Reactions at the Boron-Carbon Double Bond of Methyl(methylidene)boranes

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Abstract. The addition of Lewis bases L to the methyl(methylidene)boranes MeB=CA₂ (A = SiMe₃) and MeB=CAA' (A' = SiMe₂Cl) gives the adducts $MeB(L)=CA_2$ (1a, b; L = trimethylpyridine, PMe₃) and MeB(L)=CAA' (1c, d; L = di- and trimethylpyridine), respectively. Alcohols and amines HX are added to the BC double bond to give boranes $MeB(X)-CHA_2$ (8a-c; X = OiPr, OtBu, NiPr₂); MeB=CAA' and HNMe₂ react in the ratio 1:2, yielding $MeB(X)-CHA(SiMe_2X)$ (2d; $X = NMe_2$). From $MeB=CA_2$ and BH₃, five-membered the ring [-CA2-BH-CA2-BMe(Hm)2BMe-] (2e; 2:1) or the six-membered ring $[-CA_2-BH(H_{\mu})_2BMe-CA_2-BH(H_{\mu})_2BMe-]$ (2f; 1:1) are formed, both containing double hydrogen bridges; the product **2f** crystallizes in the space group $P\overline{1}$. The metallocene trihydrides [Cp₂MH₃] add to the BC double bond under formation of a double hydrogen bridge to give $[Me(A_2CH)B(H_u)_2MCp_2]$ (2g, h; M = Nb, Ta). MeB=CA₂ can be chloroborated, -stannated, and -phosphated with E-Cl to yield the boryldisilylmethanes MeB(Cl)-CA2-E $(2i-l; E = EtClB, tBuClB, Me_2ClSn, Cl_2P)$. The alkyloboration and -alumination with E-R leads to the boryldisilylmethanes $MeBR-SiA_2-E$ (2m-o; $E-R = Me_2B-Me$, Et_2B-Et , Cl₂Al-Et) and the bromination to MeB(Br)-CA₂Br. (2+2) Cycloadditions are achieved, when MeB=CA2 is reacted with unsaturated molecules a=b, yielding four-membered rings $[-BMe-CA_2-b-a-]$ [4a-d; a=b = fluorenone, bis(methoxycarbonyl)ethyne (reacting at both of the C=O bonds), phenylisocyan-

ate (reacting at the C=O bond), N-isopropylacetoneimine], or with triple bond systems RC=Z, yielding four-membered rings $[-BMe-CA_2-Z=CR-]$ (4e-g; RC=Z = PhC=CPh, AC=CCl, tBuC=P). With a series of six molecules with an element-oxygen double bond, a primary (2+2) cycloaddition is followed by a metathetical splitting of the transient four-membered rings 4h-m. One of the metathesis products is MeB=O, which is identified as boroxene (MeBO)₃, the other component is an alkene RR'C=CA₂ [starting from MeB=CA2 and PhCHO, PhC(Me)O] or an alkene RR'C=CAA' (starting from MeB=CAA' and PhCHO, tBuCHO) or the methylidene phosphorane Ph₃P=CA₂ (starting from MeB= CA₂ and Ph₃PO) or the dicarbadicobaltatetrahedrane $[(CA)_2 \{Co(CO)_3\}_2]$ {starting from MeB=CA₂ and $[Co_2(CO)_8]$ }. The (2+3) cyclodaddition of MeB=CA₂ to the azide X_2PN_3 (X = NiPr₂) as 1,3-dipole gives the five-membered ring $[=BMe-CA_2-N=N-NX=]$ (5a) and to RN₃ the rings [=BMe-CA=N-NA-NR=] (5'b, c; R = *i*Bu, A; formed from the cycloadducts **5b**, **c** by migration of A); analogously, [=BMe-CA'=N-NA-NA=] (5'd) is formed from MeB=CAA' and AN₃. Finally, the nitrone O-NMe=CHPh and MeB=CA₂ or MeB=CAA' give the corresponding (2+3) cycloadducts 5e, f, respectively. All of the products were characterized by their ¹H, ¹¹B, and ¹³C NMR spectra.

Keywords: Boron carbon double bond; (2+2) Cycloaddition; Metathesis; (2+3) Cycloaddition

Reaktionen an der Bor-Kohlenstoff-Doppelbindung von Methyl(methyliden)boranen

Inhaltsübersicht. Die Addition von Lewisbasen L an die Methyl-(methyliden)borane MeB=CA₂ (A = SiMe₃) und MeB=CAA' $(A' = SiMe_2Cl)$ führt zu den Addukten MeB(L)=CA₂ (1a, b; L = Trimethylpyridin, PMe₃) bzw. MeB(L)=CAA' (1c,d; L = Di- und Trimethylpyridin). Alkohole und Amine HX addieren sich an die BC-Doppelbindung unter Bildung von $MeB(X)-CHA_2$ (2a-c; X = OiPr, OtBu, NiPr2); MeB=CAA' und HNMe2 reagieren im Verhältnis 1:2 zu MeB(X)-CHA(SiMe₂X) (2d; X = NMe₂). Aus MeB=CA₂ und BH₃ bilden sich der fünfgliedrige Ring $[-CA_2-BH-CA_2-BMe(H_u)_2BMe-]$ (2e; 1:2) oder der sechsgliedrige Ring $[-CA_2-BH(H_u)_2BMe-CA_2-BH(H_u)_2BMe-]$ (2f; 1:1), die beide Wasserstoff-Doppelbrücken enthalten; der Sechsring 2f kristallisiert in der Raumgruppe $P\overline{1}$. Die Metallocentrihydride [Cp₂MH₃] addieren sich an die BC-Doppelbindung unter Bildung einer Wasserstoff-Doppelbrücke zu [Me(A₂CH)B(H_u)₂MCp₂] (2g, h; M = Hf, Ta). MeB=CA₂ kann mit E-Cl zu Boryldisilylmethanen MeB(Cl)-CA₂-E chloroboriert, -stanniert und -phosphaniert werden (2i-l; E = EtClB, tBuClB, Me₂ClSn, Cl₂P). Die Alkyloborierung und -aluminierung mit E-R ergibt die Boryldisilylmethane $MeB(R)-CA_2-E$ (2m-o; $E-R = Me_2B-Me$, Et_2B-Et , Cl₂Al-Et) und die Bromierung MeB(Br)-CA₂Br (2p). (2+2)-Cycloadditionen beobachtet man, wenn MeB=CA2 mit ungesättigten Molekülen a=b zu Vierringen [-BMe-CA₂-b-a-] [4a-d;

a=b = Fluorenon, Bis(methoxycarbonyl)ethin (an beide C=O-Bindungen wird addiert), Phenylisocyanat (an die C=O-Bindung wird addiert), N-Isopropylacetonimin] oder mit Dreifachbindungssystemen RC=Z zu Vierringen [-BMe-CA2-Z=CR-] reagiert $(4e-g; RC \equiv Z = PhC \equiv CPh, AC \equiv CCl, tBuC \equiv P)$. Mit sechs Verbindungen mit einer Element-Sauerstoff-Doppelbindung folgt auf eine primäre (2+2)-Cycloaddition eine metathetische Ringspaltung. Eines der Metatheseprodukte ist MeB=O, das als Boroxin $(MeBO)_3$ nachgewiesen wird, das andere ist ein Alken RR'C=CA₂ (aus MeB=CA₂ und PhCHO, PhMeCO) oder ein Alken RR'C= CAA' (aus MeB=CAA' und PhCHO, tBuCHO) oder das Methylidenphosphoran Ph₃P=CA₂ (aus MeB=CA₂ und Ph₃PO) oder das Dicarbadicobaltatetrahedran $[(CA)_2 \{Co(CO)_3\}_2]$ {aus MeB=CA₂ und $[Co_2(CO)_8]$. Die (2+3)-Cycloaddition von MeB=CA₂ an das Azid X_2PN_3 (X = N*i*Pr₂) als 1,3-Dipol ergibt den Fünfring [=BMe-CA₂-N=N-NX=] (5a) und an das Azid AN₃ die Fünfringe [=BMe-CA=N-NA-NR=] (5'b, c; R = *i*Bu, A; hervorgegangen aus den Cycloaddukten 5b, c durch Wanderung von A); entsprechend bildet sich [=BMe-CA'=N-NA-NA=] aus MeB=CAA' und AN₃. Schließlich entstehen aus MeB=CA₂ bzw. MeBB=CAA' und dem Nitron O-NMe=CHPh die (2+3)-Cycloaddukte 5e, f. Alle Produkte wurden mit Hilfe ihrer ¹H-, ¹¹Bund ¹³C-NMR-Spektren charakterisiert.

Introduction

In akylideneboranes $XB = CR_2$, the two-coordinated boron atom may obtain an electron octet by forming a coordinative XB- π bond, when a lone pair at the ligand X is available, e.g. when X represents an amino group [1, 2]. Otherwise, non-classical structures are formed. Describing bonds qualitatively by localized orbitals, the term "non-classical" means, that (3c2e) bonds are required in addition to (2c2e)bonds in order to supply boron with an electron octet. A broad variety of corresponding carbon-boron species had been reviewed by Berndt [3]. The short-lived parent molecule HB=CH₂ could be characterized in an argon matrix by infrared spetroscopy [4]. We had reported on a relatively simple derivative, $Me-B=CA_2$ (A = SiMe₃) [5], which can be isolated and characterized before slowly cyclodimerizing at room temperature. The same is true for the derivatives Me-B=CAA' (A' = SiMe₂Cl) and Me-B=CAA'' (A'' = SiMe₂Br), which are formed from Hal $-B=CA_2$ by a rapid exchange of Hal and Me along the B-C-Si skeleton (Hal = Cl, Br) [6]. The stabilizing effect of the silvl groups was explaind by the ability of the CSi-(2c2e) bond to be expanded to a BCSi-(3c2c) bond, thus providing boron with an electron octet [3].

It has become usual to test the reactivity of multiply bonded semimetal species by a series of reactions: the addition of Lewis bases to the unsaturated semimetal; the addition of unpolar or polar species X'-X to the B=C bond; the application of the B=C bond as a dipole in cycloadditions with 1,1 unsaturated systems a [(2+1) cycloadditions, e.g., when a is a carbene], with 1,2 unsaturated systems a=b [(2+2) cycloadditions], or with 1,3 unsaturated systems a $\overrightarrow{-}$ b $\overrightarrow{-}$ c [(2+3) cycloadditions]. A generalized and partly hypothetical application of these five types of reactions to the methyl(methylidene)borane MeB=CR₂ is shown in Eqs. (1) to (5) in the following scheme.

A few reactions of the boranes MeB=CA₂, MeB=CAA', or MeB=CAA" have already been investigated: the stabilization by cyclodimerization [a reaction of type (4)] [5, 6]; the addition of the Lewis base 2,6-dimethypyridine [a reaction of type (1)] [5], the addition of the silylene SiMe₂ [a reaction of type (3); the primary silaboracyclopropane spontaneously adds a second molecule MeB=CA₂ to give the corresponding 1-sila-3,4-diboracyclopentane] [7]; the addition of the ketone Ph₂CO or the iminoborane *t*BuB=N*t*Bu [reactions of type (4)] [5]. We report here on the reactions of MeB=CA₂ and MeB=CAA' with Lewis bases, with molecules X'-X, with unsaturated molecules, containing double and triple bonds, and with 1,3 dipolar agents, according to Eqs. (1), (2), (4), and (5).

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Addition of Lewis bases

The presumed Si–C- σ electron donation towards a BSiC-3c2e bond is weak enough to be easily replaced by the lone pair of methylpyridines as Lewis bases and even of the less basic trimethylphosphane [Eqs. (1a), (1b)]. The B atoms in the pyridine adducts are distinctly more shielded than in the starting boranes, giving a high-field shift of the NMR signals from $\delta = 69.5$, 70.8 (MeB=CA₂, MeB=CAA') to $\delta = 41-42$ (Table 1). The rotation around the BC double bond axis is restricted, making two different ¹H NMR signals for the protons of the non-equivalent SiMe₃ groups observable. Coalescence temperatures of 43 and 52 °C for the adducts of di- [5] and trimethylpyridine (1a), respectively, to MeB=CA₂ correspond to a rotation barrier of about 70 kJ/mol, comparable to the barrier around the C-N bond in carboxamides. The two different silvl groups of MeB(L)=CAA' cause isomers, which are found in the ratio 58:42 (1c) and 57:43 (1d), according to the ¹H NMR intensities. The adduct 1b, however, gives only one SiMe₃ NMR signal. A broadening of this signal below -40 °C indicates that the rotation barrier is rather small. Besides the rotation around the B=C bond axis, however, a rapid intermolecular exchange of PMe3 molecules, similar to the intermolecular exchange of PMe₃ found for BMe₃(PMe₃) [8], could give rise to the pseudo-equivalency of the SiMe₃ groups of 1b.

All of the solid adducts of methylated pyridines to MeB= CA₂ and MeB=CAA' exhibit an orange colour. The electronic situation around the boron atom is similar to that in the crystalline red adducts of pyridine to borabenzene, BC₅H₅, or 2-boranaphthalene, BC₉H₇ [9]: The nitrogen adjacent to boron is incorporated into an aromatic and boron either into an aromatic or into an "olefinic" π -electron system. The red colour of the boraarene adducts had been attributed to a charge-transfer from a HOMO, which is localized at the boraarene π -electron orbitals, to a LUMO, localized at the pyridine π -orbital system. Accordingly, the orange colour of the methylpyridine adducts of type **2** is

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probably due to charge-transfer from the $B=C-\pi$ electrons to the pyridine LUMO.

Addition of Molecules X'-X

Addition of Protic Agents

The addition of the alcohols *i*PrOH and *t*BuOH and of the amine *i*Pr₂NH to MeB=CA₂ proceeds in a straight-forward way, according to eqs. (2a) and (2b), respectively. The addition of *t*BuOH is accompanied by the formation of the diboryl oxide [Me(CHA₂)B]₂O, formed presumably from Me(HA₂C)B(OH) and unreacted MeB=CA₂, after the elimination of isobutene from **2b**. The aminoborane **2c** had been previously synthesized from the amino(methylene)borane *i*Pr₂N=B=CA₂ by first adding LiMe to the BC double bond and subsequent protolysis with HCl [10]. Upon reaction of Me₂NH with MeB=CAA', the amine is added to the BC double bond, and the SiCl bond simultaneously undergoes aminolysis, giving the aminoborane **2d** [Eq.(2c)].

The structure of the products was identified by characteristic ¹H, ¹¹B, and ¹³C NMR shifts, the intensity of the ¹H NMR signals and the expected NMR coupling schemes (Table 2). One set of signals was observed for the alkoxyboranes 2a, b. The aminoborane 2c exhibited ¹H and ¹³C NMR signals of two different *i*Pr groups at room temperature in the ratio 1:1, indicating a restriction of the rotation around the BN double bond. We interpret two ¹³C NMR signal sets in the ratio 85:15 at -30 °C by adopting conformers with respect to the central B-C axis, the rotation around which is restricted for sterical reason, i.e. an overlap of the cross-sections of one of the isopropyl and the silyl groups. The rotation around the BN double bond of 2d is also restricted, as indicated by two ¹H NMR signals for one of the NMe₂ groups. The two diastereotopic silicon-bound Me groups of $SiMe_2(NMe_2)$ give different signals in the ¹³C NMR spectrum.

Addition of Hydridic Agents

The borane MeB=CA₂ reacted with BH₃(thf) in a 2:1 ratio, according to Eq. (2d), when a 1:1 ratio was applied and the solution quickly warmed to room temperature. Two BH bonds of one molecule BH₃ are added to two molecules MeB=CA₂, according to the polarity of the correcponding bonds: hydride adds to boron and the boron of BH₃ to carbon, thus forming a B-C-B-C-B chain, the boryl ends of which then bind to one another by two BHB bridges to give 2e. A comparable product (2e') had been formed by the addition of BH₃(thf) to the diazadiboretane (RBNtBu)₂, according to Eq. (2d') [11]. Typical for the structure of 2e are two IR bands at v = 2455 and 1533 cm⁻¹, representing vibrations of the terminal and the bridging hydrogen atoms. Two ¹¹B NMR signals in the ratio 2:1 are found at characteristic values, $\delta = 27.3$ and 83.4 [12].





Applying a 1:2 ratio of $MeB=CA_2$ and $BH_3(thf)$ and conducting the reaction at -78° yielded the 1:1 product 2f, according to Eq. (2e). The structure of 2f follows from the NMR spectra. The ¹H NMR intensity ratio of 18:3:2:1 is in accord with a 1:1 reaction of the starting components. The ¹H NMR signal at $\delta = 0.58$ (BMe; ³J = 3 Hz) is related to $\delta = 1.97 (\mu$ -H) by a 2D-¹H/¹H NMR cross-peak. The ¹H NMR signal at $\delta = 3.91$ is assigned to the terminal H atom, BH_t; its coupling pattern depends on temperature as a consequence of the ¹¹B quadrupole relaxation: a quartet at 90, a doublet at 25 and a singlet at -10 °C. The coupling constant is typical for terminal H atoms (${}^{1}J = 146$ Hz). The two ¹¹B NMR signals are found at $\delta = 17.5$ and 33 in the expected range, comparable to those of triethyldiborane, HEtBH₂BEt₂ (δ = 17.2, 34.3 [12]). A 2D-¹¹B/¹H NMR spectrum relates the ¹¹B signal at $\delta = 17.2$ to the ¹H signal of H_t and H_{μ} , and the ¹¹B signal at $\delta = 33$ to that of H_{μ} only. An average coupling of J = 92 Hz is found for the ¹¹B NMR doublet at $\delta = 17.2$.

The molecular structure of 2f was finally confirmed by a crystal structure analysis (Fig. 1). The centrosymmetric molecule is built up by a planar BBCBBC-six-membered ring with ring angles of 121.21(10) (B1), 111.61(10) (C2) and $127.18(10)^{\circ}$ (B2), giving 720.00° as the sum of the six ring angles. The ring ligands H1 and C2 are situated in the ring plane; the boron atoms are planarly coodinated. The plane through B1, B2', H2 and H3 is almost orthogonal to the ring plane $[89.2(7)^{\circ}]$. The bond lengths and angles are comparable to those in similar molecules with a central *trans*-bis(trisyl)diborane(6) BH₂B unit, e.g., in (A₃C)HBH₂BH(CA₃) [13, 14].



Fig. 1 Structure of 2f (PLATON [15], 50 % displacement ellipsoids); selected distances/pm and angles/°:

The first step in the reactions (2d) and (2e) is certainly a hydroboration of the BC double bond of $MeB=CA_2$,

followed by a second hydroboration step or a head/tail cyclodimerization, respectively. With niobocenium- or tantalocenium trihydride, [Cp₂MH₃], the orientation of the addition to the BC double bond of MeB=CMe₂ is reversed: a proton is added to carbon, and the metal (Nb or Ta) is added to boron via two MHB (3c2e) bonds [Eq. (2f)]. Metal(V) is formally reduced by H^- ($\rightarrow H^+$) during this process to give metal(III), thus maintaining the 18e shell at the metal. The bonding situation is not unusual and is well known, e.g., in [Cp₂NbH₂BH₂] [16]. The NMR spectra of the products are in accord with a structure, where the C₂BM coordination sphere around boron defines a mirror plane, that makes the two silyl groups equivalent, whereas the two η^5 -Cp groups are situated one cis and the other trans to the disilylmethyl group. The BH₂M plane is orthogonal to the mirror plane, making the bridging H atoms equivalent. For details of the NMR spectra see Experimental Section!



Chloroboration, -stannation, and -phosphation

The double bond of MeB=CA₂ can be chloroborated with RBCl₂ [Eq. (2g)], chlorostannated with Me₂SnCl₂ [Eq. (2h)], and chlorophosphated with PCl₃ [Eq. (2i)] to yield the diborylmethanes **2i**, **j**, the borylstannylborane **2k**, and the borylphosphanylmethane **2l**, respectively. Again, the NMR spectra allow a unique structural identification of the products **2i**-l (see Table 3 for details). The colourless phosphanylborane **2l** is extremely sensitive towards moisture. A coupling of the SiMe and BMe protons with the phosphorus nucleus is observable through four bonds. The chloroboration of iminoboranes, RB=NR', proceeds in an analogous manner as that of MeB=CA₂ [17].



Alkyloboration and -alumination

The alkyloboration of MeB=CA₂ with BR₃ gives the diborylmethanes **2m**, **n** [Eq. (2j)]. Whereas the chloroboration is faster than the alkyloboration upon reacting RBCl₂ with MeB=CA₂, the situation is reversed, when (EtAlCl₂)₂ is applied. The structure of the ethyloalumination product **2o** [Eq. (2k)] is concluded from the NMR spectra. The dimeric structure is in accord with the ²⁷Al NMR signal at $\delta = 122$, typical for four-coordinate aluminium, and the ¹¹B NMR signal is found in a range typical for trialkylboranes, not of alkyldihaloboranes (Table 3). The product **2o** is thermolabile.



Addition of Bromine

Bromine is sponaneously added to the BC double bond of $MeB=CA_2$ at -78 °C, according to Eq. (21). The colourless solid product **2p** can be sublimated. It was characterized by elemental analysis and its NMR spectra.



We had taken into account a 1,2-dyotropic exchange of Me and Br along the B–C bond of 2p to give Br₂B-CMeA₂. Reactions of this type can be achieved thermally or also catalyzed by acids, when electronegative groups are bound to a carbon atom adjacent to boron [18]. Heating 2p in boiling toluene for 18 h, however, did not give any reaction.

[2+2] Cycloadditions

Amino(methylene)boranes like *i*PrN=B=CA₂ had been subjected to (2+2) cycloadditions with a variety of molecules with a carbon oxygen double bond like aldehydes, ketones, and carboxylic acid derivatives [10]. The methyl-(methylene)boranes MeB=CA₂ and MeB=CAA' had been subjected to a [2+2] cycloaddition with Ph₂C=O and MeB=CA₂ also with the iminoborane *t*BuB=N*t*Bu, and their stabilization by cyclodimerization represents also a [2+2] cycloaddition [5, 6]. We report here on the cyclodimerization of MeB=CA₂ with a ketone [9-fluorenone; Eq. (4a)], a carboxylic ester [MeOOC-C=C-COOMe; Eq. (4b)], an isocyanate [PhNCO; Eq. (4c)], and a ketoneimine [Me₂C=N*i*Pr; Eq. (4d)].



The characterization of the products 4a-d by NMR makes use of routine arguments. Moreover, the chemical shifts of 4a are very similar to those of the cycloadduct from MeB=CA₂ and O=CPh₂, which differs from 4a only by a Ph-Ph connection through ortho-C atoms. In the case of 4b, a 2:1 addition is achieved, even when the components are applied in a 1:1 ratio. The ¹³C NMR shift at $\delta = 92.3$ shows that the CC triple bond is still present in 4b. The polar C=O and not the unpolar C=C bond of the starting component had reacted with the B=C bond. Whereas singlebonded molecules E-X attack isocyanates preferably at the CN double bond, it is the CO double bond of PhN=C=O that undergoes the cycloaddition (4c). The ¹¹B NMR shift at $\delta = 57.3$ is found in the expected range. The analogous oxoniaboratacyclobutene from the addition of MeB=CA₂ and $O=CPh_2$ gives an ¹¹B NMR shift at $\delta = 58.7$, whereas the boron nucleus of the azoniaboratacyclobutene 4d with a nitrogen ring atom resonates at a distinctly higher fieldstrength, $\delta = 45.9$. The mass-spectrometric fragmentation of 4c gives mass peaks for the fragments M-MeBO (59 %) and M-MeBO-Me (100 %), which clearly show that boron is bound to oxygen in 4c. Analogously, the mass-spectrometric fragmentation of 4d yields the peak of M-MeBNPr-Me (100 %), establishing that the cycloaddition (4d) and the subsequent fragmentation together are representing a metathesis reaction.

Similar cycloadditions are given by MeB=CA₂ and the unpolar ethyne PhC=CPh or the polar ethyne AC=CCl or the phosphaethyne tBuC=P [Eq. (4e)]. Although the formation of **4b** had taught us, that the C=O bond of MeOOC-C=C-COOMe is more reactive than the unpolar C=C bond, diphenylethyne undergoes a quantitative 1:1 cycloaddition with MeB=CMe₂. The product **4e** gives the expected NMR data. The mass-spectrometric fragmentation follows a cycloreversion reverse to the formation (4e), whereas metathetical fragments could not be detected, in accord with a still strong double bond in the ring skeleton of **4e**. The alkyne AC=CCl adds to MeB=CA₂ in a regioselective manner, according to the polarities of the B=Cand $C \equiv C$ bonds and also according to the sterically preferable way, with the three bulky silyl groups so remote from each other as possible.-The regioselective addition of $tBuC \equiv P$, documented by only one set of NMR signals, follows again the polarities of the unsaturated components $(\delta + \text{ at boron and phosphorus}; \delta - \text{ at carbon})$ and is also in accord with the more farvourable steric situation. The ¹³C NMR signals of the ring and of the BMe carbon atoms are not observable, even not at -50 °C, a common situation in the coordination sphere of ¹¹B nuclei. The three observable ¹³C NMR signals (SiMe₃, tBu) exhibit the expected couplings with the ³¹P nucleus. The principal structure of the viscous oily 4g could be confirmed by a crystal structure analysis, after crystallizing 4g by a miniature zone melting process with a focussed infrared radiation; we do not publish the data, however, because some unusually anisotropic displacement parameters indicate disorder [19].



Aldehydes and ketones like PhCHO, tBuCHO, PhMeCO, Ph₂CO, give [2+2] cycloadducts with $iPr_2N=B=CA_2$ and the relatively bulky Ph_2CO even with $MeB=CA_2$ [5, 6]. We were not able, however, to isolate cyclodadducts from the methyl(methylene)boranes MeB=CA₂ or MeB=CAA' and the oxoalkanes PhCHO, tBuCHO, PhMeCO, according to Eq. (4f), although these cycloadducts have certainly be formed as the intermediates 4h-k, detectable in the reaction solution by an ¹¹B NMR signal in the range δ = 57-60. Instead of **4h**-**k**, we isolated the corresponding olefines as the products of a metathesis, according to Eq. (4g), and characterized them as usual by NMR methods. The oxoborane MeB=O as the second metathesis product spontaneously cyclotrimerizes to methylboroxene, which could be identified as a volatile material by its characteristic ¹¹B NMR peak. The possibility of MeB=O to appear as a short-lived intermediate is well established in the literature [20].



In analogy to Eqs. (4f), (4g), the oxophosphorane O= PPh₃ splits the BC double bond of MeB=CA₂ by metathesis, according to Eqs. (4h) and (4i). The ¹¹B NMR signal of $\delta = 55.2$ in the reaction solution indicates the transient presence of the cycloadduct **4**I. A metathetical reaction also proceeds, when MeB=CA₂ is reacted with [Co₂(CO)₈]. It is presumably one of the bridging CO units, to which MeB= CA₂ is added to give the intermediate **4m** [Eq. (4j)], which subsequently eliminates MeBO and CO to yield the wellknown dicarbadicobaltatetrahedrane [(CA)₂{Co(CO)₃}₂] [21].



[2+3] Cycloadditions

Azides RN₃ had been applied as 1,3-dipolar agents in reactions with the BC double bond of the amino(methylene)borane $iPr_2N=B=CA_2$. Instead of a cycloadduct of type **5**, according to Eq. (5a), an azaboriridine (R = Ph, Bzl) or the corresponding (aminoboryl)diazoalkane (R = A) had been isolated, both obviously formed by reaction (5b) or (5c), respectively. A third possibility would have been the formation of the amino(imino)borane $iPr_2N=B=NR$ and the diazoalkane A_2CN_2 by cycloreversion of the primary cycloadduct. A reaction of this type had been observed, at least as a side-reaction, when an azide had been applied on the methylenesilane $Me_2Si=CA_2$ [22], but had not taken place with $Pr_2N=B=CA_2$ and azides.



None of these reactions was observed, when we applied azides on MeB=CA₂ or MeB=CAA'. With the azidophosphane $(iPr_2N)_2PN_3$, the primary cycloadduct **5a** could be isolated as a thermally unstable solid. The NMR spectra support the postulated structure of **5a**: Two equivalent silyl groups are present; the ¹¹B NMR peak ($\delta = 49.7$) is found in a range typical for dialkyl(amino)boranes ($\delta = 48-52$ [12]); the ¹³C NMR signal of the ring-C atom ($\delta = 45.8$) corresponds to a saturated atom. Moreover, the mass spectrum gives the ions of A₂CN₂ and MeB=N(PX₂) (X = N*i*Pr₂) as fragments. We could not identify the decomposition products, that are formed, when **5a** is standing for a week at room temperature.



The situation is different, when the azides *i*BuN₃ or AN₃ are reacted with MeB=CA₂. The isolated products, **5'b** and **5'c**, respectively, are obviously formed from the transient cycloadducts **5b** and **5c** by the migration of one of the silyl groups from carbon to nitrogen [Eq. (5d)]. The five-membered ring is transformed thereby into an aromatic 6π -electron system, giving a characteristic change of the ¹¹B NMR signal to higher field [compare $\delta = 49.7$ (**5a**) to $\delta = 31.9$ (**5'b**), 36.3 (**5'c**)] and of the ¹³C NMR ring atom signal to lower field [compare $\delta = 45.8$ (**5a**) to $\delta = 134.4$ (**5'b**), 133.0 (**5'c**)], in accord with the generally known trend. Two and three non-equivalent silyl groups are identified by the NMR data of **5'b** and **5'c** show an intensive peak for a fragment, which is formed by the elimination of NCSiMe₃; this is not a

reasonable fragmentation of a ring of type **5**. A cation of A_2CN_2 is not detected in these mass spectra, in contrast to that of **5a**. The same arguments reveal the structure of the product **5'd**, when AN₃ is reacted with Me-B=CAA'. Only one of the groups A and A' migrates from carbon to nitrogen, since only one isomer corresponds to the NMR signals. Presumably, it is the trimethylsilyl group A that migrates, because the ¹³C NMR signal of the ring atom at $\delta = 128.3$ is significantly different from those of **5'b** and **5'c**, mentioned above; this C atom should be sensitive to the nature of the directly bound ligand.

We also reacted *N*-methylbenzaldimine-*N*-oxide as a 1,3dipolar agent with MeB=CA₂ and MeB=CAA' and characterized the products **5e**, **f** [Eq. (5e)] by their NMR spectra. The two silyl groups A are not equivalent in **5e**. Diastereomers of **5f** are identified in the ¹H NMR spetrum in the ratio 83:17. The ¹³C nuclei are not sensitive enough to make differences between the diasteromers observable, but they are sensitive enough to make the non-equivalence of the two methyl groups of A' observable.



Experimental

NMR spectra: Bruker WP80/SY (1 H; 31 P), Bruker WH 270 (13 C), Jeol JNM-PS-100 (11 B); standards: SiMe₄ (intern; 1 H, 13 C), BF₃(OEt₂) (extern; 11 B), H₃PO₄ (extern; 31 P); in CDCl₃.

Synthesis of $MeB = CA_2$ and MeB = CAA': These methyleneboranes were synthesized by thermolysis of MeB(OMe)–CA₃ and ClB(OMe)–CA₃, respectively, as described in the literature [5, 6]. We had originally obtained a 4:1 mixture of MeB=CA₂ and the trisilylmethane HCA₃ [5]. By starting from perfectly pure MeB(OMe)–CA₃ and thoroughly avoiding any moisture during the thermolysis, we now obtained pure MeB=CA₂ without any byproduct, as judged from the NMR spectra. The amounts of the two methyleneboranes, which we applied in the following syntheses, were concluded from the amounts of thermolyzed starting materials, assuming a 100 % thermolysis yield. Condensed at the walls of a cooled glass tube after passing the thermolysis tube, the methyleneborane dropped into pentane, placed at the bottom of the tube, on warming the tube from -196 to -78 °C.

Synthesis of the adducts 1a-d: The base (2 mmol) was added to the corresponding methyleneborane (2 mmol) in pentane (5 ml) at -78 °C. The colourless adduct with PMe₃ precipitates immediately; the adducts with the methylpyridine bases were stirred in pentane for several hours and then isolated by removing the solvent in vacuo. All of the four adducts crystallized from pentane at -80 °C. The adduct **1b** was extremely sensitive towards moisture. The or-

Table 1 ¹H, ¹¹B and ¹³C NMR chemical shifts of the adducts of MeB=CA₂ (**1a**, **b**) and MeB=CAA' (**1c**, **d**) with the bases 2,4,6-trimethylpyridine (**1a**, **d**), PMe₃ (**1b**), and 2,6-dimethylpyridine (**1c**)^{a)}

		1a	1b	1c ^{d)}	$\mathbf{1d}^{d)}$
¹ Η	SiMe ₃ SiMe ₂ BMe L	-0.02/0.67 / 0.70 1.57 2.43 6.11	0.45 / 0.67 0.49 ^{b)}	0.36/-0.28 -0.01/0.67 0.49/0.56 2.41/2.37 6.48 6.98	$\begin{array}{c} 0.28/-0.07\\-0.32/0.59\\0.47/0.53\\1.85/1.85\\2.40/2.38\\6.43\end{array}$
¹¹ B		40.8	53.4	41.9	40.9
¹³ C	SiMe ₃ SiMe ₂ BMe Si ₂ C L	4.4/6.1 / 9.0 70.0 20.7 22.0 124.8 151.2 153.1	6.1 / 9.9 34.8 11.3 ^{c)}	5.4/3.8 7.3/9.4 8.9 69.8 22.0 124.5/124.4 139.9/139.9 153.5/153.4	5.5/4.0 7.5/9.5 9.2/9.5 70.2 20.7/20.7 22.0/21.8 125.2/125.4 152.5/152.7 152.6/152.7

^{a)} In[D₈]toluene; ¹H NMR of **1a** in C₆D₆; ¹H, ¹¹B, ¹³C NMR of **1b** and ¹³C NMR of **1a**, **c**, **d**, at $-30 \,^{\circ}$ C. ^{b)} ²J = 9.5 Hz; ³¹P NMR: δ = 32.6. ^{c)} ¹J = 27 Hz. ^{d)} E/Z or Z/E isomers in the ratio 58/42 (**1c**) and 57/43 (**1d**).

Table 2 ¹H, ¹¹B and ¹³C NMR chemical shifts of the adducts of HX to MeB=CA₂ (**2a-c**: X = OiPr, OtBu, $NiPr_2$) and to MeB=CAA' [giving Me-(Me₂N)B-CHA(SiMe₂Nme₂), **2d**]^a)

		2a	2 b	$2c^{d)}$	2d	
¹ H	SiMe	0.02	0.03	0.03	-0.02,008	
	BMe	0.36	0.50	0.39	0.27	
	Si ₂ CH	b)	b)	0.31	0.45	
	x	1.18 ^{c)}	1.35	1.11 ^{e)}	2.65 ^{h)}	
		4.33 ^{c)}		1.19 ^{f)}	2.70^{i}	
				3.50 ^{f)}	2.75 ⁱ⁾	
				3.88 ^{e)}		
¹¹ B		52.2	52.0	45.5	44.8	
¹³ C	SiMe	1.7	1.8	2.3/0.8	j)	
	BMe	5.1	9.7	8.7/8.7	5.8	
	Si ₂ CH	20.6	21.9	16.7/12.2	16.2	
	x	24.5	30.7	21.6/21.6	38.0	
		67.3	74.1	24.6/25.7	39.2 ⁱ⁾	
				44.6/44.0	39.3 ⁱ⁾	
				48 8/49 6		

^{a)} NMR of **2d** in C₆D₆; ¹³C NMR of **2a**-c at -30 °C. ^{b)} Signal not detected. ^{c)} ${}^{3}J = 6,1$ Hz, ^{d)} Signals of two axial-symmetric isomers with respect to rotation around the B-C axis, resolved in the ¹³C NMR spectrum in the ratio 85:15. ^{e)} ${}^{3}J = 6.7$ Hz. ^{f)} ${}^{3}J = 6.1$ Hz. ^{g)} In the ratio 3:2. ^{h)} SiNMe₂ ⁱ⁾ Me I and Me II of BNMe₂.^{j)} Three SiMe signals: $\delta = 0.0$ (SiMe₃), 1.2, 1.8, (Me I and Me II of SiMe₂Cl).

ange-coloured crystals of **1a,c,d** gave the expected results on elemental analysis. The characteristic NMR data are summarized in Table 1.

(Alkoxy)[bis(trimethylsilyl)methyl]methylboranes (2a,b): A slight excess of the carefully dried alcohols *i*PrOH or tBuOH, respectively, was given to MeB=CA₂ (5 mmol) in pentane (5 ml) at -78 °C. After bringing the solution to room temperature, the product 2a was obtained by distillation (23 °C/0.7 Pa; 48 %) and characterized by elemental analysis and NMR spectra (Table 2). A 4:1 mixture of two products is obtained from the alcoholysis with *t*BuOH, the product **2b** (characterized by NMR data, Table 2) and the diboryloxide [Me(HA₂C)B]₂O, obviously formed from **2b** by the well-known elimination of isobutene and subsequent addition of the intermediate hydroxyborane to unreacted MeB=CA₂.

{*Bis(trimethylsilyl)methyl](diisopropylamino)methylborane* (2c): Excess diisopropylamine (20 mmol) was added to MeB=CA₂ (2 mmol) in pentane (5 ml) at -78 °C. After 1 h stirring, the solvent was evaporated in vacuo. The colourless product crystallized from hexane at -80 °C (81 %; m.p. 15 °C) and was characterized by elemental analysis and by the NMR data (Table 2).

(Dimethylamino) {[dimethyl(dimethylamino)sily1](trimethylsily1)methyl}methylborane (2d): The borane MeB=CAA' (8 mmol) in pentane (5 ml) was aminolyzed with dimethylamine (34 mmol) at -78 °C. Stirring at room temperature (6 h), filtration and distillation (42 °C/0.7 Pa) gave pure 2d (52 %), characterized by elemental analysis (C, H, N) and NMR spectra (Table 2).

Reaction of $MeB=CA_2$ with borane: An equimolar amount (5 mmol) of the borane BH₃ in thf (5 ml) was added to MeB=CA₂ in pentane (10 ml) at -78 °C, the solution was brought to room temperature and stirred (1 h). In spite of the equimolar amount of the starting components, the colourless 2:1 product 2e crystallized from diethylether at -80 °C (89 %, with respect to MeB=CA₂; m.p. 88 °C), characterized by elemental analysis (C, H) and NMR spectral analysis in [D₈]toluene. $- {}^{1}H$ NMR: $\delta = 0.18$, 0.57 (2 s; 6:1) (signals of BH and BH₂B not detected). $- {}^{11}B$ NMR: $\delta =$ 27.3, 38.4 (2:1). $-{}^{13}$ C NMR ($-30 \circ$ C): $\delta = 1.1$, 4.0 (2 q), 38.0 (s). - IR (in KBr): 2455, 1533 cm⁻¹ [v(BH), v(BH₂B)]. - When a large excess of BH₃(thf) (12 mmol) was added to MeB=CA₂ (6 mmol) in pentane (5 ml) at -78 °C and the solution was stirred at -78 °C (6 h), the removal of the solvents in vacuo and the extraction of the residue with diethylether at -78 °C gave a solid, from which the colourless 1:1 product 2f was obtained by crystallization from toluene at 6 °C (97 %; m.p. 123-124 °C), characterized by elemental analysis, NMR spectra in [D8]toluene (Varian Unity 500), and by crystal structure analysis. - ¹H NMR: $\delta = 0.16$ (s), 0.58 (t, ³J = 3 Hz), 1.97 (br), 3.91 (d, ${}^{1}J = 146$ Hz), in the ratio 18:3:2:1. $-{}^{11}B$ NMR: $\delta = 17.5$ (d), 33.1 (br) (1:1). $-{}^{13}$ C NMR: $\delta = 2.3, 6.8, 71.7$.

Crystal structure of 2f: Data were collected on an ENRAF-Nonius CAD4 diffractometer, using MoK_{α} radiation ($\lambda = 154.184$ pm, graphite monochromator) at 253 K. Space group: $P\overline{1}$ (Nr. 2); a =812.5(5), b = 1185.5(3), c = 760.2(2) pm; $\alpha = 102.03(5)$, $\beta =$ 108.72(5), $\gamma = 98.94(4)^{\circ}$; $V = 0.6585(6) \text{ nm}^3$; Z = 1; calculated density: 0.999 g cm⁻³; crystal size: 0.85 \cdot 0.45 \cdot 0.3 mm³; μ = 2.25 cm⁻¹; range of 2 Θ : 6–60°. The structure was solved by direct methods and refined on reflection intensities [23]. Measured reflections: 4722; independent data: 3820; observed independent reflections $[I > 2\sigma(I)]$: 3433; refined parameters: 206; R = 0.0396; wR2 =0.1242; GOF = 1.075; maximal residue electron density: 265 e nm⁻³. The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 222554.Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (e-mail: deposit@ccdc.com.ac.uk).

Niobocene- and tantalocene-di- μ -hydrido[bis(trimethylsilyl)methyl]methylborane (**2g,h**): Cp₂NbH₃ or Cp₂TaH₃ (3 mmol) in toluene (5 ml) were added to a solution of MeB=CA₂ (5 mmol) in toluene (15 ml) at -78 °C. The solution turned green. After stirring at room temperature (15 min), volatile materials were removed in vacuo. Dark-green crystals were obtained from pentane at -80 °C (68 or 84 %, respectively), which were extremely sensitive towards moisture. – NMR spectra (**2g**/**2h**) in [D₈]toluene. – ¹H NMR: $\delta = 0.06/0.04$, 0. 18/–0.01, 0.39/0.36, –14.5/–14.7, 4.80/4.75, 4.83/4.77 (6 s in the ratio 18:3:1:2:5:5). – ¹¹B NMR: $\delta = 53.9/58.1$. – ¹³C NMR: $\delta = 2.7/2.6$ (SiMe), 15.1/17.2 (BMe), 24.9/25.7 (Si₂CH), 92.9/88.7 (Cp).

Diboryldisilylmethanes (2i,j,m,n): The borane MeB=CA₂ (4 mmol) was dissolved in pentane (5 ml). A slight excess of the boranes BMe₃, BEt₃, EtBCl₂ or *t*BuBCl₂, respectively, was added at -78 °C (BEt₃ at room temperature) through a dropping funnel or (in the case of BMe₃) by condensation. After stirring at room temperature (1 h; in the case of BEt₃: 3 d), volatiles were removed in vacuo. The products were obtained by sublimation at 40/80/60/80 °C/0.7 Pa in yields of 64/85/88/78 % as colourless solids [m.p. 212 (2i), 173 (2m), or 164 °C (2n); 2j is a waxy solid]. The products **2m,n** were characterized by elemental analysis (C, H) and all of the four products by their NMR spectra (Table 3).

[*Chloro*(*dimethyl*)*stannyl*][*chloro*(*methyl*)*boryl*]*bis*(*trimethylsilyl*)*methane* (**2k**): Dichlorodimethylstannane (3.2 mmol) in diethylether (5 ml) was added to MeB=CA₂ (5.9 mmol) in pentane (5 ml) at -78 °C. After 1 h stirring, volatiles were removed in vacuo. The residue was dissolved in pentane (1 ml). Excess Me₂SnCl₂ crystallized from the solution at -80 °C and was removed by filtration. The product was obtained by condensation at 90 °C/0.7 Pa as a colourless solid (52 %) and was characterized by elemental analysis (C, H) and NMR (Table 3).

Bis(trimethylsilyl)[chloro(methyl)boryl](dichlorophosphanyl)methane (2l): A slight excess of PCl₃ was added to MeB=CA₂ (4 mmol) in pentane (5 ml) at -78 °C. After stirring at room temperature (20 min) and removal of volatiles in vacuo, the colourless product crystallized from toluene at -80 °C (77 %; m.p. 70 °C) and was characterized by elemental analysis (C, H) and NMR (Tabe 3).

1,2-Dichloro- μ -dichloro-1,2-bis {[ethyl(methyl)boryl]bis(trimethylsilyl)methyl}dialane (20): Dichloro(ethyl)alane (10 mmol) in hexane (10 ml) was added to MeB=CA₂ (10 mmol) in pentane (5 ml) at -78 °C. After 1 h stirring and removal of volatile compounds in vacuo, **20** was obtained by condensation at 60 °C/0.7 Pa and purified by crystallization from pentane at -80 °C (42 %). The colourless product decomposed slowly, even at -30 °C, but was pure, according to the NMR spectrum, measured immediately after crystallization (Table 3). [Bromo(methyl)boryl]bis(trimethylsilyl)bromomethane (2p): An equimolar amount (6 mmol) of bromine was dropped into a solution of MeB=CA₂ in pentane (5 ml) at -78 °C. The brown colour immediately disappeared. The colourless product was obtained by sublimation at 40 °C/1.3 Pa (48 %; m.p. 68 °C) and characterized by elemental analysis (C, H) and NMR (Table 3).

Boracyclobutenes (4a-g): The borane MeB=CA₂ (5 mmol) was dissolved in pentane (5 ml) or - in the case of 4a - in diethylether (5 ml). The unsaturated components (5 mmol) were added at -78 °C, either dissolved in diethylether (10 ml; in the case of 9-fluorenone to give 4a) or in pentane (10 ml; in the case of diphenylethyne to give 4e) or without solvent [in the case of bis-(methoxycarbonyl)ethyne, phenylisocyanate, 2-(isopropylimino)propane, chloro(trimethylsilyl)ethyne, tert-butylphosphaethyne to give 4b-d, f,g, respectively]. The mixture was stirred at -78 °C (1 h)in the case of **4b** or at room temperature (30 min) in all of the other cases. The colour changed in the case of 4a (orange-red \rightarrow yellow), 4b (red-brown \rightarrow colourless), and 4d (orange-red \rightarrow colourless). Volatile materials were removed in vacuo; in the case of 4g, the volume of the reaction solution was reduced in vacuo by 50 %. The products 4a,e crystallized from pentane at -80 °C; 4e was again crystallized from diethylether (80 and 86 %, m.p. 38 and 45 °C, respectively). The product 4b was twice crystallized from diethylether (54 %; m.p. 89 °C). The products 4d,f,g were transported into a cooled trap at 55 °C/0.7 Pa, 20 °C/0.1 Pa, 30 °C/1.3 Pa, respectively, and obtained as viscous oils (87, 70, 32 %, respectively). The product 4c could neither be crystallized nor transported in vacuo without decomposition; the crude oily material was pure, however. All of the products were characterized by their NMR data (Table 4) and elemental analysis.

Reaction of MeB=*CA*₂ with benzaldehyde: An equimolar mixture (5 mmol) of MeB=CA₂ and PhCHO in pentane (5 ml) was stirred at room temperature (3 d). An ¹¹B NMR signal at $\delta = 58.2$ indicated the presence of the [2+2] cycloadduct **4h**. On removing the solvent in vacuo, trimethylboroxene, (MeBO)₃, was detected among the volatiles by its NMR signals, indicating a metathesis reaction. In order to complete the reaction, pentane was replaced by hexane and the solution refluxed (4 d). A distillation gave the well-known phenyl-2,2-bis(trimethylsilyl)ethane [24] at 67 °C/1 Pa (38 %). – ¹H NMR: $\delta = 0.04$, 0.20 (2 s, 1:1, 18 H), 7.19–7.28 (5 H), 7.78 (s, 1 H). – ¹³C NMR: $\delta = 0.5$, 2.0 (2 q), 146.5 (s), 155.0 (d); additional: 3 d, 1 s (Ph).

Table 3 1 H, 11 B, and 13 C NMR chemical shifts of the boryldisilylmethanes MeB(X)–C(SiM₃)₂–Y (2i–p)

X Y		2i Cl BEtCl	2j Cl B <i>t</i> BuCl	2k Cl SnMe ₂ Cl	21 C1 PCl ₂	2m Me BMe ₂	2n Et BEt ₂	20 ^{g)} Et AlCl ₂	2p Br Br
ΙΗ	SiMe BMe X,Y	0.25 1.07 0.87-1.38	0.31 1.16 1.04	0.30 1.07 0.83 ^{c)}	0.41 ^{e)} 1.25 ^{f)}	0.11 0.79 0.79	0.10 0.80 1.00-1.11	0.29 0.99 1.05, 1.34 ^{h)}	0.29 1.31 /
¹¹ B		73.1	72.3	71.4	70.6	82.9	85.7	82.4	73.5
¹³ C ^{a)}	SiMe BMe Si ₂ C X,Y	2.6 19.5 50.9 9.9 ^{b)} 26.0	3.8 20.0 58.5 28.8 ^{b)} 30.1	3.7 18.1 40.2 6.6 ^{d)}	3.6 18.2 /	3.1 19.2 50.3 19.2 /	3.4 16.0 50.4 9.7, 9.8 ^{b)} 23.6, 27.4	4.5 16.7 33.3 9.8 ^{b)} 26.7 ⁱ⁾	1.2 23.0 49.2 /

^{a)} At -50 °C (except **2p**). ^{b)} Quartet. ^{c)} $^{2}J = 56$ Hz (¹¹⁷Sn), 59 Hz (¹¹⁹Sn). ^{d)} $^{1}J = 205$ Hz. ^{e)} $^{4}J = 1.7$ Hz. ^{f)} $^{4}J = 4.1$ Hz. ^{g)} Varian Unity 500; in [D₈]toluene. ^{h)} t and q; $^{3}J = 7$ Hz. ⁱ⁾ 27 Al NMR: $\delta = 122$.

Table 4 1 H, 11 B, 13 C NMR chemical shifts of the (2+2) cycloadducts 4a-g

		4a	4b	4c	4d	4e	4f ^{g)}	4g ^{g)}
ΙΗ	SiMe BMe Etc.	0.03 0.84 7.11-7.66	0.09 0.61 3.70	0.18 1.06 7.12-7.50	0.10 0.38 _{d)}	0.07 1.02 7.01-7.46	0.14 0.93 0.14	0.04 0.53 1.25 ^{j)}
¹¹ B		58.6	53.8	57.3	45.9	54.2	69.0	41.0
¹³ C ^{a)}	$\begin{array}{c} \text{SiMe} \\ \text{BMe} \\ \text{Si}_2\text{C} \\ \text{Si}_2\text{C} \\ \text{Si}_2\text{C} \\ \text{Etc.} \end{array}$	3.8 4.6 42.2 96.4 b)	3.2 5.1 39.8 153.2 54.7 92.3	0.0 1.8 44.2 176.0 c)	4.4 1.7 33.1 67.1 e)	1.4 4.2 39.9 158.8 155.2	$\begin{array}{c} 0.18^{\rm h)} \\ 8.65 \\ 52.8 \\ 71.7 \\ 0.24^{\rm h)} \\ 62.5^{\rm i)} \end{array}$	1.7 ^{k)} 1) m) 31.6 ⁿ⁾ 39.9 ^{o)}

^{a)} **4a**, **d**, **e** at -30, **4c** at -50 °C. ^{b)} 119.8, 125.6, 126.5, 129.2 (4d), 139.7, 147.2 (2s). ^{c)} 120.1, 124.5, 129.0 (3d), 137.2 (s). ^{d)} 1.36, 1.14, 3.09 (s, d, sept, in the ratio 6.6:1; ³J = 6.6 Hz.) ^{e)} 25.3, 28.2, 42.4 (q, q, d). ^{f)} 126.0, 126.8, 128.0, 129.9, 131.5 (6 d), 135.2, 135.4 (2 s). ^{g)} Varian Unity 500. ^{h)} Arbitrary assignment of the two SiMe₃ signals. ⁱ⁾ Observable at -30 °C (BC). ^{j)} $^{4}J = 9.92$ Hz. ^{k)} $^{3}J = 3.57$ Hz. ¹⁾ Signals not resolved. ^{m)} ^{31}P NMR: $\delta = 301.93$. ⁿ⁾ $^{3}J = 205$ Hz (tBu). ^{o)} $^{2}J = 33.90$ Hz (tBu).

Reaction of MeB=*CA*₂ with acetophenone: Proceeding analogously as just described makes an ¹¹B NMR signal detectable at $\delta = 57.5$. The product PhMeC=CA₂ was distilled at 83 °C/1 Pa (55 %). - ¹H NMR: $\delta = -0.23$, 0.29 (2 s, 1:1, 18 H), 2.25 (s, 3 H), 7.08-7.32 (5 H). - ¹³C NMR: $\delta = 2.4$, 2.7, 30.1 (3 q), 149.3, 164.8 (2 s); additional: 3 d, 1 s (Ph).

Reaction of MeB=CAA' with benzaldehyde: An equimolar mixture (16 mmol) of MeB=CAA' and PhCHO was stirred (2 h) in hexane (15 ml). The product, PhCH=CAA' was obtained by distillation at 61 °C/0.7 Pa (37 %). - ¹H NMR (two isomers in the ratio 68:32): $\delta = 0.28/0.03$ (s, 9H), 0.26/0.62 (s, 6 H), 7.21-7.36 (5 H), 7.86/7.98 (s, 1 H). - ¹³C NMR: $\delta = 0.5/1.8$ (q), 5.4/3.8 (q), 144.3 (s), 152.2 (d); additional: 3 d, 1 s (Ph).

Reaction of MeB=*CAA' with dimethylpropanal:* An analogous procedure gave the olefine *t*BuCH=CAA' at 30 °C/0.7 Pa (32 %). - ¹H NMR (two isomers in the ratio 60:40): $\delta = 0.16/0.29$ (s, 9 H), 0.64/0.50 (s, 6 H), 1.12/1.12 (s, 9 H), 6.82/6.98 (s, 1 H). - ¹³C NMR: $\delta = 1.3/3.6$ (q), 7.5/4.4 (q), 30.5 (q), 36.8 (s), 133.4/133.9 (s), 171.6/170.9 (d).

Reaction of MeB=CA₂ with triphenylphophine oxide: A solution of Ph₃PO (4 mmol) in toluene (10 ml) was added to MeB=CA₂ (4 mmol) in toluene (5 ml) at -78 °C. After stirring at room temperature (30 min), an ¹¹B NMR signal at $\delta = 55.2$ was observed, attributed to the formation of **4**l, besides the signal of (MeBO)₃ at $\delta = 31.9$. After further stirring (18 h), volatile materials were removed in vacuo, pentane was added to the residue, and still unreacted Ph₃PO was removed by filtration. After the removal of pentane, the known phosphorane Ph₃P=CA₂ [25] crystallized from CHCl₃ at -40 °C. Since traces of the cycloadduct **41** were still present, a sublimation (105 °C/0.7 Pa) was performed, that gave the pure phosphorane (30 %). - ¹H NMR: $\delta = -0.21$ (s, 18 H), 7.24–7.84 (5 H). - ¹³C NMR: $\delta = 5.2$ (q), 127.8 (d/d), 134.0 (d/d), 130.6 (d), 134.7 (d, ¹J = 79.8 Hz).

Reaction of $MeB=CA_2$ *with octacarbonyldicobalt*: The borane MeB=CA₂ (6 mmol) was condensed to $[Co_2(CO)_8]$ (3 mmol) in

toluene (10 ml) at -196 °C. Warming to room temperature gave a black solution. After 1 h stirring, volatile materials, including the excess of the starting borane, were removed in vacuo. The dicarbadicobaltatetrahedrane, [(CA)₂{Co(CO)₃}₂], a known substance [21], was twice crystallized from pentane at -80 °C (81 %). - ¹H NMR: $\delta = 0.32$. - ¹³C NMR: $\delta = 1.0$ (q), 92.9 (s), 201.1 (s).

3-[Bis(diisopropylamino)phosphanyl]-4-methyl-5,5-bis(trimethylsilyl)-1,2-diaza-3-azonia-4-borata-1,3-cvclopentadiene (5a): Azidobis-(diisopropylamino)phosphane [26] (8 mmol) in pentane (5 ml) was added to MeB=CA₂ (6 mmol) in pentane (5 ml) at -78 °C. After stirring the mixture at -78 °C (30 min), all volatile substances were removed at -30 °C/0.7 Pa. Colourless solid product precipitated from diethylether at -80 °C and was characterized by elemental analysis and NMR. $- {}^{1}H$ NMR: $\delta = -0.02$ (18 H), 0.67 (3 H), 0.97 (d, 12 H), 1.18 (d, 12 H), 3.68 (sept, 4 H). – ¹¹B NMR: δ = 49.7. $-{}^{13}$ C NMR (-50 °C): $\delta = 0.0$ (q, SiMe), -2.4 (q, BMe), 45.8 (s, Si₂C), 23.3, 47.1 (q, d, *i*Pr). – On standing at room temperature, the thermolabile product decomposed slowly. An ¹¹B NMR signal at $\delta = 33.7$ grew, together with a 1:1 set of ¹H NMR signals in the range typical for SiMe₃. An IR band at v = 2047 cm^{-1} grew simultaneously, indicating a diazo group. In order to obtain a complete decomposition with a well-defined product, the mixture was heated in boiling toluene (5 d), yielding an orange, viscous material, from which no pure product, however, could be isolated.

3-Isobutyl-4-methyl-2,5-bis(trimethylsilyl)-1,2-aza-3-azonia-4-borata-3,5-cyclopentadiene (5'b): Isobutylazide (7 mmol) was added to MeB=CA₂ (5 mmol) in pentane (5 ml) at -78 °C. After stirring at -30 °C (8 h), an ¹¹B NMR signal at $\delta = 45.5$ was detected in the reaction mixture, attributed to the primary cycloadduct **5b**. After removal of the volatiles, the product **5'b** was obtained on distillation at 70 °C/0.7 Pa (74 %) as a yellow liquid, characterized by elemental analysis (C, H, N) and NMR. - ¹H NMR: $\delta = 0.25$ (s, 9 H), 0.51 (s, 12 H; SiMe, BMe), 0.87 (d, 6 H), 1.97 (mc, 1 H), 3.72 (d, 2 H). - ¹¹B NMR: $\delta = 31.9$. - ¹³C NMR (-50 °C): $\delta = 1.6$, 2.8 (2 q, SiMe), -4.2 (q, BMe), 134.4 (s, BCSi), 20.7, 30.7, 55.4 (q, d, t; *i*Bu).

4-Methyl-2,3,5-tris(trimethylsilyl)-1,2-diaza-3-azonia-4-borata-3,5cyclopentadiene (5'c): An equimolar mixture (8 mmol) of MeB= CA₂ and azidotrimethylsilane was prepared at -78 °C and brought to room temperature. A sublimation at 45–55 °C/0.7 Pa gave the product (16 %; m.p. 55–58 °C), characterized by elemental analysis (C, H, N) and NMR. – ¹H NMR: $\delta = 0.27$, 0.40, 0.54 (3 s, 1:1:1, 27 H), 0.64 (s, 3 H). – ¹¹B NMR: $\delta = 36.3$. – ¹³C NMR (-30 °C): $\delta = 0.3$, 1.3, 2.6 (3 q, SiMe₃), 3.4 (q, BMe), 133.0 (s, BCSi).

4-Methyl-5-(chlorodimethylsilyl)-2,3-bis(trimethylsilyl)-1,2-diaza-3-azonia-4-borata-3,5-cyclopentadiene (5'd): Starting from MeB= CAA' and AN₃ and proceeding as described for 5'c, the product was obtained by sublimation at 50–60 °C/0.7 Pa (36 %; m.p. 58–60 °C). – ¹H NMR: δ = 0.41, 0.59, 0.65 (3 s, 1:1:1, 27 H); the signal for BMe is hidden under the signal of SiMe₂Cl (3+6 H), presumably at δ = 0.65. – ¹¹B NMR: δ = 36.8. – ¹³C NMR: δ = 0.2, 1.3 (2 q, SiMe₃), 5.6 (q, SiMe₂Cl), –3.8 (q, BMe), 128.3 (s, BCSi).

2,5-Dimethyl-3-phenyl-4,4-bis(trimethylsilyl)-1-oxonia-2-aza-5-borata-5-cyclopentene (5e): N-Methylbenzaldimine-N-oxide, PhCH= NMe-O, (4.5 mmol) in toluene (5 ml) was added to MeB=CA₂ (5 mmol) in pentane (5 ml) at -78 °C. After stirring the mixture at room temperature (2 h), volatiles were removed in vacuo. The product crystallized from pentane at -80 °C (92 %; m.p. 42 °C) and was characterized by elemental analysis (C, H, N) and NMR. - ¹H NMR: $\delta = -0.10, 0.27$ (2 s, 1:1, 18 H), 0.52 (s, 3 H), 2.73 (s, 3 H), 4.27 (s, 1 H), 7.24–7.59 (5 H). - ¹¹B NMR: $\delta = 51.9. -$ ¹³C NMR: $\delta = 1.8, 2.4, 46.2$ (3 q), 38.6 (s), 78.7 (d); additional: 3 d, 1 s (Ph).

4-(Chlorodimethylsilyl)-2,5-dimethyl-3-phenyl-4-(trimethylsilyl)-1oxonia-2-aza-5-borata-5-cyclopentene (**5f**): A procedure as described for **5e** gave the product **5f** (58 %; m.p. 82 °C). – ¹H NMR (diasteromers in the ratio 83:17): $\delta = 0.07/0,57$ (SiMe₃), 0.30/0.55 (SiMe₂), 0.66/0.59 (BMe), 2.73/2.71 (NMe), 4.58/4.27 (PhCH), 7.23-7.62 (Ph). – ¹¹B NMR: $\delta = 51.9$. – ¹³C NMR: $\delta = 2.0$ (SiMe₃), 5.8 (Me I of SiMe₂), 6.0 (Me II of SiMe₂), 45.7 (NMe), 78.7 (PhCH); additional: 3 d, 1 s (Ph); the signals of BMe and Si₂CB were not detected.

References

- [1] B. Glaser, H. Nöth, Angew. Chem. 1985, 97, 424; Angew. Chem. Int. Ed. Engl. 1985, 24, 416.
- [2] R. Boese, P. Paetzold, A. Tapper, Chem. Ber. 1987, 120, 1069.
- [3] A. Berndt, Angew. Chem. 1993, 105, 1034; Angew. Chem. Int. Ed. Engl. 1993, 32, 985.
- [4] P. Hassanzadeh, Y. Hannachi, L. Andrews, J. Chem. Phys. 1993, 97, 6418.
- [5] R. Boese, P. Paetzold, A. Tapper, R. Ziembinski, *Chem. Ber.* 1989, 122, 1057.
- [6] P. Paetzold, T. Schmitz, A. Tapper, R. Ziembinski, *Chem. Ber.* 1990, 123, 747.
- [7] U. Englert, R Finger, P. Paetzold, B. Redenz-Stormanns, Organometallics 1995, 14, 1507.
- [8] B. E. Alaluf, K. J. Alford, E. O.Bishop, J. D. Smith, J. Chem. Soc., Dalton Trans. 1974, 669.

- [9] R. Boese, N. Finke, J. Henkelmann, G. Maier, P. Paetzold, H. P. Reisenauer, G. Schmid, *Chem. Ber.* 1985, 118, 1644.
- [10] A. Tapper, T. Schmitz, P. Paetzold, Chem. Ber. 1989, 122, 595.
- [11] S. Küpper, U. Englert, P. Paetzold, *Heteroatom Chem.* 1990, 1, 479.
- [12] H. Nöth, B. Wrackmeyer in *NMR Basic Principles and Progress* (P. Diehl et al., Eds.), Vol. 14, Springer, Berlin 1978.
- [13] S. S. Al Juaid, C. Eaborn, P. B. Hitchcock, K. K. Kundu, M. E. Molla, J. D. Smith, *J. Organomet. Chem.* **1990**, *385*, 13.
- [14] P. Paetzold, L. Geret, R. Boese, J. Organomet. Chem. 1990, 385, 1.
- [15] A. L. Spek, PLATON 94, University of Utrecht, The Netherlands, 1994.
- [16] C. R. Lucas, M. L. H. Green, J. Chem. Soc., Chem. Commun. 1972, 1005.
- [17] P. Paetzold, Adv. Inorg. Chem. 1987, 31, 123.
- [18] P. Paetzold, H. Grundke, Synthesis 1973, 635.
- [19] We are greatly indebted to R. Boese (Universität-Gesamthochschule Essen, Germany) for the collection and interpretation of the crystal diffraction data.
- [20] H. Bock, L. S. Cederbaum, W. von Niessen, P. Paetzold, P. Rosmus, B. Solouki, Angew. Chem. 1989, 109, 77; Angew. Chem. Int. Ed. Engl. 1989, 28, 88.
- [21] P. Galow, A. Sebald, B. Wrackmeyer, J. Organomet. Chem. 1983, 259, 253.
- [22] N. Wiberg, P. Karampatses, C.-K. Kim, Chem. Ber. 1987, 120, 1203.
- [23] G. M. Sheldrick, SHELXS 97, Program for Structure Solution, and SHELXL 97, Program for Structure Refinement, University of Göttingen, Germany, 1997.
- [24] B. T. Gröbel, D. Seebach, Chem. Ber. 1977, 110, 852.
- [25] H. Schmidbauer, H. Stuhler, W. Vornberger, Chem. Ber. 1972, 105, 1084.
- [26] A. Baceiredo, G. Bertrand, J.-P. Majoral, F. El Anba, G. Manuel, J. Am. Chem. Soc. 1985, 107, 3945.