject to more theoretical studies than the corresponding boryl complexes.

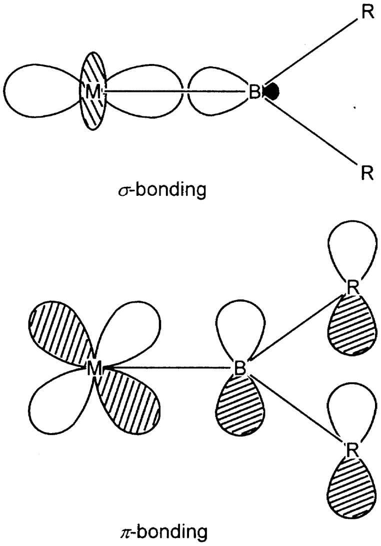
Applying a very simple model to the covalent bonding in compounds [L_xM–BR_2], the sp^2-hybridized boron atom adopts a trigonal planar co-ordination and forms σ-bonds with the metal fragment L_xM and both ligands R. To compensate for the electron deficiency at boron, the competitive π-donation from L_xM and R into the vacant p orbital at boron is possible (Scheme 5).

Hence, the electronic stabilisation of the boron atom is strongly affected by both the metal fragment L_xM and the boron-bound ligands R. A similar situation is known for isoelectronic cationic carbene complexes [122,123]. Late transition metals without π-acceptor ligands L, should stabilise the metal–boron bond most effectively; however, there seem to be no major restrictions to the use of suitable precursor complexes for the synthesis of boryl complexes as pointed out in Section 3.1. In the case of boron-bound ligands R, however, compounds with catechol



122

Fig. 3. [(η^1-$Ph_2PCH_2PPh_2$)$(CO)_2$Co(μ-$Ph_2PCH_2PPh_2$)(BH_2)] (**120**) and [{HB(1,2-N_2-3,5-$Me_2C_3H)_3$}-$(CO)_2W${BEt(CH_2-4-MeC_6H_4}] (**122**).



Scheme 5. Model for σ- and π-bonding in boryl complexes.

groups and related cyclic ligands are particularly stable, thus representing the largest group of boryl complexes. Other ligands are still a minority and obviously, most boranes do not form stable boryl complexes. Besides, the choice of R may even lead to complexes with different co-ordination modes for the boryl groups as already pointed out for some niobium complexes in Scheme 4. Although the effect of the π-bonding on the stability is not completely resolved yet, two series of fully characterised compounds [CpFe(BR_2)$(CO)_2$] and [R_2BOsCl(CO)$(PPh_3)_2$] with various boryl groups BR_2, allow now for a useful comparison of the boron-bound groups R with respect to their influence on the metal–boron linkage.

3.2.1. Thermodynamic and theoretical aspects

Although the metal–boron bond in boryl complexes can be regarded to be of predominantly covalent character, very recent ab initio calculations showed electrostatic interactions between the positively charged boron and the negatively charged metal atom to additionally contribute to the overall bond strength [124]. The question of the thermodynamic stability of this bond with respect to homolytic dissociation was addressed by both experimental and theoretical investigations. An initial estimation of the bond dissociation energy (BDE) of a boryl complex was obtained from the determination of the reaction enthalpy for the formation of *trans*-[CatBIrHCl(CO)$(PPh_3)_2$] (**72**), which was subsequently characterised [88] from *trans*-[IrCl$(PPh_3)_2$(CO)] and CatBH. Under the consideration of the calculated BDEs of CatB–H and CatB–CH_3 and the experimentally available heat of formation for the iridium–hydrogen bonds in [Ir$(H)_2$Cl$(PPh_3)_2$(CO)], the BDE for a cleavage of the iridium–boron bond in **72** was determined to be 66 kcal mol^{-1} [125]. This value exceeds iridium–carbon BDEs in related complexes by more than

30 kcal mol^{-1}. Similarly, high BDEs were calculated subsequently for complexes of the type *cis*-[$(R_2B)_2M(PH_3)_2$] (R = H, OH; M = Pd, Pt), being 51.0 (R = OH, M = Pd), 64.8 (R = H, M = Pt), and 62.9 (R = OH, M = Pt) kcal mol^{-1}. These BDEs again exceed those of the corresponding metal–carbon bonds by at least 25 kcal mol^{-1} [126]. A very recent detailed theoretical study on the electronic structure of five- and sixfold co-ordinated osmium complexes with various boryl ligands such as H_2B–, F_2B, $(HO)_2B$–, and CatB– gave corresponding BDEs ranging from 80 to 90 kcal mol^{-1}, thus being even higher than for the dissociation of a carbonyl ligand from [$Os(CO)_5$] which was calculated to be 42.9 kcal mol^{-1} [127]. Another study focussed on the influence a positively charged transition metal has on the metal–boron bond, by calculating a series of scandium, cobalt, rhodium, and iridium boryl complexes in comparison with their cationic counterparts [128]. Although the contribution of the π-backbonding to the stability of the molecules is judged differently by those studies, they all agree that the investigated metal–boron bonds are thermodynamically much more stable than corresponding metal–carbon bonds with respect to homolytic dissociation. However, that does not imply boryl complexes to be generally unreactive compounds. As a matter of fact, many of them are rather labile and readily accessible to nucleophilic attack with cleavage of the metal–boron bond, thus initiating degradation processes. The lability of the metal–boron bond, on the other hand, allows for the various metal-mediated functionalisations of hydrocarbons by boranes.

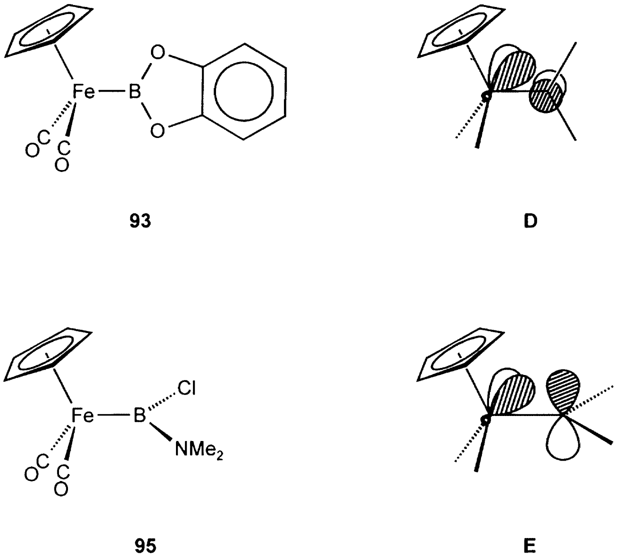
3.2.2. Spectroscopic and structural aspects

Earlier studies on boryl complexes had to rely solely on NMR- and IR-spectroscopic studies to prove the proposed molecular structure. Corresponding ^{11}B-NMR resonances were reported to be strongly shielded up to $\delta = -23.5$ which was explained by strong metal–boron π-interaction [32]. Recent re-examinations on now structurally authentic compounds such as [$CpFe(BPh_2)(CO)_2$] (**94**) have proved the ^{11}B-NMR shifts to be much more deshielded [103]. Obviously, those earlier reported values seem not to correspond to the proposed constitutions. As a matter of fact, ^{11}B-NMR signals for boryl complexes range from 24 ppm for [$Cp^*IrH(BF_2)(PMe_3)$] (**112**) to over 30–70 ppm for catecholboryl complexes, and 90–120 ppm for dialkyl- and diarylboryl complexes and up to 141 ppm for the silylboryl complex [$CpFe\{B\{Si(SiMe_3)_3\}Cl\}(CO)_2$] (**96**). Hence, boryl complexes cover a wider ^{11}B-NMR range than any other class of compounds with threefold co-ordinated boron, exceeding the common dispersion known for the ^{11}B nucleus [129] by some 50 ppm to a lower field. This significant deshielding is the most characteristic spectroscopic feature all boryl complexes have in common, and generally, the resonance of the yielded boryl complex is shifted to a lower field with respect to that of the corresponding borane precursor. Due to the increased co-ordination number of boron, borane complexes and base adducts of boryl complexes, display much more shielded ^{11}B-NMR resonances up to -25 ppm (Table 1).

More recent studies on boranes BR_3 stated the difficulties in correlating ^{11}B-NMR shifts with possible π-backdonation from the ligands R [129], and also it turns out to be very difficult to find a similar relation for boryl complexes. For example, complexes for which the presence of metal–boron π-backbonding appears to be confirmed by further spectroscopic and structural data (vide infra) show similarly deshielded resonances like compounds without evidence for π-donation. Almost impossible, is a comparison of the relative amount of π-donation different metal moieties provide to the same boryl ligand. For example, a comparison of the ^{11}B-NMR shifts of [$Cp_2WH(BCat)$] (**87**) ($\delta = 57.0$) and [$CpFe(BCat)(CO)_2$] (**93**) ($\delta = 51.8$) implies the [$CpFe(CO)_2$] moiety to be a stronger π-donor towards the catecholboryl ligand than [Cp_2WH]; for the corresponding diphenylboryl complexes [$Cp_2WH(BPh_2)$] (**123**) ($\delta = 114.0$) [75] and [$CpFe(BPh_2)(CO)_2$] (**94**) ($\delta = 121.0$), however, a reversed order is found [97,104]. The bisboryl complex *cis*-[$(Cat{*}B)_2Fe(CO)_4$] (**8**) shows one boron resonance at $\delta = 45$, which is shielded by about 10 ppm with respect to the signal of the anionic boryl complex Li[-Cat*BFe($CO)_4$] (**124**); this finding does not correspond with the expected better π-donor abilities of the anionic [$Fe(CO)_4$]$^-$ moiety compared to the neutral [$Fe(CO)_4$] fragment [54]. A better description of the metal–boron bond, however, can be provided by the interpretation of structural and IR-spectroscopic data. Especially, the metal–boron distance and the geometry of a ligand that is located *trans* to the boryl group, and hence competing for the possible π-donation from the central metal, are useful parameters.

The strongly nucleophilic Na[$CpFe(CO)_2$] gave access to a range of structurally characterised boryl complexes [$CpFe(BR_2)(CO)_2$], and allows for a comparison of the effects the different boron-bound groups R may have on the geometry of the molecule. The schematic structure of the catecholboryl complex [$CpFe(BCat)(CO)_2$] (**93**) in the crystal is depicted in Scheme 6. In this case, the plane being defined by the iron- and the two oxygen atoms (i.e. the bonding plane of boron) is orientated almost co-planar to another plane which is defined by the iron- and the boron atoms and the centre-point of the cyclopentadienyl ligand; the corresponding dihedral angle was determined to be 7.9°. This particular arrangement of the boryl ligand allows for a π-donation from the metal-like a″-symmetrical HOMO into the vacant p-orbital at boron (**D**). The metal–boron distance for **93** was found to be 195.9(6) pm, thus being slightly shorter than the sum of the covalent radii of Fe and B, and indicating the presence of a weak π-bond. This geometry is unique for the compound type [$CpFe(BR_2)(CO)_2$]. For all other examples, such as the aminoboryl complex [$Cp{*}Fe\{B(NMe_2)Cl\}(CO)_2$] (**99**), the bonding plane of boron is twisted by about 90° (Scheme 6), and this arrangement of the boryl ligand does not allow for the aforementioned π-backbonding (**E**) (note that there is a HOMO-1 being orthogonal to the HOMO, thus being in the appropriate position for π-bonding; there is, however, no structural or spectroscopic evidence for such an interaction).

As a consequence, **99** ($d_{B-Fe} = 202.7(5)$ pm) and the corresponding diborane(4)yl and η^1-borazine complexes [$CpFe\{B(NMe_2)B(NMe_2)Cl\}(CO)_2$] (**105**) ($d_{B-Fe} = 209.0(3)$ pm) and [$\{(C_5H_4Me)Fe(CO)_2\}_2(B_3N_3H_3Cl)$] (**110**) ($d_{B-Fe} = 204.5(1)$ pm) show boron–metal distances which exceed the sum of the covalent radii of boron and iron. These findings may be explained by the different influence of the boron-bound groups R, as the catechol ligand is the least effective π-donor in this



Scheme 6. Bonding situation in boryl iron complexes $[CpFe(BR_2)(CO)_2]$; schematic structures of **93** and **95** in the crystal (left) and possible orbital interactions (right).

series. Interestingly, however, even $[CpFe(BPh_2)(CO)_2]$ (**94**), showing phenyl groups without π-donating character at boron, adopts in the solid state a geometry similar to **E** and displays a rather long iron–boron bond of 203.4(3) pm, giving no evidence of π-stabilisation from the iron centre.

A similar bonding situation for those iron boryl complexes in solution is reflected by the carbonyl stretching frequencies in the IR spectra. The corresponding frequencies of all non-catecholboryl complexes such as **94**, **95**, **105**, **110** resemble those of the related methyl complex $[CpFeMe(CO)_2]$, thus corroborating the lack of iron–boron π-bonding also in solution [130]. $[CpFe(BCat)(CO)_2]$ (**93**), however, shows significantly blue-shifted CO bands, which gives further evidence for the π-stabilisation of the catecholboryl ligand by the iron centre.

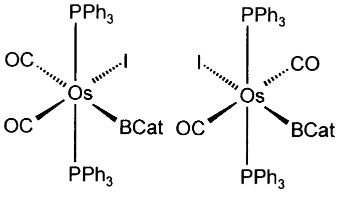
Detailed investigations on the osmium boryl complexes $[CatBOsCl(CO)(PPh_3)_2]$ (**59**), $[\{(EtO)_2B\}OsCl(CO)(PPh_3)_2]$ (**125**), and $[\{B\{1,2\text{-}(NMe)_2C_6H_4\}\}OsCl(CO)(PPh_3)_2]$ (**126**) gave similar results for the role of the boron-bound ligands. Again, the catecholboryl complex **59**, which shows the least effective π-donating groups R at boron, is characterised by the shortest osmium–boron bond in the crystal and the highest CO stretching frequencies in the IR spectrum. The π-back-bonding from osmium to boron appears to decrease with increasing π-donation from R to boron in the series **59** > **125** > **126** as proven by structural and IR-spectroscopic data [131,132].

Besides the geometry of the boryl group itself, structural data of ligands being located *trans* to BR_2 provide information about the metal–boron interactions. Boryl complexes with carbonyl CO-ligands such as *cis*-$[(Cat^*B)_2Fe(CO)_4]$ (**8**) and

[CatBMn(CO)$_5$] (**91**) do not show particularly short metal–boron bonds. The geometry of the *trans* CO-ligand, however, indicates the presence of some π-interaction. Carbonyl ligands in *trans* position to pure σ-donors such as hydride or alkyl ligands show shorter metal–carbon bonds than CO groups being mutually *trans* [133,134]. In the case of **8** and **91** no such metal–carbon bond shortening is observed, thus giving evidence for the π-acceptor abilities of the CatB group. Particularly useful, is the comparison of structural data of the compounds [CatBOsI(CO)$_2$(PPh$_3$)$_2$] (**127a**, **b**) (Scheme 7). In this case, it was possible to study two isomers with either a carbonyl (**127a**) or an iodine ligand (**127b**) in *trans* position to the CatB group. The longest Os–CO distance was found for the carbonyl group being *trans* with respect to BCat, again indicating metal–boron π-interaction [132].

Another source of structural information derives from ^1J coupling constants between the ^{31}P and the ^{195}Pt nuclei in square planar complexes of the type [(R$_3$P)$_2$Pt(BR$_2$)$_2$]. The bisboryl complexes *cis*-[(CatB)$_2$Pt(PPh$_3$)$_2$] (**24**), *cis*-[(PinB)$_2$Pt(PPh$_3$)$_2$] (**10**), *cis*-[(CatB)$_2$Pt(dppe)] (**128**) and *cis*-[(CatB)$_2$Pt-(Ph$_2$PC$_3$H$_6$PPh$_2$)] (**129**) [64], for example, show coupling constants $|^1J_{\mathrm{Pt,\ P}}|$ in the range of 1500–1600 Hz, which fall below those of corresponding platinum aryl complexes by some 200 Hz, thus indicating the strong *trans* effect of the boryl groups [135]. Considering the different covalent radii of boron and carbon, those platinum boryl complexes are furthermore characterised by metal–boron distances which are shorter than platinum–carbon distances in related aryl complexes [136]; both findings again demonstrate the presence of metal–boron π-bonding.

The structural and spectroscopic data being discussed so far underline the importance of π-stabilisation for boryl complexes, especially in the case of corresponding catecholboryl derivatives. Obviously for this reason, catecholboranes proved to be the most useful starting materials for the synthesis of this compound type. However, it must be noted that the multiple bond character for metal–boron linkages appears to be weak, since so far it was not possible to determine a corresponding rotational barrier by NMR experiments even at very low temperatures [52,53]. Furthermore, the metal–boron π-bonding is not a general feature of boryl complexes. There are a large number of rhodium and iridium complexes without any structural or spectroscopic indication for such interaction, even in the case of CatB ligands. Examples include compounds like [CatBRh(PMe$_3$)$_4$] (**22**), [(CatB)$_3$Rh(PMe$_3$)$_3$] (**23**), [(CatB)$_2$RhCl(PPh$_3$)$_2$] (**11**), *trans*-[CatBRhHCl(P*i*Pr$_3$)$_2$]



127a **127b**

Scheme 7. Two structurally characterised isomers of [CatBOsI(CO)$_2$(PPh$_3$)$_2$] (**127a**, **b**).

(**66**), and *mer*-[CatBIrHCl(PMe$_3$)$_3$] (**70**). In the case of the trigonal-bipyramidal rhodium complex **22**, the X-ray structure analysis revealed the CatB ligand even to adopt an axial position, which is usually occupied by ligands with strong σ-donor and weak π-acceptor abilities [137].

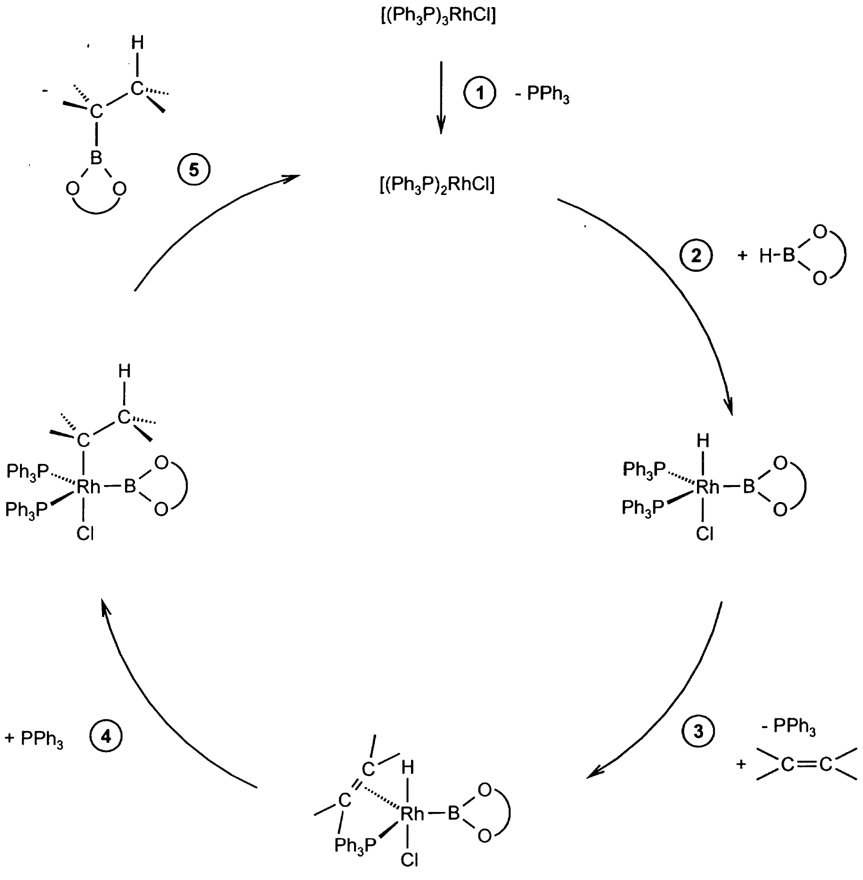
3.3. Reactivity

The increasing interest in boryl complexes over the past decade is mainly due to their possible applications for the functionalisation of hydrocarbons. Especially, the metal-catalysed hydroboration of unsaturated organic molecules, which involves boryl complexes as key intermediates, is about to become a valuable tool with broad usability in organic and organometallic synthesis. More recently, the stoichiometric [101,138] and catalytic [139] use of boryl complexes even led to selective borylation of alkanes by photochemically induced C–H activation. Besides the interest in synthetic applications of boryl complexes, their general reactivity was also subject to detailed studies. Corresponding investigations aimed at the reactivity of (a) the metal centre, (b) the metal–boron linkage, and (c) the boron centre. This section will refer to some more general aspects of the reactivity of boryl complexes and their applications, since both subjects have been already reviewed in full detail [140–144].

3.3.1. Transition metal-catalysed hydroboration and related reactions

The hydroboration of unsaturated hydrocarbons was discovered some 40 years ago [145] and has ever since developed into one of the most useful methods for the functionalisation of organic compounds [146–148]. Similar to the related metal-mediated hydrosilylation [149–151], suitable transition metal complexes were investigated with respect to their catalytic effect on the corresponding hydroboration. Since boryl complexes were supposed to be intermediates in this catalytic process, they became of increasing interest and were synthesised for modelling the single steps of the catalysis and revealing its mechanism. The first reports on metal-mediated hydroboration of olefins referred to the use of Wilkinson's catalyst [RhCl(PPh$_3$)$_3$] [83,84], initiating detailed studies on low-valent rhodium species and related complexes and their catalytic efficacy. According to the rhodium-catalysed hydroboration of acrylic esters with carbaboranes [152], a similar mechanism was suggested for the hydroboration of olefins (Scheme 8) [84].

Starting from [RhCl(PPh$_3$)$_3$], this mechanism involves the following steps: (1) elimination of PPh$_3$, (2) oxidative addition of a boron–hydrogen bond to the metal centre, (3) elimination of a second PPh$_3$ and side-on co-ordination of the incoming olefin, (4) addition of PPh$_3$ and insertion of the olefin into the rhodium–hydrogen bond, (5) reductive elimination of the borylalkane and restoration of the reactive metal species. Subsequently, experimental evidence was provided for this proposed mechanism [69,141,153] and suitable boryl complexes were found to model single steps of this cycle such as the reductive elimination of a borylalkane [154] and the insertion of an alkyne into the metal–boron bond [81]. As already pointed out in Section 3.1.1.2, the reaction of [RhCl(PPh$_3$)$_3$] with boranes such as CatBH, how-



Scheme 8. Mechanism for the transition metal-catalysed hydroboration of olefins.

ever, is more complex than Scheme 8 suggests, and affords a series of side- and degradation products. The mechanism of the rhodium-catalysed hydroboration was also subject to theoretical studies [155,156]. Although both studies agree with steps (1)–(3) and (5), in one case, the insertion of the side-on co-ordinated olefin into the Rh–B instead of the Rh–H bond was favoured [156]. This alternative insertion of an olefin into metal–boron bonds was also reported from some experimental studies [85,157].

The metal-mediated hydroboration provides some advantages and useful synthetic completions with respect to the non-catalytic reaction [141–144]. For example, it allows for the use of less reactive or thermally sensitive boranes that are not suitable for hydroborations under non-catalytic conditions. Furthermore, in many cases the chemo-, regio-, and stereoselectivity may be reversed, which greatly increases the applicability of the hydroboration. It is thus possible to carry out the hydroboration of C=C double bonds even in the presence of keto groups, or to functionalise cyclohexenone derivatives in the 3-position; in the latter case, non-catalysed reactions lead to boration in 2-position. Chiral complexes allow for stereoselective reactions even with achiral boranes, and the use of optically active material can be restricted to the relatively small amount of catalyst required. Very recently, it was demonstrated that the catalytic hydroboration is similarly successful under heterogeneous conditions. That was achieved by introducing $P[CH_2CH_2(CF_2)_nCF_3]_3$ ligands to the Wilkinson's catalyst and corresponding reactions in fluorous biphase systems [158].

Although to a lesser extent, low-valent complexes of iridium [64], palladium [159], and nickel [160] were also investigated with respect to their possible catalytic activities, and a similar mechanism was suggested for the hydroboration in these cases.

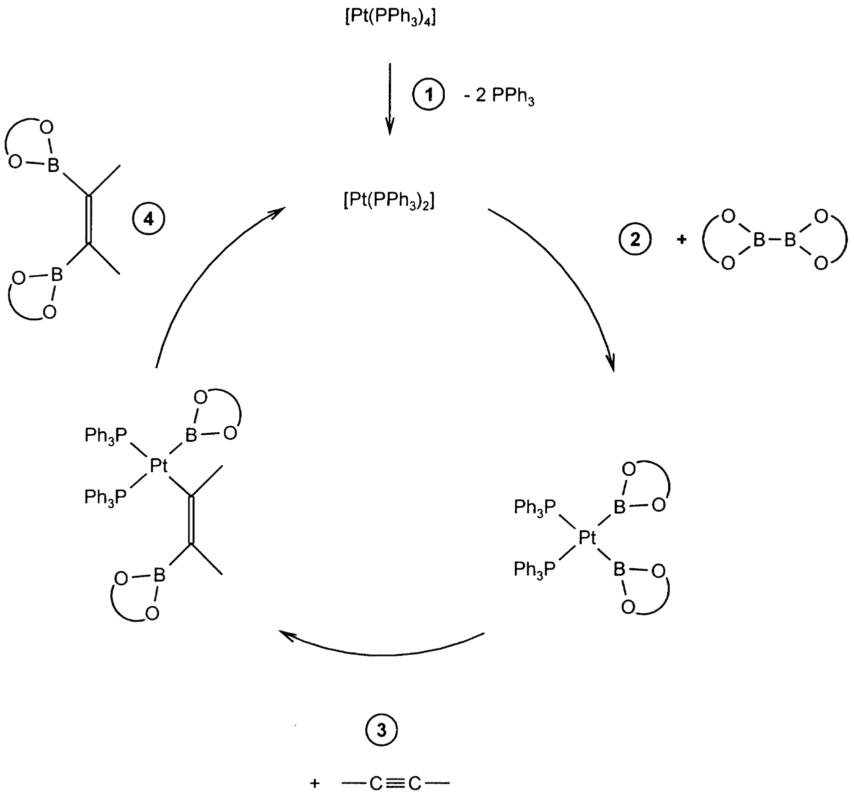
It should be noted that the formation of an intermediate boryl complex is not observed for all metal-mediated hydroborations of unsaturated organic molecules. There are certain cases where the borane adds directly to the co-ordinated multiple bond system rather than to the metal centre itself. Examples include the hydroboration of alkenes and alkynes in the presence of lanthanum [161], titanium [162,163] or zirconium [164,165], and the hydroboration of imines with copper, silver or gold complexes as catalysts [166].

Closely related to the metal-mediated hydroboration, are corresponding additions of boranes with B–B, B–Si, B–Sn, and B–S bonds, respectively, to unsaturated hydrocarbons. For the platinum-catalysed boroboration of alkenes and alkynes with B_2Cat_2 or B_2Pin_2, a mechanism according to Scheme 9 was suggested [57,64,166]. Similar to the hydroboration, this catalytic cycle involves the oxidative addition of the boron–boron bond to the metal centre (step 2), insertion of the incoming alkyne into one metal–boron bond (step 3), and reductive elimination of the bisborylalkene (step 4).

So far, various combinations of diboranes(4) or heteroboranes and transition metal catalysts were successfully applied to the functionalisation of organic molecules. Examples include the following reactions (boron–element bond/organic substrate/transition metal): B–B/vinylarenes/Rh and Au [167], B–B/1,3-dienes/Pt [66], B–B/ketimines/Rh [168], B–Si/alkynes/Pd and Pt [169], B–Si/diynes/Pd [170], B–Si/alkenes/Pt [171], B–Si/1,2-dienes/Pd [172], B–Sn/alkynes/Pd and Pt [173], B–Sn/diynes/Pd [60], B–Sn/1,2-dienes/Pd [172], B–S/alkynes/Pd and Pt [60]. Although the non-catalysed boroboration of multiple bonds was known before, it is restricted to highly reactive tetrahalodiboranes(4) [145,174]. The metal-mediated boroboration allows now for the use of tetraaryloxydiboranes(4), which are less reactive, and hence much more convenient in synthesis and handling.

3.3.2. Reactions of boryl complexes

As pointed out in Section 3.2.1, the strength of a metal–boron bond in boryl complexes may well exceed that of a metal–carbon bond, as far as homolytic dissociation is concerned. The broad applicability of the metal-catalysed hydroboration and its related reactions, however, is based on the facile cleavage of metal–boron bonds, thus giving evidence for their kinetic lability [54]. Many



Scheme 9. Mechanism for the transition metal-catalysed boroboration of olefins.

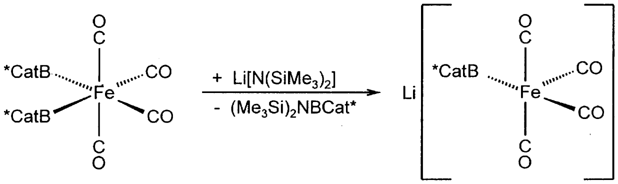
reactions of boryl complexes thus occur with cleavage of the metal–boron linkage. As far as phosphanes and similar Lewis bases are concerned, however, they may well undergo additions to or substitutions at the metal centre with retention of the boryl ligand. The substitution of metal-bound carbonyl or phosphane ligands by mono- or bidentate phosphanes, for example, was reported for many boryl complexes of tungsten [101], manganese [125], iron [138], rhodium [60,157], and platinum [64,68]. Corresponding additions of neutral Lewis bases such as carbonyl or isonitriles to metal centres were especially observed in the case of fivefold co-ordinated and hence, unsaturated boryl complexes of ruthenium and osmium [132].

Reactions of boryl complexes with protic reagents such as water, alcohols, amines, and HCl proceed, apart from very few exceptions (vide infra) with cleavage of the metal–boron bond and formation of oxy-, amino- and chloroboranes. Such protolytic cleavage reactions were reported for boryl complexes of tungsten [52,53], iron [54,104], and rhodium [60]. Few examples for reactions of iron boryl complexes with non-polar reagents such as H_2 or Br_2 are known, also occurring with cleavage of the metal–boron bond and formation of the corresponding boranes and bromoboranes, respectively [103,104].

Several experimental studies addressed the question, whether the substitution of a metal co-ordinated boryl ligand by another boryl- or stannyl group occurs via σ-bond metathesis. Corresponding reactions were carried out with diboranes(4) and distannanes and boryl complexes of rhodium [59] and platinum [63,64,175].

The chemistry of transition metal complexes of boron although being generally extensive and versatile, displays a certain lack with respect to reactions at the metal co-ordinated boron atom with retention of the metal–boron linkage. Only one boryl complex and one bridged borylene complex (vide infra) are known to undergo such reactions. Typically, both compounds show boron–chloride bonds that are easily available to substitution reactions. $[Cl_2BOsCl(CO)(PPh_3)_2]$ (**64**), which is besides *cis*-$[(F_2B)_2Pt(PPh_3)_2]$ (**38**) and $[Cp^*IrH(BF_2)(PMe_3)]$ (**112**), the only dihaloboryl species, undergoes clean reactions with alcohols and secondary amines yielding products of the type $[\{(RO)_2B\}OsCl(CO)PPh_3)_2]$ and $[\{(R_2N)_2B\}OsCl(CO)PPh_3)_2]$, respectively, with elimination of HCl and retention of the metal–boron bond [132].

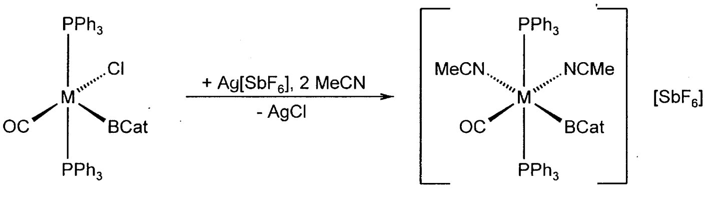
Two reactions of boryl complexes are especially noteworthy, since they gave access to the first charged species of this compound type. According to Eq. (22), the bisboryl complex *cis*-$[(Cat^*B)_2Fe(CO)_4]$ (**8**) reacts with a bulky lithium amide with formation of the anionic boryl complex $Li[Cat^*BFe(CO)_4]$ (**124**) and cleavage of the corresponding aminoborane [54].



8 **124**

(22)

Upon treatment with $Ag[SbF_6]$ in acetonitrile, the fivefold co-ordinated ruthenium complex $[CatBRuCl(CO)(PPh_3)_2]$ (**52**) yields the six co-ordinated cationic compound $[CatBRu(CO)(MeCN)_2(PPh_3)_2]$ $[SbF_6]$ (**130**) with addition of two molecules of acetonitrile and elimination of AgCl (Eq. (23)) [29]. Correspondingly, the osmium analogue $[CatBOs(CO)(MeCN)_2(PPh_3)_2]$ (**131**) was obtained from $[CatBOsCl(CO)PPh_3)_2]$ (**59**) [131].



52, M = Ru
59, M = Os

130, M = Ru
131, M = Os

(23)

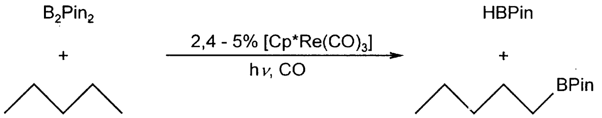
3.3.3. C–H activation by boryl complexes

Besides the metal-mediated hydroboration, boryl complexes were more recently reported to provide an alternative functionalisation of hydrocarbons. Photolysis of certain boryl complexes in the presence of the organic substrate leads to C–H activation with formation of the corresponding borylated hydrocarbon. The catecholboryl complexes [CatBMn(CO)$_5$] (**91**), [CatBRe(CO)$_5$] (**92**), and [CpFe(B-Cat)(CO)$_2$] (**93**) convert benzene into PhBCat upon irradiation according to Eq. (24) with formation of the corresponding dinuclear carbonyl complexes. In this case, the iron complex **93** proved to yield 100% of PhBCat, while reactions of **91** and **92** were accompanied by the formation of boron-containing side products [103,138].

$$[L_xM\text{-}BCat] \xrightarrow{h\nu,\ C_6H_6} \begin{array}{c} CatBPh \\ + \\ [(L_xM)_2] \end{array}$$

$$\begin{array}{rl} L_xM & = CpFe(CO)_2 \\ & = Mn(CO)_5 \\ & = Re(CO)_5 \end{array} \qquad (24)$$

Similar photolyses of those boryl complexes in 1-hexene gave terminal hexenylboronate esters $C_4H_9CH{=}C(H)BCat$ as the major product together with smaller amounts of the saturated hexylboranate ester $C_6H_{13}BCat$. Mechanistic investigations on the aforementioned arene and alkene functionalisation rule out a radical reaction involving a homolytic cleavage of the metal–boron bond. Most likely, the reaction is induced by photochemical cleavage of a carbonyl ligand [138]. The corresponding C–H activation of alkanes by boryl complexes is of certain interest, since there are only very few examples for complexes which simultaneously activate and functionalise unreactive hydrocarbons [176,177]. [Cp*W(B-1,2-O_2-3,5-$Me_2C_6H_2$)(CO)$_3$] yields, upon photolysis in pentane, the corresponding alkylboronate ester C_5H_{11}(B-1,2-O_2-3,5-$Me_2C_6H_2$) in 85% with selective addition of the boryl group in the terminal position of the alkane. The corresponding iron- and ruthenium complexes were reported to be similarly reactive, however less efficient [101]. Very recently, even a corresponding catalytic process was reported. Irradiation of B_2Pin_2 in pentane under an atmosphere of CO and in the presence of catalytic amounts of [Cp*Re(CO)$_3$] yielded $C_5H_{11}BPin$ in 95% again by selective addition of the boryl group in terminal position of the alkane (Eq. (25)). For this reaction, a mechanism was suggested involving photochemically induced cleavage of one carbonyl group and oxidative addition of the boron–boron bond to the rhenium centre [178].



(25)

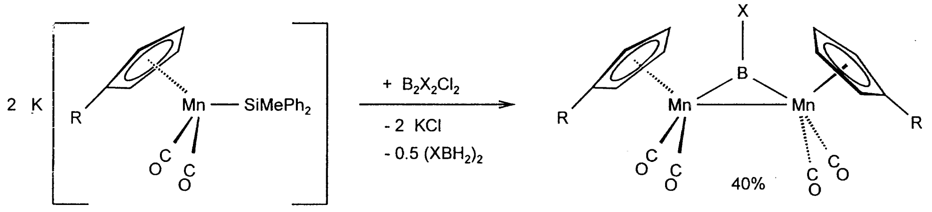
4. Borylene complexes

Two different co-ordination modes of borylene ligands BR to transition metal centres are possible: the BR moiety may either adopt a bridging position between two metal centres with a threefold co-ordinated boron, or alternatively, the borylene may bind terminally to one metal atom, thus showing boron in co-ordination number two. Both bridging and terminal borylene complexes were realised only very recently, and are in comparison to boryl complexes far less numerous. The first examples of such compounds were already reported in the 1960s [32], however, as in the case of boryl complexes, without structural evidence. Spectroscopic data, especially ^{11}B-NMR shifts are in strong contrast to those of recently characterised borylene complexes, thus disproving the earlier proposed constitutions. Although being still rare, borylene complexes have attracted considerable interest [180–182], and have been subject to various theoretical studies which addressed especially the nature of the metal–boron linkage in terminal borylene complexes (vide infra).

4.1. Bridged borylene complexes

4.1.1. Synthesis

4.1.1.1. From diboranes(4). The first formation of bridged borylene complexes resulted from an unexpected and unprecedented reaction of various 1,2-dihalodiboranes(4) with K[(C_5H_4R)Mn($SiMePh_2$)$(CO)_2$] (R = H, Me) according to Eq. (26).



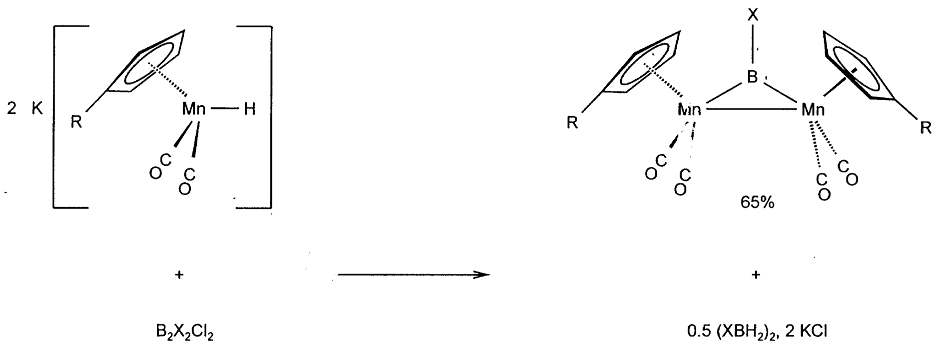
132a, b R = H, Me; X = NMe$_2$

132c R = Me; X = *t*Bu

(26)

Previous studies always reported diboranes(4) to undergo oxidative additions with suitable precursor complexes, yielding bisboryl complexes, and to a lesser extent, boryl- and trisboryl complexes [53–55,58–65] (see Section 3.1.1), and subsequently, salt elimination reactions of 1,2-dihalodiboranes(4) with anionic transition metal compounds were reported, which led to the formation of diborane(4)yl complexes with retention of the boron–boron linkage [99,100,107,115] (see Section 3.3.2). The dinuclear borylene complexes [μ-B(NMe_2){CpMn$(CO)_2$}$_2$]

(**132a**), [μ-B(NMe$_2$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132b**), and [μ-B*t*-Bu{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132c**), however, were formed with cleavage of the boron–boron bond and co-ordination of the borylene ligand to two metal centres. This reaction was accompanied by the formation of corresponding diborane(6) derivatives (XBH$_2$)$_2$ (R = NMe$_2$, *t*-Bu); the origin of the hydrogen and the fate of the metal-bound silyl group, however, remained unclear [183]. An improved synthesis yielding **132a–c** in higher yields as products of a stoichiometric reaction was reported for similar reactions with the corresponding anionic manganese hydride complex K[(C$_5$H$_4$R)MnH(CO)$_2$] (Eq. (27)) [184].



132a, b R = H, Me; X = NMe$_2$

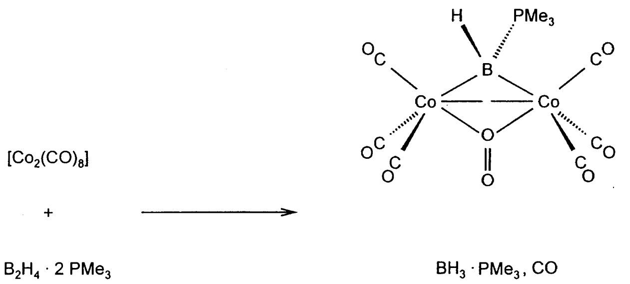
132c R = Me; X = *t*Bu

132d, e R = Me; X = N(C$_4$H$_8$)$_2$, N(C$_5$H$_{10}$)$_2$

(27)

In this case, a hydrogen transfer from manganese to boron occurred and resulted in the formation of the diboranes(6). Further studies have shown that the cleavage of the boron–boron bond in the starting diboranes(4) decisively contributes to the formation of the borylene complexes **132a–c**, as no products with B–Mn bonds were formed when monoboranes RBCl$_2$ were used [184]. Recently, two further borylene complexes [μ-B(NC$_4$H$_8$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132d**) and [μ-B(NC$_5$H$_{10}$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132e**) were reported, being obtained by the latter improved method from K[(C$_5$H$_4$Me)MnH(CO)$_2$] and the diboranes(4) B$_2$X$_2$Cl$_2$ (X = N(C$_4$H$_8$)$_2$, N(C$_5$H$_{10}$)$_2$) (Eq. (27)) [107].

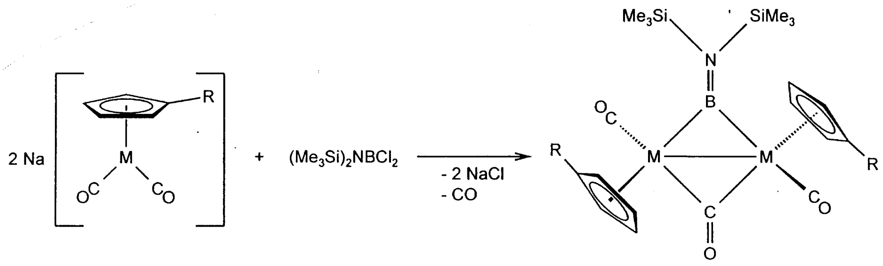
Another approach to bridged borylene complexes was succeeded by in 1998 [185]. By using [Co$_2$(CO)$_8$] and B$_2$H$_4$ · 2PMe$_3$ as starting materials, the cobalt borylene complex [μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**133**) is formed in a similar cleavage reaction of a diborane(4). The fragmentation of the 1,2-bis(trimethylphosphane)diborane(4) into BH$_3$ · PMe$_3$ and BH · PMe$_3$ and liberation of one CO group led to **133** (Eq. (28)), representing the only example of a donor-stabilised bridged borylene complex.



133

(28)

4.1.1.2. From monoboranes. The aforementioned syntheses of dinuclear borylene complexes are very specific and restricted to the two examples discussed. In order to gain a more general access to bridged borylene complexes, the reactions of aminodihaloboranes with anionic transition metal compounds in a 1:2 ratio were investigated. According to Eq. (29), the bridged borylene complexes [μ-B{N(SiMe$_3$)$_2$}(μ-CO){(C$_5$H$_4$R)Fe(CO)}$_2$] (**134a**, R = H; **134b**, R = Me) [105] and [μ-B{N(SiMe$_3$)$_2$}(μ-CO){CpRu(CO)}$_2$] (**135**) [106] were obtained from (Me$_3$Si)$_2$NBCl$_2$ and Na[(η^5-C$_5$H$_4$R)M(CO)$_2$] (M = Fe, R = H, Me; M = Ru, R = H) with salt elimination and loss of one carbonyl group.



(29)

134a, b R = H, Me; M = Fe
135 R = H; M = Ru

The formation of the iron borylene complexes **134a**, **b** was observed under all conditions, while the formation of the corresponding ruthenium complex **135** depends on the reaction conditions and stoichiometry employed, such as only an excess of Na[(η^5-C$_5$H$_5$)Ru(CO)$_2$] and slow addition of the borane led to **135** as the sole product. Interestingly, sterically less demanding aminodichloroboranes such as Me$_2$NBCl$_2$ reacted in both cases with substitution of only one boron-bonded chloride and formation of the corresponding boryl complexes (see Section 3.1.2). This result was attributed to the electron-withdrawing effect of the silyl group, which in the case of (Me$_3$Si)$_2$NBCl$_2$ makes the boron centre more electrophilic and hence, more reactive [105,106].

4.1.2. Structure

Due to the formation of two metal–boron bonds, all bridged borylene complexes show characteristically deshielded ^{11}B-NMR signals. In the case of (amino)borylene complexes **132a**, **b**, **d**, **e**, **134a**, **b**, and **135**, where a B–N π-bonding component is expected, low-field shifted ^{11}B-NMR signals in the range of $\delta = 100-120$ are observed (Table 2). For the (*tert*-butyl)borylene complex **132c**, which is free of boron–ligand π-interaction, an even stronger deshielded signal is observed at $\delta = 170.0$. The good agreement between the CO stretching frequencies (and structural data, vide infra) of these bridged borylene complexes and those of corresponding μ-methylene complexes [186–188], supports their description as dimetallaboriranes. The NMR data of the dinuclear cobalt borylene complex **133** indicate a different constitution with respect to the compounds mentioned above. The ^{11}B-NMR signal at $\delta = 17.5$ is significantly high-field shifted which is an

Table 2
Borylene complexes and base adducts of borylene complexes

Compound	Synthesis	*d*(M–B) (pm)	δ ^{11}B	Ref.
[μ-B(NMe$_2$){CpMn(CO)$_2$}$_2$] (**132a**)	b	203(1)	103.0	183
[μ-B(NMe$_2$){CpMn(CO)$_2$}$_2$] (**132a**)	–	204.9 [a]	y	192
[μ-B(NMe$_2$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132b**)	b	x	102.8	183
[μ-B(*t*-Bu){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132c**)	b	x	170.0	183
[μ-B(NC$_4$H$_8$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132d**)	b	x	100.3	107
[μ-B(NC$_5$H$_{10}$){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**132e**)	b	x	101.1	107
[μ-BH(PMe$_3$)(μ-CO){Co(CO)$_3$}$_2$] (**133**)	b	211.2(9) 210.8(11)	17.5	185
[μ-B{N(SiMe$_3$)$_2$}(μ-CO){CpFe(CO)}$_2$] (**134a**)	a	x	118.4	105
[μ-B{N(SiMe$_3$)$_2$}(μ-CO){(C$_5$H$_4$Me)Fe(CO)}$_2$] (**134b**)	a	200.7(3) 200.2(3)	119.1	105
[μ-B{N(SiMe$_3$)$_2$}(μ-CO){CpRu(CO)}$_2$] (**135**)	a	x	105.9	106
[μ-BCl{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**136**)	c	x	133.5	193
[μ-B(NH*t*-Bu){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**137a**)	c	x	102.4	193
[μ-B(NHPh){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**137b**)	c	x	107.6	193
[μ-B(OMe){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**137c**)	c	x	98.8	193
[μ-B(OEt){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**137d**)	c	198.8(2) 202.1(2)	97.6	193
[μ-B(OH){(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$] (**137e**)	c	x	101.6	193
[(CO)$_5$Cr{BN(SiMe$_3$)$_2$}] (**139a**)	a	x	92.3	181
[(CO)$_5$W{BN(SiMe$_3$)$_2$}] (**139b**)	a	215.1(7)	86.6	181
[(CO)$_4$FeBN(SiMe$_3$)$_2$] (**139c**)	a	x	88.2	181
[(CO)$_5$W{BN(SiH$_3$)$_2$}] (**139d**)	–	215.2 [a]	y	199, 200
[(η^5-Me$_5$C$_5$)BFe(CO)$_4$] (**140**)	a	201.0(3)	−35.3	197
[(η5-Cp)BFe(CO)4]	–	196.2 [a]	y	199, 200
[Os(=BNHC$_9$H$_6$N)Cl$_2$(CO)(PPh$_3$)$_2$] (**141a**)	c	x	y	202
[Os(=BNHC$_9$H$_6$N)ClI(CO)(PPh$_3$)$_2$] (**141b**)	c	205.5(8)	51.7	202

a: From monoboranes; b: from diboranes(4); c: other method; x: no X-ray data available; y: no ^{11}B-NMR data available.

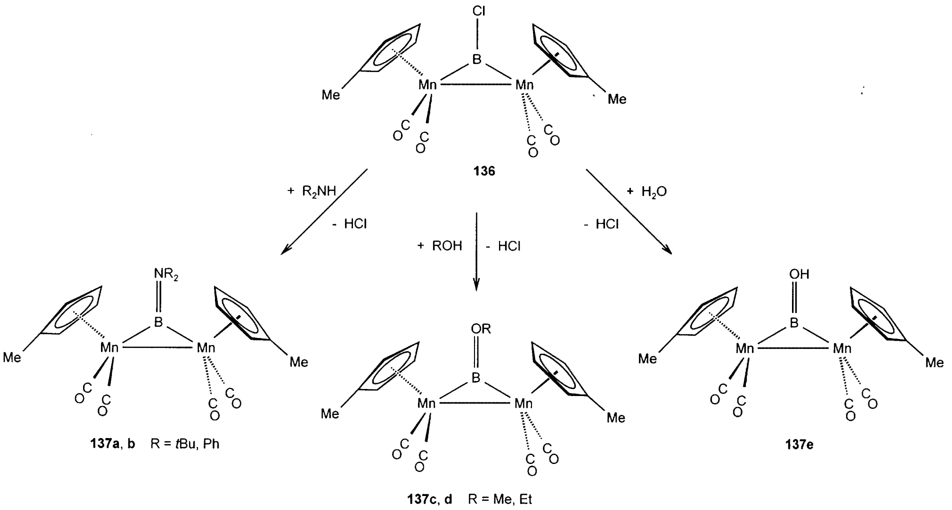
[a] Geometry from ab initio calculation.

expected result for complexes bridged by borylene–Lewis base adduct ligands containing boron in the co-ordination number four.

The results of the X-ray structure analyses of **132a** and **134b** show that these molecules adopt approximate C_2 symmetry in the crystalline state. In both cases, the metal atoms and boron form an isosceles triangle with metal–metal and metal–boron distances (Table 2) which are in the expected range for corresponding single bonds. In **132a**, the Me_2N group and the central Mn_2B three-membered ring are almost co-planar and the B–N distance of 139.0 pm is characteristic for a B=N double bond. Due to the bulky $(Me_3Si)_2N$ group in **134b**, however, the Si_2B plane is more twisted with respect to the Fe_2B plane. Hence, in connection with the extended B–N distance of 141.2 pm, a less effective backbonding from the nitrogen to the boron atom can be assumed. The overall molecular structure data resemble those of the isoelectronic vinylidene manganese [189] and iron complexes [190], respectively, which can be considered as dimetallacyclopropane derivatives.

The X-ray structure analysis of **133** shows boron to adopt a pyramidal geometry induced by the co-ordination of the lone electron pair of the trimethylphosphine phosphorous atom to the borylene ligand. Probably due to the steric demand of PMe_3, the ideal tetrahedron is not formed. The Co–B bond lenghts of **133** range as expected, between those in the boryl complex $[Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm} \cdot BH_2)]$ (**120**) [119] (222.7 pm) and those in cobaltaborane clusters with μ_3-BH ligands $[\{(C_5Me_5)Co\}_3(\mu\text{-H})_2(\mu_3\text{-BH})_2]$ [191] (201.3 and 198.5 pm, respectively).

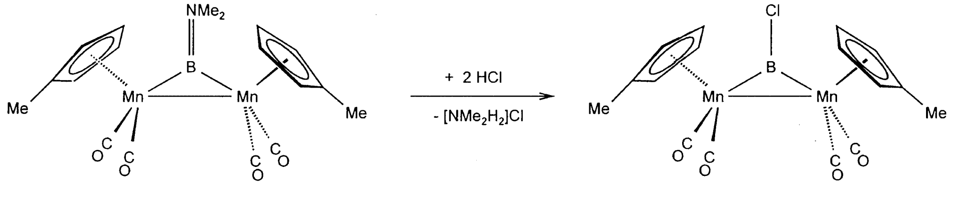
Recently, **132a** was the object of theoretical investigations concerning the metal-binding capabilities of a series of borylene ligands BX ($BX = BF$, BNH_2, BO^-) which are isolobal to CO [192]. The theoretically predicted and the experimentally derived structural parameters were found to be in very good agreement (Table 2). From density-functional theoretical studies, it occurred that borylenes BX, co-ordinating through boron, can be viable ligands in the design of transition metal complexes being thermodynamically stable with respect to a homolytic metal–boron bond dissociation. On the one hand, the high thermodynamic stability is traced 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 a 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 leads to a positive charge on BX and advances nucleophilic attack. In the complex **132a**, 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 bulky methyl substituents. The binuclear $Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ fragment reduces also the build-up of positive charge at $BNMe_2$, as 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.



Scheme 10. Reactions of bridged borylene complexes [μ-BX{(C_5H_4Me)Mn$(CO)_2$}$_2$] with retention of the metal–boron bonds.

4.1.3. Reactions

4.1.3.1. Reactions with retention of the metal–boron bond. The (amino)borylene complexes **132a**, **b** showed, in correspondence with the results of theoretical investigations, significantly low reactivity against nucleophilic substitutions at the bridged boron atom. Consequently, they have high stability against both air and moisture for long periods. These compounds even can be obtained in high yields by an aqueous work-up of the reaction mixture under air [184]. The substitution of the boron-bonded amino group was achieved by the reaction of **132b** with an excess of HCl, giving the corresponding (chloro)borylene complex [μ-BCl{(C_5H_4Me)Mn-$(CO)_2$}$_2$] (**136**) (Eq. (30)) in high yields [193].



132b **136**

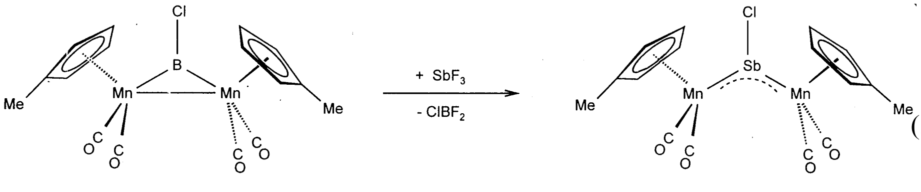
(30)

In agreement with the known properties of amino- and chloroboranes, **136** proved to be significantly more reactive than the amino derivative **132b** and served as starting material for further substitution reactions at the borylene bridge. Protic reagents such as primary amines, alcohol and water led to the corresponding substituted borylene complexes **137a**–**e** in good yields with elimination of HCl (Scheme 10) [193].

These products represented the first derivatives of transition metal complexes in general, which were obtained by substitution reactions at the boron atom with retention of the metal–boron linkage (see Section 3.3.3 for further examples). As expected, all spectroscopic and structural data of **136**, **137a**–**e** are in good agreement with those of **132a**, **b**. Reactions of the borylene complexes without cleavage of the metal–boron bond are interesting, as they open an access to various bridged borylene complexes, which cannot be obtained by the methods discussed in Section 4.1.1.

Additionally, it has to be mentioned that the dinuclear cobalt complex **133** undergoes substitution of two cobalt-bound CO ligands with PPh_3 and formation of the complex [μ-$BH(PMe_3)$(μ-CO){$Co(PPh_3)(CO)_2$}$_2$] which was characterised in solution [185].

4.1.3.2. Reactions with cleavage of the metal–boron bond. Recent investigations [179] showed some reactions of the (chloro)borylene complex **136** with cleavage of the Mn–B bonds. According to Eq. (31), the reaction with SbF_3 yields $ClBF_2$ and the chlorostibinidene complex [μ-SbCl{$(C_5H_4Me)Mn(CO)_2$}$_2$] (**138**), which was previously reported [194].



(31)

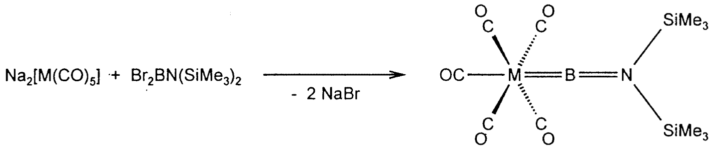
136 **138**

In contrast to the preceding reaction, by employing I_2 in the reaction with **136**, a complete decomposition of the dinuclear transition metal framework was observed and MnI_2 was found as the only isolated and characterised compound [179].

4.2. Terminal borylene complexes

A structurally authentic terminal borylene complex showing boron in co-ordination number two was reported in 1998 [181]. The reaction of $Na_2[M(CO)_5]$ with $Br_2BN(SiMe_3)_2$ gave the borylene complexes [$(CO)_5M${$BN(SiMe_3)_2$}] (**139a**, M = Cr; **139b**, M = W) by salt elimination (Eq. (32)). Both products show considerable stability in solution at ambient temperature and in the solid state. The corresponding iron complex [$(CO)_4FeBN(SiMe_3)_2$] (**139c**) was obtained similarly from $K_2[Fe(CO)_4]$ [181].

The ^{11}B-NMR signals of these terminal borylene complexes at $\delta = 92.3$ (**139a**), 86.8 (**139b**), and 88.2 (**139c**) are, compared to those of amino-substituted boryl complexes, substantially low-field shifted and close to the range observed for bridged (amino)borylene complexes. The IR spectra of these octahedral complexes display the expected three bands for the carbonyl groups that are considerably shifted to lower wavenumbers with respect to those of corresponding vinylidene complexes [195].

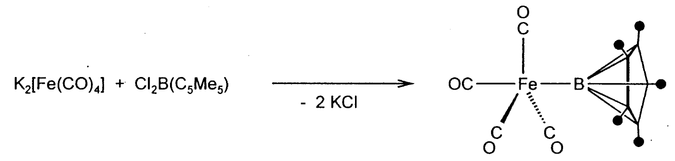


(32)

139a, M = Cr
139b, M = W

In the crystal, **139b** shows approximately C_{4v} symmetry for the $W(CO)_5$ moiety with C–W–C angles of about 90° and very similar W–C and C–O distances. The three central atoms are arranged almost linearly with an angle W–B–N of 177.9(5)°, and the W–B distance is 215.1(7) pm. Hence, it is shorter by about 22 pm than the W–B bond in the only structurally characterised amino-substituted boryl complex of tungsten $[(C_5H_5)(CO)_3W\{B(NMe_2)\text{-}BCl(NMe_2)\}]$ (**88**) [99] but 8 pm longer than that of the alkyl-substituted boryl complex $[(tpb')(CO)_2W\{BEt(CH_2\text{-}p\text{-}MeC_6H_4)\}]$ (tpb′ = tris(3,5-dimethylpyrazl-1-yl)hydroborate) [121]. The structural data give no evidence for a *trans* effect of the borylene ligand, and this, together with the IR data led to a description of the metal=boron double bond in terms of strong boron-to-metal σ-donation and weaker π-backbonding. For (amino)borylene complexes of first row transition metal complexes, this situation was predicted on the basis of ab initio calculations [192].

The first borylene complex $[(\eta^5\text{-}C_5Me_5B)Fe(CO)_4]$ (**140**) displaying a sterically demanding terminal-bound borylene ligand, too, was reported in 1998 [196]. The reaction of the dianion $K_2[Fe(CO)_4]$ and $Cl_2BC_5Me_5$ led via salt elimination to **140** (Eq. (33)), which in contrast to **139a**–**c** comprises a sixfold co-ordinated boron.



(33)

140

The ^{11}B-NMR shift at $\delta = -35.3$ is characteristic for apical boron atoms in *nido*-carboranes. The Fe–B distance in the crystal was determined to be 201.0(3) pm, which corresponds to an iron–boron single bond. The borylene ligand adopts an axial position and both boron and iron and the Cp-centre point are arranged in a linear fashion. Terminal borylene complexes were also subject to several theoretical studies [192,197–200], and especially the selected examples $[(CO)_5W\{BN(SiH_3)_2\}]$ (**139d**)and $[(\eta^5\text{-}CpB)Fe(CO)_4]$ (**140a**) were investigated as model compounds for the aforementioned complexes **139b** and **140**. 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 at the boron atom, for example, $N(SiMe_3)_2$ or η^5-C_5Me_5 [192]. The nature of the transition metal–boron bond in L_xMBR is obviously strongly influenced by the boron-bonded ligand R. Descriptions based on calculations range from an almost purely $RB \rightarrow TM$ σ-bonded model for R being a good π-donor, up to a strong $TM \rightarrow BR$ π-backdonation when R is a weaker π-donor [197–199]. However, very recent studies 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 [198,199].

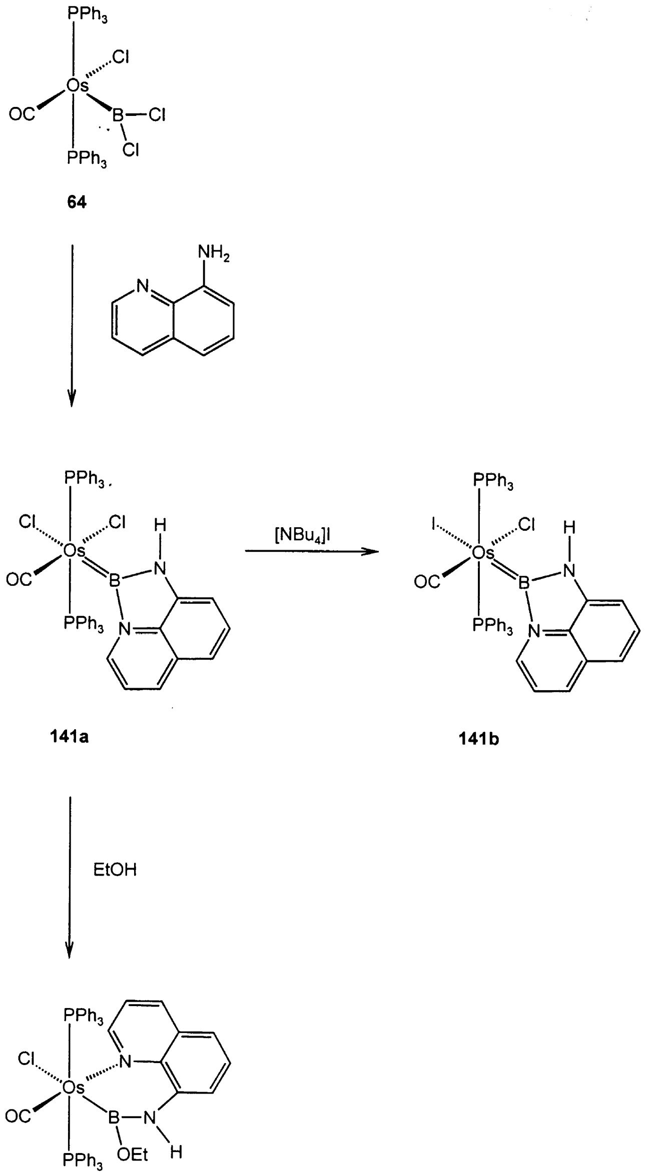
Recently, the first base-stabilised terminal borylene complex was reported [202]. The reaction of the boryl complex $[Cl_2BOsCl(CO)PPh_3)_2]$ (**64**) with 8-aminoquinoline yielded $[Os(=BNHC_9H_6N)Cl_2(CO)(PPh_3)_2]$ (**141a**) according to Scheme 11.

Subsequent treatment of **141a** with tetrabutylammonium iodide led to the corresponding borylene complex $[Os(=BNHC_9H_6N)ClI(CO)(PPh_3)_2]$ (**141b**), in which the chloro ligand *trans* to the boron atom is replaced by iodine, thus giving evidence for the *trans* influence of the borylene ligand. The better solubility of **141b** led to complete spectroscopic characterisation in solution. Due to the higher co-ordination number of boron, **141b** shows an ^{11}B signal at $\delta = 51.7$ which is shielded with respect to base-free terminal borylene complexes with twofold co-ordinated boron. In the crystal, an osmium–boron distance of 205.5(8) pm was found for **141b**, which is longer than an expected double bond. Corresponding findings were made for related base-stabilised silylene complexes [26,27,202].

Additionally, it has to be mentioned that the reaction of the complex **141a** with methanol leads to the structurally characterised ethoxy(amino)boryl complex $[\{B(OEt)NHC_9H_6N\}OsCl(CO)(PPh_3)_2]$ (**142**) (Scheme 11) and a shift of the quinoline nitrogen atom from the boron to the osmium atom is observed [201]. The reaction of **141a** with methanol indicates, that even the boron atom in base-stabilised borylene complexes shows some electrophilic character, which was predicted in a theoretical study [192].

5. Conclusions

Transition metal complexes of boron have been established over the past decade as a further class of compounds being characterised by direct metal–boron interactions. There are now a variety of synthetic methods at hand allowing for the preparation, and thus broader application of these compounds. In particular, boryl complexes have already proven to be valuable compounds for the functionalisation of organic molecules and the number of publications reporting metal-mediated hydroboration and related reactions is still growing fast. Obviously, transition metal complexes of boron are becoming rewarding targets with respect to both



Scheme 11. Formation and reaction of the terminal borylene complexes [Os(=BNHC$_9$H$_6$N)-ClX(CO)(PPh$_3$)$_2$] (**141a**, X = Cl; **141b**, X = I).

fundamental and applied organometallic chemistry. Novel compounds of this class, such as terminal borylene or borane complexes were realised only very recently, showing the ongoing effort and development in this area of research.

Acknowledgements

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