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Review

The chemistry of bridged borylene complexes

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Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

Abstract

The stabilisation of borylenes (BX, X = various ligands) in the sphere of a transition metal was achieved for the first time in the case of bridged borylene complexes of the type $[(L_xM)_2BX]$. These compounds are characterised by 2c–2e bonds between metal and boron, thus belonging to the class of transition metal complexes of boron. Over the past 5 years different synthetic approaches were made, yielding the first structurally authentic metal complexes with a bridging BX ligand. Their synthesis, structure and reactivity is the subject of this paper. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Iron; Manganese; Borylene complexes

1. Introduction

Combinations between boron and transition metals are rather unique with respect to their structural variety. The following classes of compounds with direct metal–boron interactions are known for decades: (1) transition metal borides consisting of almost 1000 examples in about 130 different structural types [1a–c]; (2) metalla- [2a–c] and metallacarbaboranes [3a–c] with several hundred examples; and (3) complexes with boron-containing π-ligands [4], which are less numerous, nevertheless exhibit a rich structural diversity. Much more recently, during the 1990s[1], a fourth class of such compounds was established, the transition metal complexes of boron, which has attracted considerable interest since then [6a–c]. In contrast to compounds (1)–(3) these complexes are characterised by 2c–2e bonds between metal and boron and can be systematically classified as borane (**I**), boryl (**II**), and bridged (**III**) as well as terminal (**IV**) borylene complexes (Scheme 1). Complexes **I** – containing boron in co-ordination number four – can be described as Lewis acid–base adducts between basic metal centres and acidic boranes BR_3. Boryl transition metal complexes **II** are characterised by a terminal σ-bonded boryl group BR_2 and the co-ordination number of boron is reduced to three. For the borylene ligand BR there are two possible co-ordination modes: either bridging between two metal centres (**III**) also containing three-co-ordinated boron, or terminal with formation of a metal–boron double bond (**IV**) and boron with co-ordination number two (see Fig. 1). Among compounds **I**–**IV** the bridged borylene complexes **III** are of some special relevance since they represent the first examples for the stabilisation of the borylene moiety B–R in the sphere of a transition metal. A survey of their chemistry shall be given here, including the most recent results.

2. Related compounds of other main group elements

In contrast to the bridged borylene complexes corresponding compounds of carbon are more numerous and longer known. $[\mu\text{-CH}_2((\eta^5\text{-C}_5H_4R)Mn(CO)_2)_2]$ (R = H,

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[1] Between 1963 and 1970 a substantial amount of such compounds was already described, however, without structural evidence. These results are reviewed in [5a]. The proposed constitution of these products was disproved to a great extent by recent findings. See for example: [5b–e].

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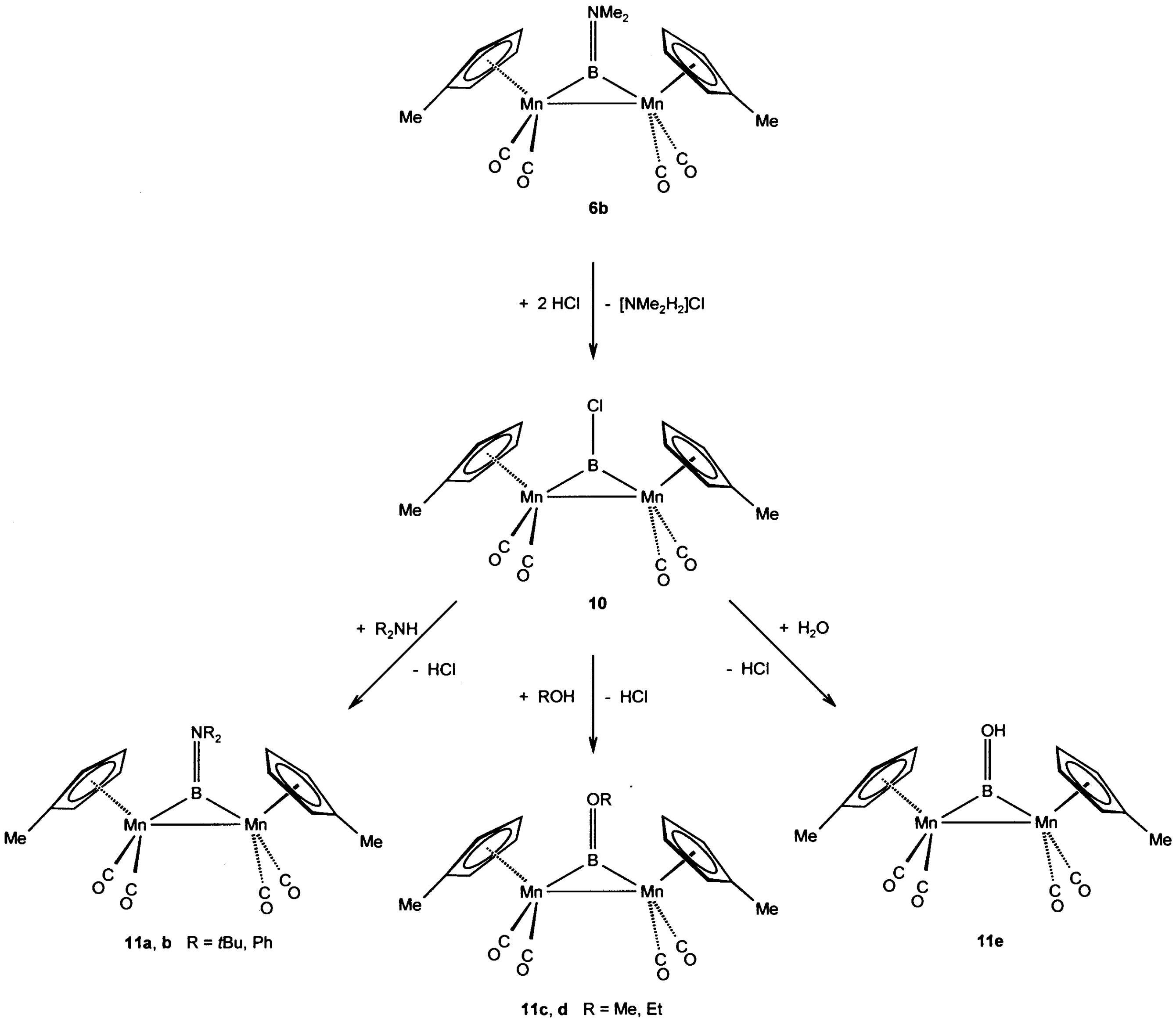
CH_3) (**1a**,**b**) the first methylene-bridged complexes were described in 1975. In contrast to the experience with the reactivity pattern of other diazoalkanes the low-temperature reaction of [(η^5-C_5H_4R)Mn$(CO)_2$THF] with diazomethane did not yield the expected mononuclear carbene complex, but the dinuclear CH_2-bridged compound **1** [7a,b]. In the following years several synthetic methods – for instance the diazo method as a direct and the carbene and acetylene path as indirect methods – have proven to form methylene-, alkylidene- and vinylidene-bridged complexes containing μ-CH_2, μ-CRR′, and μ-C=CH_2 ligands. Due to the bonding situation between the methylene group and the organometallic frame these compounds can be considered as dimetallacyclopropane derivatives [8].

The corresponding bridged silylene complexes – owing to the diagonal relationship in the periodic table, silicon shows some parallels to boron in its chemical behaviour – are far less common. For the compounds which are known today, two classes must be considered: first, SiR_2-bridged complexes lacking metal–metal interactions such as [(μ-SiH_2)$_2${(η^5-C_5H_5)Ti}$_2$] (**2**) [9] and, second, compounds with metal–metal bonds in addition to bridging silylene functionalities such as [μ-Si$(C_6H_5)_2$]$_2$[Mn$(CO)_4$]$_2$ (**3**) [10]. For example [μ-Si(H)CH_3][(η^5-C_5H_5)Fe$(CO)_2$]$_2$ (**4**), which is prepared in a clear-cut synthesis from its mononuclear precursor and Na[(η^5-C_5H_5)Fe$(CO)_2$], as one complex belonging to the first subgroup can be transferred into the silylene- and additionally CO-bridged compound [μ-Si(H)CH_3](μ-CO)[(η^5-C_5H_5)Fe(CO)]$_2$ (**5**) with an Fe–Fe bond by photochemical induced CO elimination [11].

Even compounds with the havier congeners of carbon and silicon in bridging positions are reported, strikingly, in higher number than the above described



Scheme 1. Substitution reactions at the metal co-ordinated borylene with retention of the metal–boron linkages.

μ-silylene complexes. All in all they are structurally similar to the latter, but there has to be mentioned an interesting fluxional behaviour specifically of the μ-(dialkyl)germylene complexes [8].

Transition metal complexes of the havier Group 13 metals Al, Ga and In are also known, but it is notable, that the examples from indium chemistry are dominant, followed by gallium, whereas the aluminium chemistry takes a special position. With concentration on the bridged complexes there are μ^2- and μ^3-bridged representatives known, which have been synthesised by various methods, such as pressure carbonylation, salt elimination and ligand substitution, in dependance of the selected metal combination. The majority of the described compounds contain metal carbonyl fragments $\{L(CO)_nM\}$ (L = CO, PR_3, Cp); complexes without CO ligands are extremely rare [12].

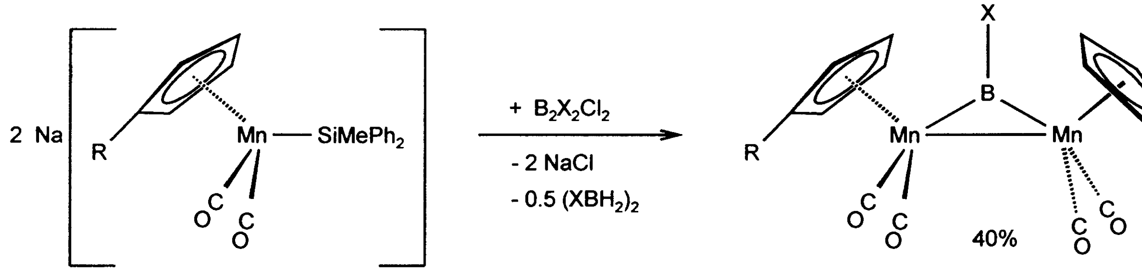
3. Synthesis

3.1. From diboranes(4)

First of all, the formation of bridged borylene complexes from diboranes(4) was really unexpected, because in previous studies these compounds generally underwent oxidative additions to metal centres giving mono-, bis- and trisboryl complexes [13a–k].

Nevertheless, in 1995 we synthesised the first dinuclear complexes **6a–c** with a bridging borylene ligand according to Eq. (1).

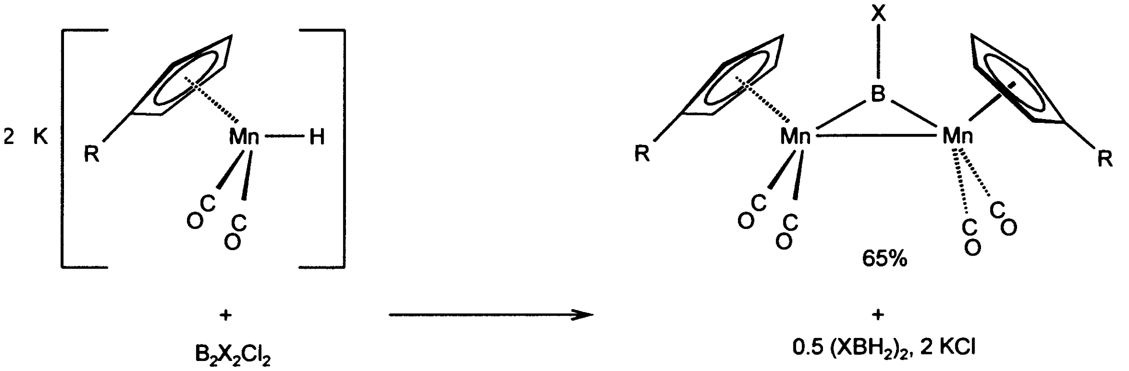
From this reaction we expected the formation of diborane(4)yl complexes, a group of compounds which was realised subsequently [14a–d]. However, reaction of the anionic manganese complex K[(η^5-C_5H_4R)Mn($SiMePh_2$)$(CO)_2$] (R = H, Me) with the diborane(4) derivatives $B_2X_2Cl_2$ (X = NMe_2, ^{t}Bu) surprisingly led to the diboranes(6) $(XBH_2)_2$ and the manganese borylene complexes [μ-BX{(η^5-C_5H_4R)Mn$(CO)_2$}$_2$] (**6a–c**) in yields of about 40% [15]. The stoichiometry of the reaction, the origin of the proton bonded to boron in the diborane(6) and the fate of the silyl group were unclear. Two years later this synthesis was improved significantly by employing the anionic manganese hydride complex K[(η^5-C_5H_4Me)MnH$(CO)_2$] as starting compound instead of the corresponding silyl complex. The reaction with the diborane(4) derivatives $B_2X_2Cl_2$ led stoichiometrically in considerably higher yields of more than 65% to the same products (Eq. (2)) [16].



(1)

6a, b R = H, Me; X = NMe_2

6c R = Me; X = *t*Bu



(2)

6a, b R = H, Me; X = NMe_2

6c R = Me; X = *t*Bu

6d, e R = Me; X = $N(C_4H_8)_2$, $N(C_5H_{10})_2$

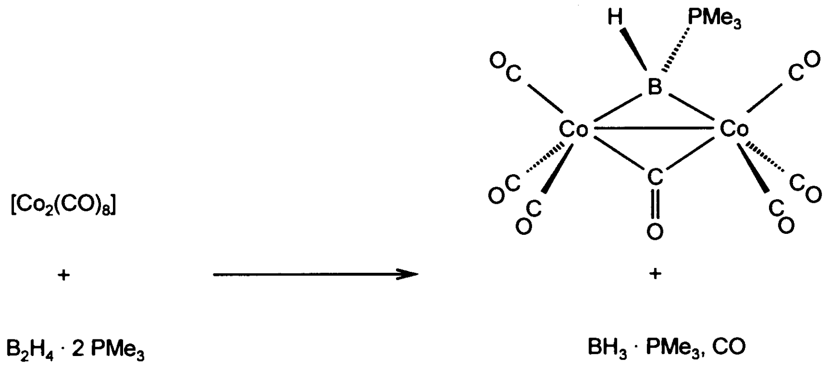
In this case, a hydrogen transfer from manganese to boron occurs and results in the formation of the diboranes(6). Further studies have shown that the cleavage of the boron–boron bond in the starting diboranes(4) decisively contributes to the formation of the borylene complexes **6a–c**, as no products with B-Mn bonds are formed when aminodichloroboranes are used [16]. Recently, two further examples **6d**,**e** were reported, being obtained by the latter improved method from $K[(C_5H_4R)MnH(CO)_2]$ and the diboranes(4) $B_2X_2Cl_2$ ($X = N(C_4H_8)_2$, $N(C_5H_{10})_2$) (Eq. (2)) [14d].

Another approach to bridged borylene complexes was achieved by Shimoi et al. in 1998 [17]. Starting from $[Co_2(CO)_8]$ and $B_2H_4{\cdot}2PMe_3$ the cobalt borylene complex $[\mu\text{-}BH(PMe_3)(\mu\text{-}CO)\{Co(CO)_3\}_2]$ (**7**) is formed in a similar cleavage reaction of a diborane(4). Via the fragmentation of the 1,2-bis(trimethylphosphane)diborane(4) into $BH_3{\cdot}PMe_3$ and $BH{\cdot}PMe_3$ and liberation of one CO, group **7** is obtained in 66% yield (Eq. (3)) representing the only example of a donor-stabilised borylene complex.

3.2. From monoboranes

The syntheses being described in Section 3.1 are very specific and restricted to the examples mentioned above. In order to gain a more general access to bridged borylene complexes we investigated the reactions of aminodihaloboranes with anionic transition metal compounds in a 1:2 ratio.

The first bridged complex which was obtained by this method is the dinuclear iron complex $[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_4R)Fe(CO)\}_2]$ (**8a**, R = H; **b** = Me) [18] followed by its ruthenium analogue $[\mu\text{-}B\{N(SiMe_3)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2]$ (**9**) [19]. Starting from $(Me_3Si)_2NBCl_2$ and $Na[(\eta^5\text{-}C_5H_4R)M(CO)_2]$ (M = Fe, R = H, Me; M = Ru, R = H) the metal–boron linkage is formed by nucleophilic substitution of the chloride ligand by the transition metal moiety and salt elimination. Additionally, with loss of one CO group from the initial anionic transition metal complex, the products are obtained in 25, respectively, 20% yield according to Eq. (4).



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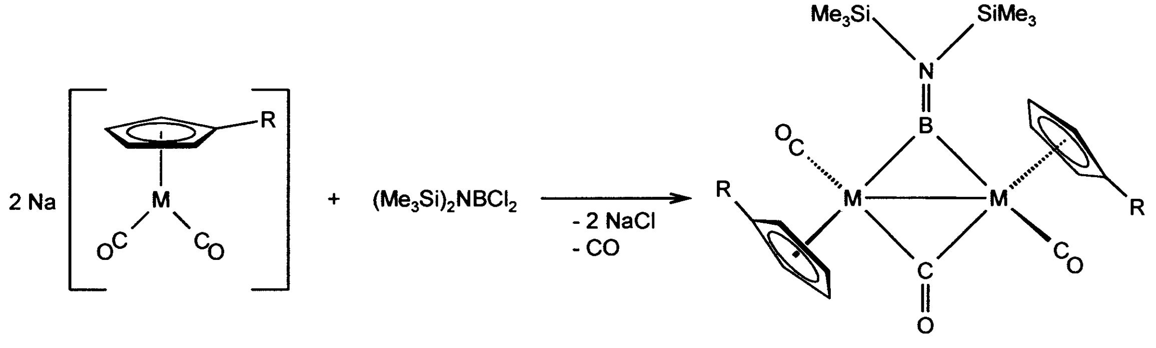
(3)



(4)

8a, **b** R = H, Me; M = Fe
9 R = H; M = Ru

Table 1
Spectroscopic and structural data of bridged borylene complexes

Compound no.	δ (^{11}B)	ν_{CO} (cm^{-1})	d (M–B) (pm)	d (M–M) (pm)	d (B–R) (pm)	d (B–L) (pm)	Ref.
6a	103.0	1960, 1917, 1883	203(1)	279.0(2)	139(1)	–	[14]
6a$_{calc}$	–	–	204.9	282.7	141.1	–	[23]
6c	170.0	1951, 1922, 1878	–	–	–	–	[14]
6d	100.3	1954, 1916, 1885	–	–	–	–	[13d]
6e	101.1	1955, 1917, 1887	–	–	–	–	[13d]
7	17.5	2080–1949, 1795	211.2(9), 210.8(11)	248.6(2)	102(7)	192.1(10)	[16]
8b	119.1	1925, 1770	200.7(3), 200.2(3)	254.8(1)	141.2(4)	–	[17]
9	105.9	1932, 1776	–	–	–	–	[18]
10	133.5	1969, 1941, 1912	–	–	–	–	[24]
11a	102.4	1932, 1921, 1852	–	–	–	–	[24]
11b	107.6	2025, 1943, 1927	–	–	–	–	[24]
11c	98.9	1978, 1930, 1900	–	–	–	–	[24]
11d	97.6	1978, 1937, 1910	198.8(2), 202.1(2)	281.75(5)	134.2(3)	–	[24]
11e	101.6	2018, 1969, 1926	–	–	–	–	[24]

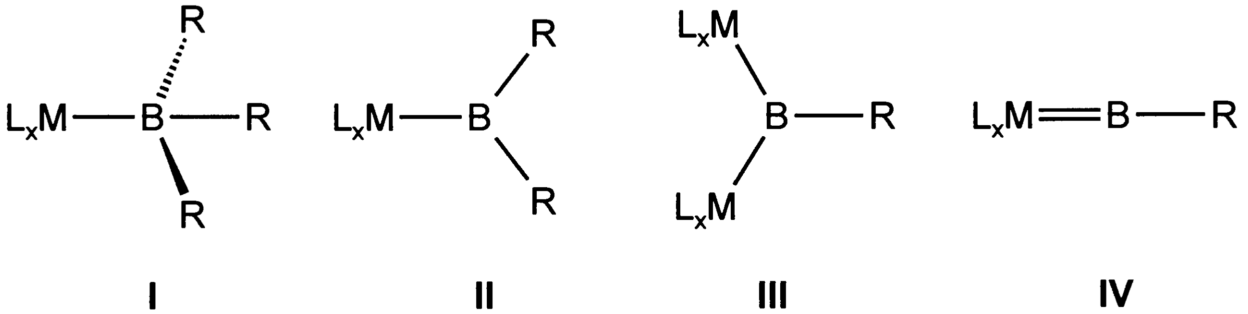


Fig. 1. Transition metal complexes of boron; borane- (**I**), boryl- (**II**), bridged borylene (**III**), and terminal borylene complexes (**IV**).

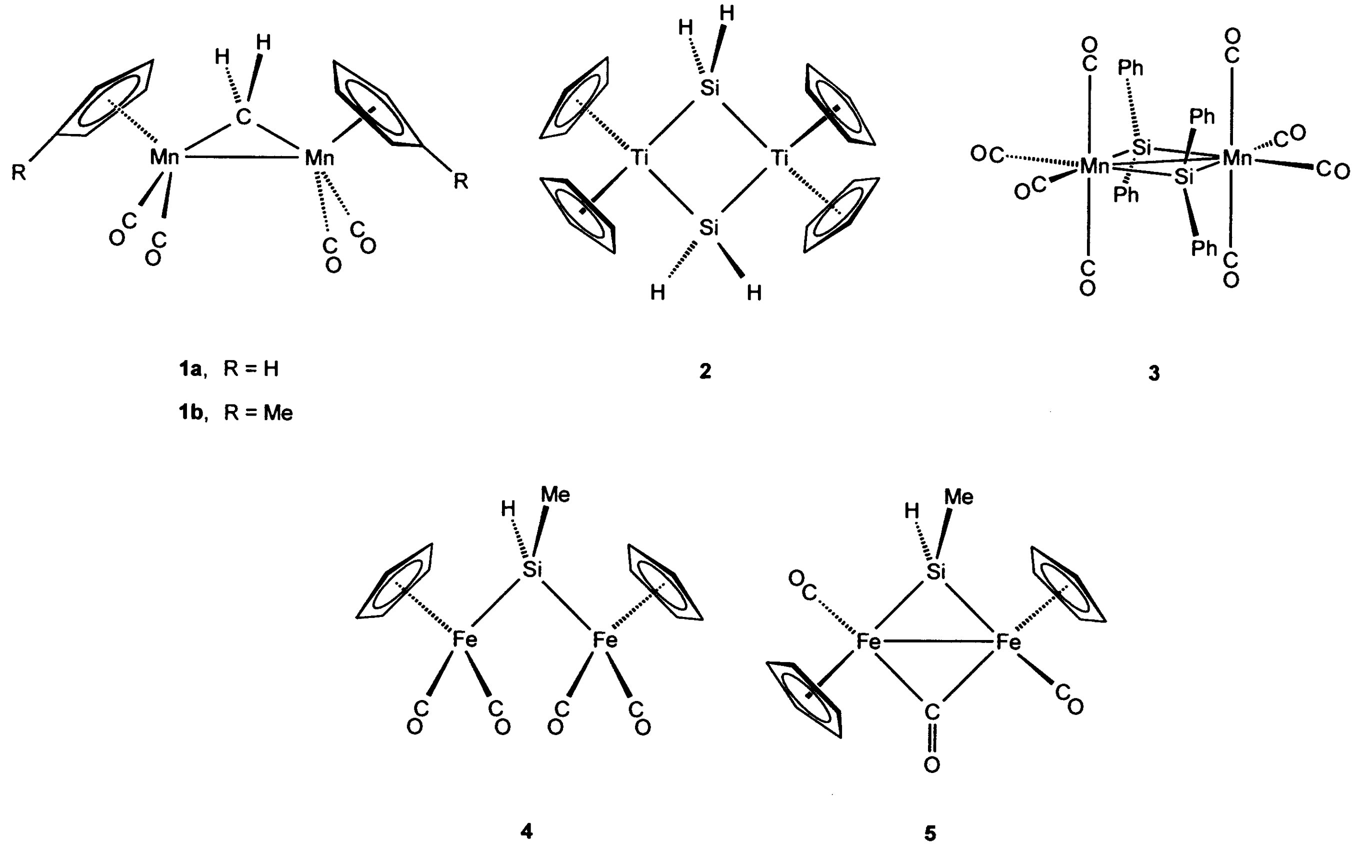
Interestingly, the formation of the iron borylene complexes **8a**,**b** is observed under all conditions, while the formation of the corresponding ruthenium complex **9** depends on the reaction conditions and stoichiometry employed, such as only an excess of Na[(η^5-C_5H_5)Ru(CO)$_2$] and slow addition of the borane leads to **9** as the sole product. Interestingly, in both cases the use of sterically less demanding aminodichloroboranes such as Me_2NBCl_2 leads to the formation of boryl complexes with substitution of only one boron bonded chloride. This result is attributed to the electron withdrawing effect of the silyl group, which in the case of $(Me_3Si)_2NBCl_2$ makes the boron centre more electrophilic and hence, more reactive.

4. Structures

The constitution of the borylene complexes **6**–**9** in solution was derived from multinuclear NMR and IR data. In the case of all (amino)borylene complexes **6a**,**b**,**d**,**e**, **8a**,**b**, and **9**, the B–N π-bonding component is expected. Despite this fact, low field shifted ^{11}B-NMR signals ranging from about $\delta = 100-120$ are observed (Table 1). This significant deshielding with respect to the signals of the starting boranes is characteristic for all transition metal complexes of boron [6a–c]. In the case of the (*tert*-butyl)borylene complex **6c**, which is free of boron–ligand π-interaction an even stronger deshielded signal is observed at $\delta = 170.0$. C_2 symmetry which is established in the solid state by single-crystal X-ray studies for **6a** and **8b**, respectively, also derives for all complexes in solution from ^{1}H- and ^{13}C-NMR data. The good agreement between the CO stretching frequencies (and structural data, vide infra) of these compounds and those of corresponding μ-methylene complexes [7a,b,8] supports their description as dimetallaboriranes.

The NMR data of the dinuclear cobalt borylene complex **7** indicate a different constitution with respect to the compounds mentioned above. The ^{11}B-NMR signal at $\delta = 17.5$ is shifted significantly highfield compared to the complexes containing boron in co-ordination number three. This is an 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 **6a** and **8b** (Figs. 2–4) 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 1) which are in the expected range for corresponding single bonds. In **6a** the Me_2N group and the central Mn_2B three-membered ring are almost coplanar 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 **8b**, 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



1a, R = H

1b, R = Me

2

3

4

5

Fig. 2. Bridged element diyl complexes of carbon and silicon.

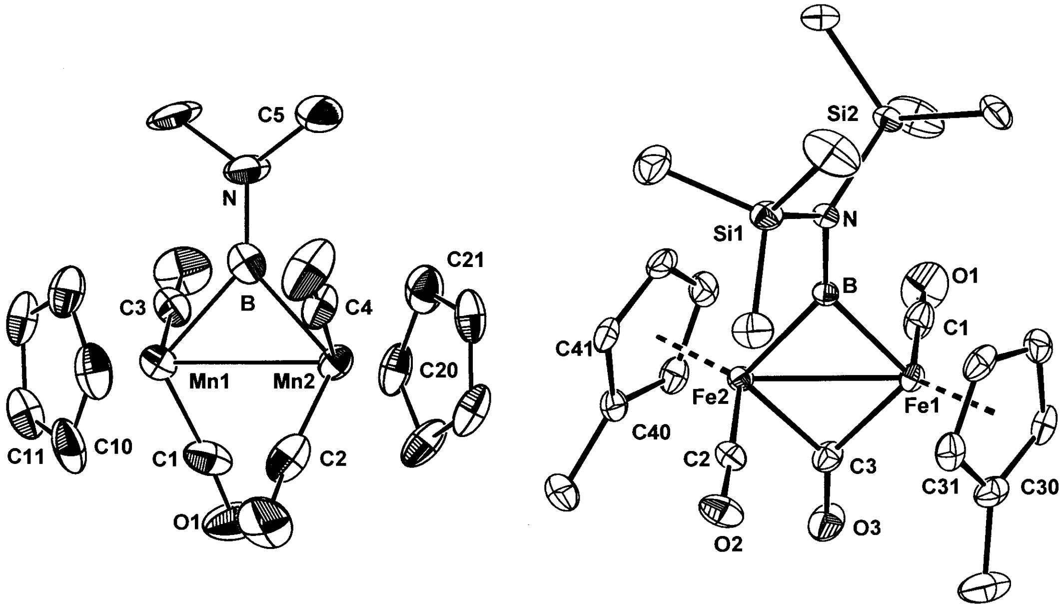


Fig. 3. Structures of **6b** and **8a** in the crystal.

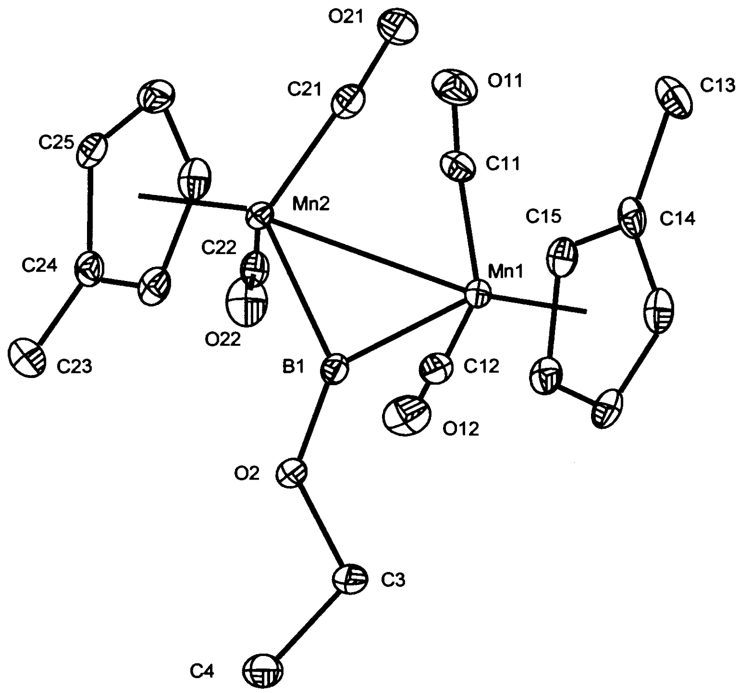


Fig. 4. Structure of **11d** in the crystal.

data resemble those of the isoelectronic vinylidene manganese [20] and iron complexes [21], respectively, which can be considered as dimetallacyclopropane derivatives.

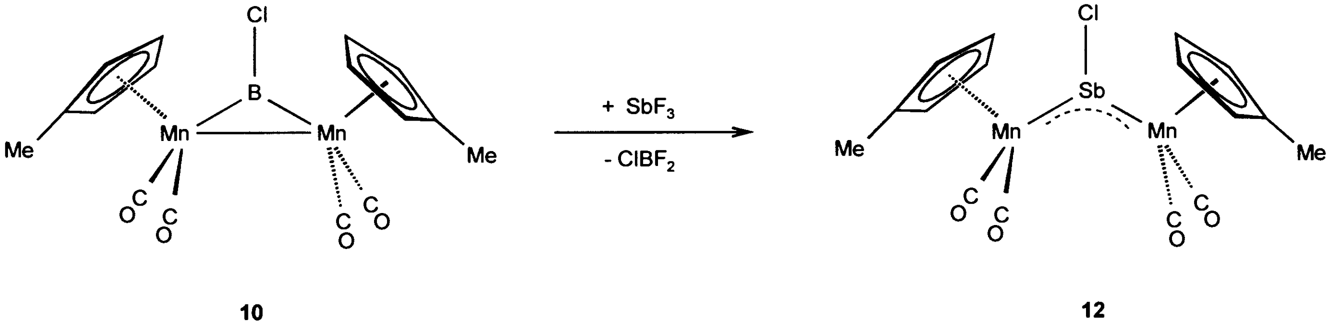
The X-ray structure analysis of **7** shows boron to adopt a pyramidal geometry induced by the co-ordination of the lone electron pair of the trimethylphosphine phosphorous atom to the borylene ligand. Probably due to the steric demand of PMe_3 the ideal tetrahedron is not formed. The Co–B bond lengths of **7** range as expected between those in the boryl complex $[Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm}\cdot BH_2)]$ [22] (222.7 pm) and those in cobaltaborane clusters with μ_3-borylene ligands $[\{(\eta^5\text{-}C_5Me_5)Co\}_3(\mu\text{-}H)_2(\mu_3\text{-}BH)_2]$ [23] (201.3 and 198.5 pm, respectively).

Recently **6a** was the object of theoretical investigations concerning the metal-binding capabilities of a series of borylene ligands BX ($BX = BF$, BNH_2, BO^-) isolobal to CO [24]. The theoretically predicted and the experimentally derived structural parameters were found to be in very good agreement (Table 1). From density-functional theoretical studies it occured 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 un-co-ordinated 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 **6a** 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 built-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.

5. Reactions

5.1. Reactions with retention of the metal–boron bond

The aminoborylene complexes **6a**,**b** show, in correspondence with the results of theoretical investigations, significantly low reactivity against nucleophilic substitutions at the bridged boron atom. As a consequence, they show high stability against both air and moisture for long periods. For example, these compounds can be obtained in high yields by an aqueous work-up of the reaction mixture under air [16]. Only



(5)

the reaction of **6b** with an excess of HCl leads to substitution of the amino group with formation of the corresponding chloroborylene complex [μ-BCl{(η^5-C_5H_4Me)$Mn(CO)_2$}$_2$] (**10**), which is isolated in high yields of about 75% [25]. In agreement with the known properties of amino- and chloroboranes, **10** proved to be significantly more reactive than the amino derivative **6b** and served as starting material for further substitution reactions at the borylene bridge. With protic reagents such as primary amines, alcohol and water, the corresponding substituted borylene complexes **11a**–**e** are formed in good yields with elimination of HCl (Scheme 1) [25]. These products represent 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. All products are characterised by multinuclear NMR methods in solution – ^{11}B-NMR shifts are given in Table 1 – and, in addition, the structure of the (ethoxy)borylene complex **11d** in solid state is determined by a single-crystal X-ray study (Table 2). As expected, all spectroscopic and structural data are in good agreement with those of **6a**,**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 3.

Additionally, it has to be mentioned that the dinuclear cobalt complex **7** undergoes substitution of two cobalt-bounded CO ligands with PPh_3 and formation of complex [μ-$BH(PMe_3)$(μ-CO){$Co(PPh_3)(CO)_2$}$_2$] [17]. This compound is characterised in solution and retention of the Co–B linkages was observed.

5.2. Reactions with cleavage of the metal–boron bond

Recent investigations [26] show some reactions of the chloroborylene complex **10** with cleavage of the Mn–B bonds. Reaction with SbF_3 yields $ClBF_2$ and the chlorostibinidene complex [μ-SbCl{(C_5H_4Me)-$Mn(CO)_2$}$_2$] (**12**) [27] are formed according to Eq. (5).

In contrast to the preceding reaction, by employing I_2 in the reaction with **10** a complete decomposition of the dinuclear transition metal frame is observed and MnI_2 as the only isolated and characterised compound is found [26].

6. Summary and outlook

In contrast to the well-developed chemistry of transition metal boryl complexes and bridged element diyl complexes of Al, Ga, In, C, Si, Ge, and Sn, examples of bridged borylene complexes are still very rare. This is obviously due to synthetic difficulties involved with their preparation. Initially, the access to these complexes was limited to the rather special and unexpected cleavage of diboranes(4), most recent results, however, show that salt elimination reactions starting from suitable dihaloboranes could find a wider scope of applicability here. All compounds being described here show as a common structural feature the presence of a central M_2B (M = transition metal) moiety with a metal–metal bond. The structural and spectroscopic findings suggest the description of bridged borylene complexes as dimetallaboriranes.

Future investigations on this subject are expected based on the interesting reactions of the few known representatives of this class described here.

Acknowledgements

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