Unusual Mono- and Dinuclear Cobalt and Platinum Complexes of Rearranged Boriranylideneborane and Diboretanylideneborane Ligands: Dicobalt-μ-diborylcarbene Complexes as Derivatives of Planar Methane

Anuradha Gunale, Dirk Steiner, Dieter Schweikart, Hans Pritzkow, Armin Berndt,* and Walter Siebert*

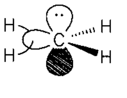
Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday

Abstract: The reactivity of boriranylideneboranes **4** and diboretanylideneborane **8** towards metal complex fragments was investigated. The reactions of **4** proceed with cleavage of the C–C bond in the three-membered ring and migration of substituents to form mono- and dinuclear complexes of varying structure depending on electronic and steric effects. The duryl and mesityl derivatives **4a** and **4b** react with [Co(C_5H_5)(C_2H_4)$_2$] with evolution of ethene to form dicobalt complexes **5a** and **5b**, which can be viewed as the first examples of complex-stabilized diborylcarbenes **6a** and **6b**. The crystal structure analysis shows an unusual structure in which a C-B-C-B chain and two cobalt atoms lie in one plane to give a planar-tetracoordinate carbon (ptC) atom C2; the sum of angles at C2 is 359.9°. Quantum-mechanical calculations show that this unusual structure is stabilized by interactions of **6d** with the cobalt atoms. The ptC in complex **5d**, which is surrounded by four electropositive substituents, has increased σ and decreased π electron density. Complexes **5** are therefore the first examples of metal-substituted analogues of planar methane (Hoffmann model). Reaction of the *tert*-butyl derivative **4c** with [Co(C_5H_5)(C_2H_4)$_2$] provides only the mononocobalt complex [Co(C_5H_5)(C_2H_4)C_2($SiMe_3$)$_2B_2t$$Bu_2$] (**7c**), independent of reaction stoichiometry; this indicates that an aromatic group is required for formation of the dinuclear complex. Characterization of the metalacycle **7c** was facilitated by replacing the ethene ligand by CO and *t*BuNC. Reaction of the diboretanylideneborane **8** with [Co(C_5H_5)(C_2H_4)$_2$] does not provide another complex with a ptC atom, but instead the sandwich complex **10**, a complex-stabilized 1,3-dibora-5-silapenta-1,4-diene. Boriranylideneborane **4a** reacts with [Pt(C_8H_{12})$_2$] at room temperature to form the diplatinum compound **11**, which can be viewed as being formed from diborylcarbene **12**.

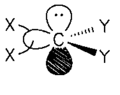
Keywords: boron • cobalt • diborylcarbenes • planar-tetracoordinate carbon • platinum

Introduction

In 1970 Hoffmann et al.[1] reported the electronic structure of planar methane (**A**): Two hydrogen atoms form two-center two-electron (2c–2e) bonds to the sp^2-hybridized carbon atom, and the other two hydrogen atoms form a 3c–2e bond with the empty hybrid orbital. The remaining two electrons at carbon are located in the high-lying p_z orbital. This unusual structure can be stabilized by σ-donor/π-acceptor substituents (**B**; X, Y = silyl, boryl). Schleyer et al.[2] carried out MO calculations on a large number of molecules with electropositive substitutents (X, Y = Li, SiH_3, BH_2) and on compounds in which the planar-tetracoordinate carbon (ptC) functions as a bridging atom in two rings. Their studies show that in the case of 1,1-dilithiocyclopropane, the planar geometry is favored over tetrahedral coordination by 7 kcal mol^{-1}.



A



B

C

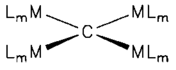
Over the past two decades numerous compounds with a ptC have been reported; in addition to being structurally characterized by X-ray crystallography, their electronic structures were often analyzed as well. A recent review by Röttger and Erker[3] summarizes the rapidly expanding chemistry of ptC compounds.

---

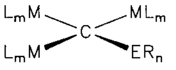
[*] Prof. Dr. W. Siebert, Dr. A. Gunale, Dr. H. Pritzkow
Anorganisch-Chemisches Institut der Universität
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Fax: Int. code + 49 6221 545-609
Prof. Dr. A. Berndt, Dr. D. Steiner, Dr. D. Schweikart
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: Int. code + 49 6421 288-917

0947-6539/98/0401-0044 $ 17.50+.50/0

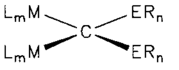
In almost all these compounds the ptC is connected not only to Lewis acid centers (transition metals ML_m and main group elements ER_n) but also to electron-precise or electron-rich atoms such as carbon, nitrogen, oxygen, and sulfur. When the ptC is part of an aromatic, acetylenic, olefinic, or imino π system, it does not require the stabilization expected for the ptC in the planar methane derivatives **E**–**J**.



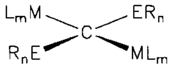
E



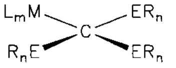
F



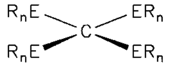
G



H



I

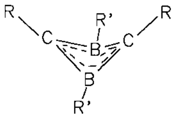


J

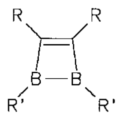
As a result of chelation in many mono- and dinuclear complexes,[3] the ptC is geometrically forced to be near the metal center(s), and its connectivity increases to four. Recently, Huttner et al.[4] noticed that in η^2-carboxylatocobalt complexes the Co⋯C distance (2.35 Å) is only 0.3 Å longer than that of a covalent Co–C bond. They concluded: "The chelating therefore exhibits the characteristic, but hitherto never discussed peculiarity of an idealized square-planar coordinated carbon atom". Many other carboxylato metal complexes exhibit similar geometries.[5]

Our interest in compounds with a ptC focuses on methane derivatives of the type **E**–**J**, in which the Lewis acid substitutents ML_m and ER_n should function as σ donors and π acceptors, and interact with each other. A carbidotetrarhenium cluster[6] could be regarded as an example of tetrametalamethane **E**. However, in the complex anion $[\{I(OC)_3Re\}C\{Re(CO)_4\}_3]^-$ the carbon atom is located at the center of a tetrahedrally distorted square of rhenium atoms. The Re_4 ring is folded by 42°, which is explained by repulsive interactions between ligands on adjacent metals. Attempts[7] to synthesize tetraborylmethane derivatives **J** to prove the prediction[2a] that a ptC could be stabilized by four boryl groups have not yet been successful.

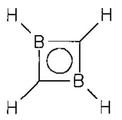
While investigating the ligand properties of boron heterocycles,[8] we found that among the 1,3-dihydro-1,3-diboretes[9–12] **1**—which are not planar as in **3** but puckered (predicted by Schleyer et al.)[13]—**1b** does not show any complex chemistry due to weakening of the acceptor abilities of the boron atoms by the π-donor amino substituents. Attempts to complex **2b**[12] with Pd^0 or Pd^{II} compounds unexpectedly resulted in catalytic dimerization of the boron heterocycle and formation of the eight-membered tetraborocine derivative.[14] The reaction of **2b** with $[Ru_3(CO)_{12}]$ provides a CO-insertion product instead of a new metal complex.[15] Therefore, it was decided to investigate the complexation chemistry of B-organyl derivatives of C_2B_2 heterocycles, in particular boriranylideneboranes **4** (the classical, nonexisting representation is **4***).[16]



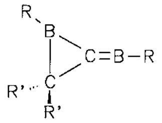
1	R	R'
a	H	H
b	H	N*i*Pr_2



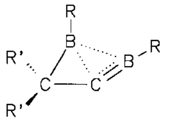
2	R	R'
a	H	H
b	H	N*i*Pr_2



3



4*

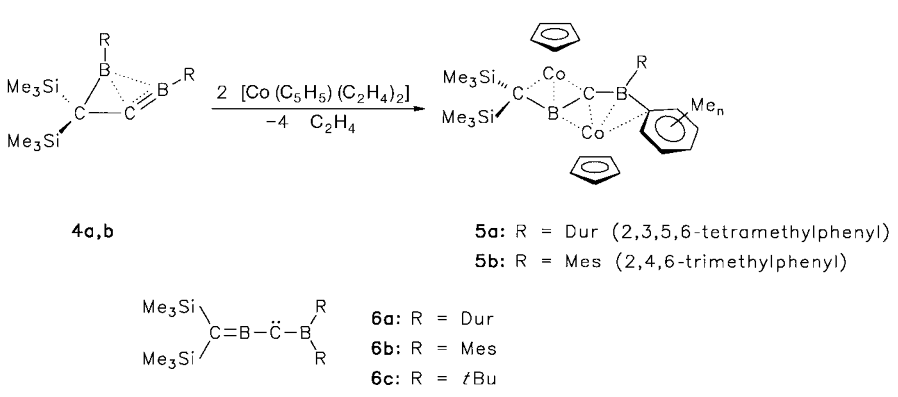


4a: R = Dur, R' = $SiMe_3$
4b: R = Mes, R' = $SiMe_3$
4c: R = *t*Bu, R' = $SiMe_3$

The nonclassical structure of **4** was predicted for $(CH_2)C(BH)_2$ by Schleyer and others[17,18] years before proof was provided by an X-ray structure determination of the B-duryl, C-trimethylgermyl derivative of **4** (R = Dur, R′ = $GeMe_3$).[19] The organic chemistry of **4** has been extensively studied and is characterized by cleavage of bonds in the three-membered ring and migration of substituents.[16] The topomerization of **4** proceeds readily via a cyclic diborylcarbene,[17] and the facile isomerization of borylmethyleneboranes was explained with linear diborylcarbenes as intermediates.[16c] Recently, **4** itself was recognized to be a carbene stabilized by the nearby B–B moiety, which acts as a π acceptor as well as a σ donor.[16d] However, relatively little is known about the reactivity of **4** with respect to metal complex fragments. Here we report the complexation chemistry of the nonclassical boriranylideneboranes **4a**–**c**. With respect to CoCp (Cp = C_5H_5) moieties, **4a** and **4b** formally act as diborylcarbenes and are complexed twice to yield the first examples of the planar methane derivative **C** with the substitution pattern shown in **H**.[20] Quantum-chemical methods were employed to study the electronic stabilization of these complexes.[21]

Results and Discussion

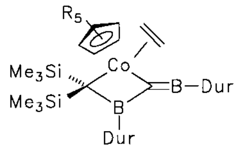
Synthesis and Reactivity: Two equivalents of $[Co(C_5H_5)(C_2H_4)_2]$[22] react with **4a** and **4b** in hexane with evolution of ethene to form unexpectedly **5a** and **5b** (Scheme 1). These dinuclear complexes are the first examples of complex-stabilized diborylcarbenes **6a** and **6b**.[20] The reaction of **4a** proceeds spontaneously at room temperature, whereas that of **4b** requires photochemical activation. Chromatographic workup and recrystallization from hexane provides the dark green crystalline products in 48 and 19% yields, respectively. Complex **5b** can also be obtained by the reaction of **4b** with $[Co(C_5H_5)(C_6Me_6)]$[22] at 60 °C, but the yields (12%) are similarly low. The mesityl complex is less stable than the duryl derivative, as seen from its rapid decomposition in solution at room temperature. The low yield is probably due to decomposition during the reaction or subsequent workup. Complexes **5a** and **5b** are soluble in common organic solvents and decompose in halogenated solvents.



Scheme 1. Reaction of **4a**,**b** with $[Co(C_5H_5)(C_2H_4)_2]$.

The ^{11}B NMR spectra of the isolated complexes show only one broad signal at $\delta = 43$ for **5a** and $\delta = 46$ for **5b**. Apparently, the electronic environments of the chemically different boron atoms are similar enough that their resonances cannot be resolved at 64 MHz. ^1H and ^{13}C NMR spectra of the two complexes exhibit highly unsymmetrical structures in which the aromatic groups are not free to rotate. The strongly low field shifted signal for the central C atom in **5a** ($\delta = 194.5$) supports its description as a carbene, since similar chemical shifts were observed for other dinuclear carbene complexes ($\delta = 165-235$).[24]

In the reaction of **4a** with $[Co(C_5H_5)(C_2H_4)_2]$, traces of a red, boron-containing fraction were isolated in addition to the main product **5a**. The mass spectrum of the red compound showed a mole peak at $m/z = 610$, which corresponds to the formula $[Co(C_5H_5)(C_2H_4)C_2(SiMe_3)_2B_2Dur_2]$ (**7a**). Attempts to synthesize **7a** in larger quantities, for example with a 1:1 ratio of **4a** and $[Co(C_5H_5)(C_2H_4)_2]$, were unsuccessful due to its extreme instability; **5a** was always the main product in the reactions. The bound ethene acts as a classical two-electron ligand and, as in $[Co(C_5H_5)(C_2H_4)_2]$, is easily lost. This leads to the formation of a very reactive species.

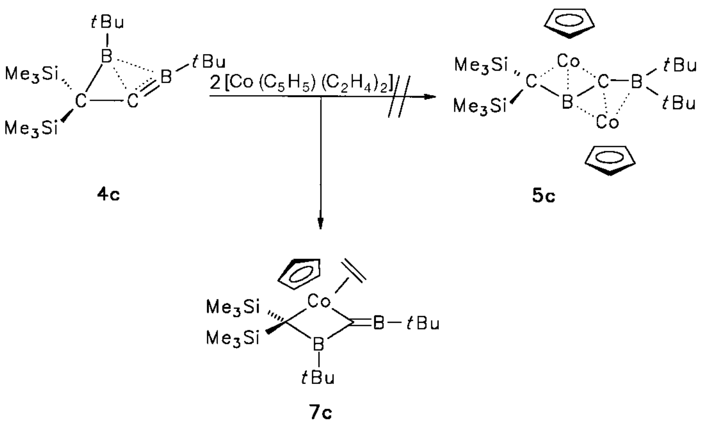


7a: R = H

7b: R = Me

Since $[Co(C_5Me_5)(C_2H_4)_2]$[25] is known to be more stable than $[Co(C_5H_5)(C_2H_4)_2]$, it was allowed to react with **4a** in the hope of isolating a Cp* derivative (Cp* = C_5Me_5) of **7a**. A boron-containing fraction was isolated whose mass spectrum showed a mole peak at $m/z = 680$, which corresponds to the mononuclear complex $[Co(C_5Me_5)(C_2H_4)C_2(SiMe_3)_2B_2Dur_2]$ (**7b**). Unfortunately, this complex was also very unstable and decomposed upon removal of solvent. Attempts to replace the ethene ligand by CO resulted in quantitative formation of $[Co(C_5Me_5)(CO)_2]$.[26] Interestingly, by the reaction of $[Co(C_5Me_5)(C_2H_4)_2]$ with **4a** there was no evidence for the formation of a dinuclear complex, that is, a Cp* derivative of **5a**. This is most likely due to steric reasons.

As the X-ray crystal structure of **5a** shows (see below), there is a definite interaction between one duryl moiety and one of the CoCp fragments. To test the importance of the aromatic system for the stabilization of this complex, the *tert*-butyl derivative **4c** was allowed to react with $[Co(C_5H_5)(C_2H_4)_2]$ (Scheme 2). In this case, reaction does not take place at room temperature, but requires heating in hexane at reflux. The diborylcarbene complex **5c** is not formed; only the monocobalt complex **7c** is obtained independent of reaction stoichiometry. Thus, dinuclear complexes are stable only when aromatic substituents are attached to the boron atoms. A 1,3-shift of such a substituent—known only for aryl groups—is required for the formation of the skeleton of the dinuclear complexes. The unstable intermediate **7a′** (see Scheme 4) with a dicoordinate boron atom is probably formed, which can be attacked by another equivalent of $[Co(C_5H_5)(C_2H_4)_2]$ to provide **6a**. Quantum-mechanical investigations for **5d** (see below) identify a weak interaction between one aryl ring and the nearby cobalt atom.[21]

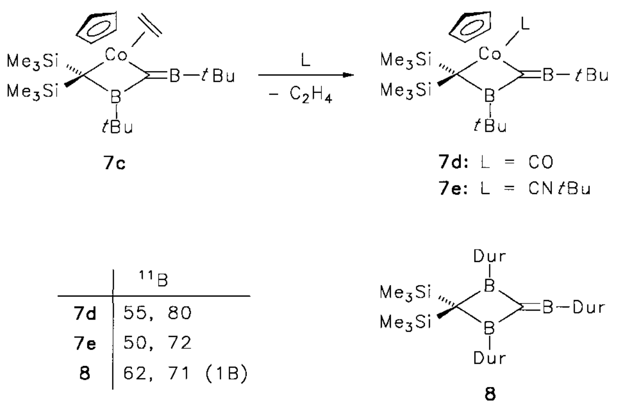


Scheme 2. Reaction of **4c** with $[Co(C_5H_5)(C_2H_4)_2]$.

As in the case of **7a** and **7b**, the ethene ligand in **7c** is responsible for the instability of the complex. It was therefore decided to replace it by a ligand that binds more strongly. Although no exchange was observed with MeCN and PPh_3, reactions with CO and *t*BuNC resulted in the more stable complexes **7d** and **7e** (Scheme 3).

Bubbling CO through a freshly prepared solution of **7c** followed by chromatographic workup provided **7d** as a red oil ($\nu_{CO} = 1979\ cm^{-1}$). The ^{11}B NMR spectrum of **7d** shows two signals at $\delta = 55$ and 80 in a 1:1 intensity ratio.

A solution of **7c** was also treated with *t*BuNC. Chromatographic workup and recrystallization from hexane provided red, microcrystalline **7e** ($\nu_{CN} = 2107\ cm^{-1}$). The ^{11}B NMR spectrum of **7e** also shows two signals in a 1:1 intensity ratio at $\delta = 55$ and 72. Comparison of the chemical shifts of **7d** and **7e** with those of diboretanylideneborane **8**[27] supports the proposed metalacyclic structure: **8** shows an ^{11}B resonance at $\delta = 71$ for the exocyclic boron atom, and the signal for the

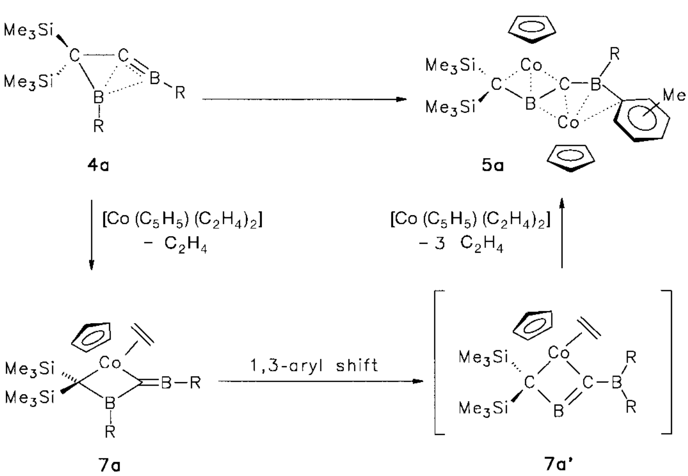


	^{11}B
7d	55, 80
7e	50, 72
8	62, 71 (1B)

Scheme 3. Replacement of C_2H_4 in **7c** by CO and *t*BuNC.

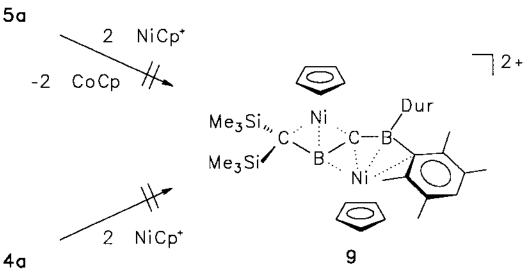
two ring boron atoms is at $\delta = 62$. The appearance of two singlets for the $SiMe_3$ groups and three signals for the *tert*-butyl groups in the ^{1}H and ^{13}C NMR spectra of **7e** indicates that a highly unsymmetrical structure is present. Because the microcrystals of **7e** were not suitable for X-ray structure analysis, attempts were made to replace ethene in **7c** with 2,6-dimethylphenylisocyanide. However, $[Co(C_5H_5)(2,6\text{-}Me_2\text{-}C_6H_3NC)_2]$[28] was the only cobalt-containing product isolated. Unfavorable steric interactions between the dimethylphenyl group and the *tert*-butyl groups apparently preclude formation of the desired product.

Since traces of **7a** were isolated from the reaction of **4a** with $[Co(C_5H_5)(C_2H_4)_2]$, it is likely that it represents an intermediate in the formation of **5a**. The following mechanism can therefore be postulated (Scheme 4): Insertion of a CoCp fragment into the C–C bond of the three-membered ring in **4a** leads to unstable **7a**. A subsequent 1,3-aryl shift is followed by attack of a second CoCp unit on the formed C=B bond of **7a′** and loss of ethene to provide **5a**.



Scheme 4. Possible mechanism for the formation of **5a**.

The reactivity of **5a** was investigated to test the possibility of exchanging the CoCp units in **5a** with the isolobal $NiCp^+$ fragments, which would lead to another metal-substituted planar methane derivative $[\{Ni(C_5H_5)\}_2(\mu\text{-}C_2(SiMe_3)_2B_2Dur_2)]^{2+}$ (**9**, Scheme 5). The triple-decker $[Ni_2(C_5H_5)_3]BF_4$[29] was chosen as the reagent since it decomposes to provide the reactive $NiCp^+$ fragment and nickelocene. Although the characteristic color for the formation of $[Ni(C_5H_5)_2]$ was observed, no dinuclear nickel complex could be isolated from the reaction mixture. Furthermore, the starting material **5a** could not be recovered, since it apparently decomposes in the presence of $NiCp^+$. The direct reaction of **4a** with $[Ni_2(C_5H_5)_3]BF_4$ also did not provide the expected dinuclear complex **9**.

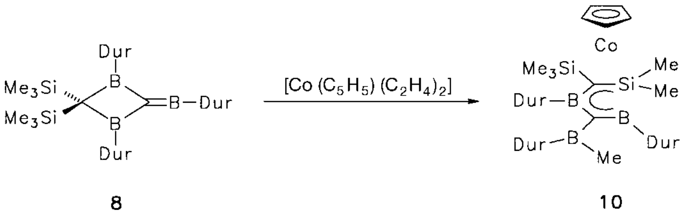


Scheme 5. Attempted syntheses of **9**.

Quantum-mechanical calculations (see below) show that the central carbon atom in **5d** has a configuration of $\sigma^{3.994}\pi^{1.356}$ and is electron-rich.[21] It was therefore expected that **5a** would readily react with electrophiles such as $[AuPPh_3Cl]$ to form cationic compounds. Surprisingly, this was not the case; the starting materials could be recovered almost quantitatively.

Attempts were made to isolate cation $(\mathbf{5a})^+$, whose presence was indicated by the cyclovoltammogram of **5a** (see below). However, reaction of **5a** with $[Fe(C_5H_5)_2]BF_4$ or $AgBF_4$ led only to decomposition products. Similarly, reaction of **5a** with potassium or lithium led to insoluble black products, and the expected product $K^+(\mathbf{5a})^-$ could not be isolated, even when [18]crown-6 ether was added as ligand.

Due to the similarities in structure between **7** and **8**, it was expected that **8** would react with $[Co(C_5H_5)(C_2H_4)_2]$ to provide a complex of type **I** with a planar-tetracoordinate carbon atom. Instead, **10** was obtained as dark red crystals in very low yields (Scheme 6).

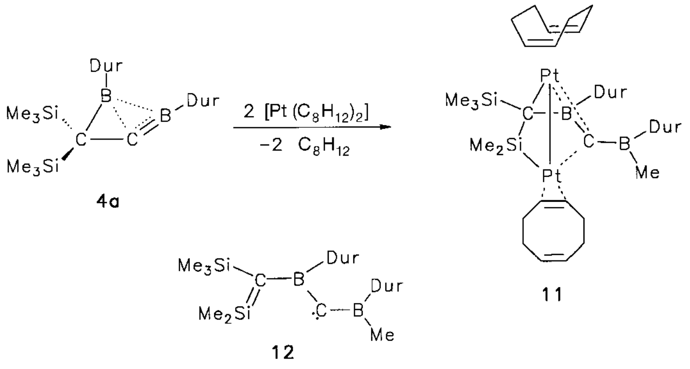


Scheme 6. Reaction of **8** with $[Co(C_5H_5)(C_2H_4)_2]$.

The sandwich complex, which is soluble in hexane and toluene, proved to be very unstable, and decomposed in THF as solvent and upon attempted chromatography or sublimation. The ^{11}B NMR spectrum exhibits two signals at $\delta = 29$ and 70 in an intensity ratio of 2:1. The ^{1}H NMR spectrum shows that a methyl group has migrated from a silicon to a boron atom; the signal for the Cp protons appears in the expected region ($\delta = 4.94$). The aromatic groups are not free to rotate on the NMR time scale, and there are 11 signals for the 12 methyl groups.

0947-6539/98/0401-0047 $ 17.50+.25/0

The reactivity of **4a** was also investigated with respect to other metal complex fragments. Although reactions with $[Ni(C_8H_{12})_2]$[30] and $[Fe(CO)_3(C_8H_{14})_2]$[31] did not result in boron-containing complexes, $[Pt(C_8H_{12})_2]$[32,33] reacted readily with **4a** at room temperature to form the diplatinum complex **11** (Scheme 7). It can be viewed as being formed by oxidative addition of two Pt(cod) (cod = 1,5-cyclooctadiene) moieties onto the unknown diborylcarbene **12**.[20] The schematic representation of **12** indicates the position of this bent moiety in the complex; however, the free diborylcarbene should have a linear B-C-B geometry.[*]



Scheme 7. Reaction of **4a** with $[Pt(C_8H_{12})_2]$.

NMR spectroscopy of **11** indicated a highly unsymmetrical structure: There are two signals at $\delta = 41$ and 65 in the ^{11}B NMR spectrum. The ^{1}H and ^{13}C NMR spectra indicate the migration of a methyl group from a silicon to a boron atom, and there are eight signals for the methyl groups on the rigid aromatic rings. In the ^{195}Pt NMR spectrum two signals appear at $\delta = -4429$ and -3882; the low-field shift is assigned to the platinum center in the ring, which has σ interactions with the neighboring atoms.

Crystal structures: Crystals of **5a** that were suitable for an X-ray structure analysis were grown from a hexane solution (Figure 1). Microcrystals of the mesityl derivative **5b** were also obtained and studied with an image plate (IPDS, Stoe). The quality of the latter crystals was very poor: The refinement of the weak-intensity data yielded a structure similar to **5a**, but did not allow the discussion of any structural details.

Table 1. Selected bond lengths [Å] and angles [°] in **5a**.

Co1–B1	2.276(6)	B1–C2	1.522(10)
Co1–C2	2.009(6)	B1–C5	1.601(10)
Co1–B3	2.081(8)	C2–B3	1.474(9)
Co1–C5	2.180(7)	B3–C4	1.483(10)
Co2–C2	1.887(6)	C4–Si1	1.851(8)
Co2–B3	1.973(7)	C4–Si2	1.887(8)
Co2–C4	2.114(6)		
B1-C2-B3	150.3(6)	C2-B3-C4	138.0(6)
B1-C2-Co1	78.9(4)	C2-B1-C5	114.4(6)
B1-C2-Co2	139.0(5)	B3-C4-Si1	119.0(6)
B3-C2-Co1	71.5(4)	B3-C4-Si2	116.2(6)
B3-C2-Co2	70.7(4)	Si1-C4-Si2	119.4(3)

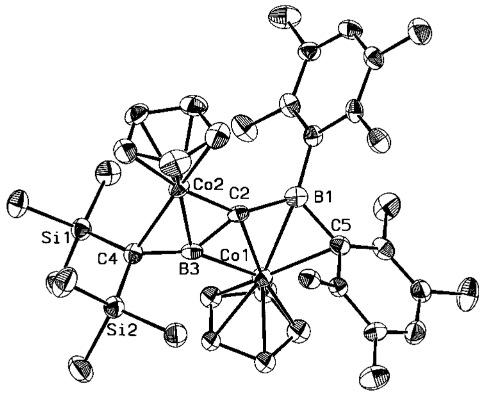


Figure 1. Crystal structure of **5**.

The C–C bond of the boriranylideneborane **4a** has been cleaved, and a bent C-B-C-B chain is now present. The C4-B3-C2 part of the C-B-C-B chain in **5a** is *trihapto*-coordinated to a CoCp moiety. The second CoCp fragment is bonded *tetrahapto* to the other side of the ligand through the B3-C2-B1 atoms as well as to one duryl substituent. The distances between the central C2 atom and the two cobalt atoms are short (Co1–C2 2.009(6), Co2–C2 1.887(6) Å) and can be compared with the length of a C=Co bond (1.881(6) Å)[34] (Table 1). Cobalt–boron distances of 1.9–2.1 Å have been observed.[35] The corresponding distances in **5a** are in this range, although Co1–B1 is a little longer (2.276(8) Å).

The atoms of the C4-B3-C2-B1 chain as well as the two Co atoms lie in a plane. The plane through Si1-C4-Si2 is perpendicular to this plane, and that through C5-B1-C15 forms an angle of approximately 30° to it. The bonds B3–C4 and C2–B3 are very short and in the region of a metal-coordinated B=C bond.[36] The sum of the angles at the central carbon atom is 359.9°. Therefore, C2 is planar-coordinated by four electropositive centers (maximum deviation from the best plane 0.05 Å).

Monocobalt complex **10** has the sandwich structure (Figure 2) that has been seen for mononuclear complexes of diborole.[8] Starting from diboretanylideneborane **8**, a methyl

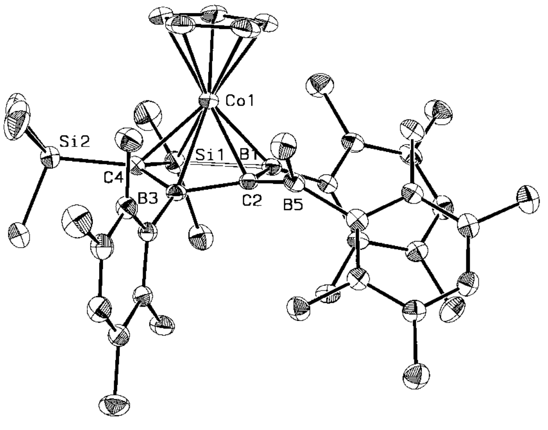
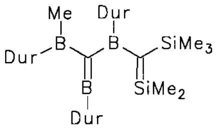


Figure 2. Crystal structure of **10**.

---

[*] According to density functional theory calculations (6-311G* basis) by I. Hyla-Kryspin and R. Gleiter, no imaginary frequencies are detected for the optimized structures **4** (R = R′ = H) and **6d**. The local minimum **6d** lies only 21.4 kcal mol^{-1} higher in energy than the global minimum **4**. Therefore, derivatives of **6** might be within experimental reach.



13

substituent from one $SiMe_3$ group has migrated to the exocyclic boron atom. Ring opening results in the 1,3-dibora-5-silapenta-1,4-diene derivative **13**, which is complexed to the CoCp fragment.

The B1–Si1 bond (2.405(3) Å, Table 2) is definitely longer than that typically seen for B–Si (1.91–2.09 Å).[37] The B–C bonds around B3 and B5 (1.538–1.624 Å) are in the region of single bonds. In contrast, B1–C2 is shorter (1.488(4) Å), and can be compared to the metal-coordinated B=C bonds in **5a**. The Si1–C4 distance (1.809(3) Å) is shorter than that of C4 to the exocyclic Si2, which is proof of its double-bond character. Therefore, **10** may be considered as a metal-stabilized pentadiene derivative.

Table 2. Selected bond lengths [Å] and angles [°] in **10**.

B1–C2	1.488(4)	C4–Si1	1.809(3)
B1–C6	1.567(4)	C4–Si2	1.868(3)
C2–B5	1.573(4)	Si1–B1	2.405(3)
B5–C16	1.592(5)	Co1–B1	2.058(3)
B5–C26	1.576(5)	Co1–C2	2.090(3)
C2–B3	1.596(4)	Co1–B3	2.311(3)
B3–C27	1.624(5)	Co1–C4	2.116(3)
B3–C4	1.538(5)	Co1–Si1	2.322(1)
B1-C2-B3	117.9(3)	C4-Si1-B1	88.6(1)
C2-B3-C4	114.7(3)	Si1-B1-C2	99.4(2)
B3-C4-Si1	113.3(2)		

The X-ray crystal structure analysis of the diplatinum complex **11** (Figure 3) confirmed the highly unsymmetrical structure shown by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy. The complex is best described as a five-membered ring (made up of Si1, Pt2, C2, B3, and C4) that is *tetrahapto*-bonded to Pt1. The distance between Pt1 and Si1 is 2.913(4) Å and too long for a bonding interaction (Table 3). Normal Pt–Si bonds are in the region of 2.2 to 2.4 Å.[38]

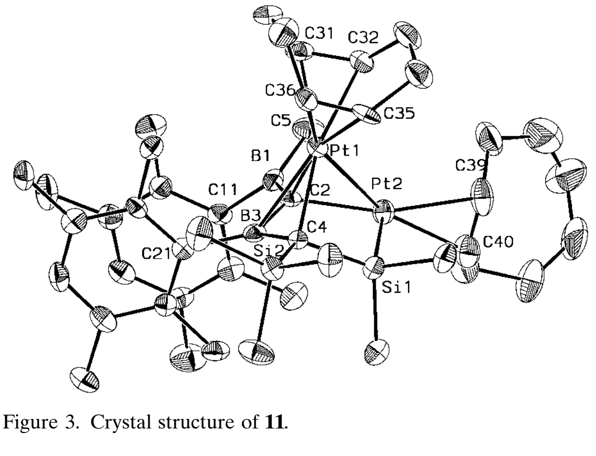


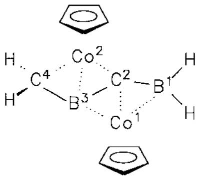
Figure 3. Crystal structure of **11**.

Although the Pt1–Pt2 distance of 2.864(2) Å is a little longer than typically observed, there is a bonding interaction present. This is supported by the small angle of about 86° for Pt1-C2-Pt2. In known μ-methylene diplatinum complexes, a Pt–Pt bond is described for distances between 2.5 and 2.8 Å and Pt-C-Pt angles of 75–78°. There is no bond assumed for complexes with a Pt–Pt distance of longer than 3 Å or angles at the carbene carbon of more than 100°.[39] The Pt1 atom can be assigned an 18 VE configuration (cod as an η^4-ligand, σ bonds to C4 and Pt2, and a 3c–2e bond Pt1-C2-Pt2). On this basis Pt2 formally has a 16 VE configuration, since it is only *dihapto*-coordinated to its cod ligand. This may be due to steric reasons.

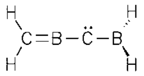
Table 3. Selected bond lengths [Å] and angles [°] in **11**.

Pt1–Pt2	2.864(2)	Pt2–C40	2.154(12)
Pt1–C2	2.118(10)	B1–C2	1.583(18)
Pt1–B3	2.409(12)	B1–C5	1.582(17)
Pt1–C4	2.166(10)	B1–C11	1.584(17)
Pt2–C2	2.084(10)	B3–C21	1.597(15)
C2–B3	1.528(16)	C4–Si2	1.868(11)
B3–C4	1.556(16)	Pt1–C31	2.234(11)
Si1–C4	1.897(10)	Pt1–C32	2.234(11)
Si1–Pt2	2.304(4)	Pt1–C35	2.225(11)
Pt2–C39	2.176(12)	Pt1–C36	2.181(12)
C2-B3-C4	107.4(9)	Pt2-C2-B3	122.5(8)
B3-C4-Si1	105.3(7)	B1-C2-B3	132.3(9)
C4-Si1-Pt2	102.9(4)	Pt1-C2-Pt2	86.0(4)
Si1-Pt2-C2	81.3(3)	Pt2-Pt1-C4	80.6(3)

Electronic structure and bonding: The electronic factors responsible for the stabilization of the planar-tetracoordinate carbon atom in **5a** and **5b** were investigated with extended Hückel and ab initio methods by I. Hyla-Kryspin and R. Gleiter on the model compounds **5d**, **6d**, and [{CoCp}$_2$].[21]



5d



6d

The frontier MOs of the bridging ligand **6d** are as follows: The HOMO of **6d** is strongly localized on the carbene C atom (C̈) and has almost pure 2pπ character. The low-lying LUMO is an out-of-phase combination of the in-plane 2p orbitals and can accept σ electron density from the metal dimer fragment. Through interactions with the appropriate Co orbitals, a synergistic ligand →metal and metal →ligand shift of electron density is possible. A natural population analysis showed that the electron density at the ptC in free diborylcarbene **6d** (C̈ $\sigma^{2.978}\pi^{1.501}$) is different from that in planar methane (C̈ $\sigma^2\pi^2$)[1]: 0.499 e of C π electron density has already been delocalized onto the boron atoms, and the σ electron density of C in **6d** has increased by 0.978 e.

Upon complexation, an additional shift in electron density of 1.233 e from the CoCp units to **6d** is observed, and the final electronic configuration at the ptC in **5d** is $\sigma^{3.944}\pi^{1.356}$. The natural charge accompanying the carbene carbon increases from −0.482 in **6d** to −1.310 in **5d**. The ptC receives a total of 0.828 e from its neigboring groups or atoms. The in-plane σ density increases from 2.978 to 3.944 e, and the out-of-plane π electron density decreases from 1.501 to 1.356 e. Thus, in **5d** the overall stabilization manner of the ptC is exactly that predicted by Hoffman et al.[1] as required for stabilizing this unusual geometry: **5a** is a derivative of planar methane.

The natural charges accompanying the cobalt atoms change from +1.022 to +0.955 for Co1 and from +1.021 to +1.437 for Co2 upon complexation. An analysis of the occupancies of the in-plane and out-of-plane natural atomic orbitals shows that Co1 can be characterized as a strong σ donor (decrease from 5.007 to 4.157 upon complexation) and a strong π acceptor (increase from 2.968 to 3.886), whereas Co2 has weak σ-acceptor (increase from 5.007 to 5.206) and moderate π-donor properties (decrease from 2.970 to 2.340). Therefore, electron density is transferred from Co1 through the ptC atom to Co2 in the σ plane, while π electron density reorganizes in the opposite direction in the perpendicular plane. This push–pull interaction is responsible for the stabilization of the ptC. In addition, one aryl group (duryl or mesityl) accepts electron density into a π* MO.

Electrochemistry: To evaluate the electrochemical behavior of complexes with a planar-tetracoordinated carbon atom, cyclic voltammograms of **5a** and **5b** were recorded. The measurements were performed on solutions of the complexes with $n\mathrm{Bu_4NPF_6}$ (0.1M) in dimethoxyethane (DME) with glassy-carbon working electrodes. The one-electron nature of the observed reversible redox processes was established by comparison with the one-electron standard $[\mathrm{Fe(C_5H_5)_2}]^{+/0}$. Differences between cathodic and anodic peak potentials (ΔE_p) were measured and compared to the results for $[\mathrm{Fe(C_5H_5)_2}]$ (70–100 mV for reversible waves at scan rates of 0.05–0.5 V s^{-1}). A voltage range of +2.0 to −3.1 V versus SCE was investigated at a ground-current sensitivity of 5 μA cm^{-1}.

The duryl derivative **5a** shows two reversible reductions and one reversible oxidation. A further oxidation to a dication is irreversible. The redox processes for **5b** are not so well defined. The two reductions as well as the oxidation to a monocation are semireversible. Furthermore, an oxidation to a dication was not observed. The electrochemistry data are summarized in Table 4, and Figure 4 shows the cyclovoltammogram for **5a**.

ESR spectroscopy: The monoanion $(\mathbf{5a})^-$ could also be produced by reduction of **5a** in THF with a potassium mirror. At 100 K, a THF glass of the ion showed a broad signal at $g = 2.10$ (Figure 5). There is a weak hyperfine structure ($a_1 \approx 65$ G).

Attempts were made to obtain the dianion $(\mathbf{5a})^{2-}$ to see if it is paramagnetic or diamagnetic. Upon further exposure of a solution of $(\mathbf{5a})^-$ to potassium, a sharp signal appeared at $g = 2.004$, which is characteristic for an organic radical. The decomposition of **5a** upon reduction was further evidenced by a change in the color of the solution from green to brown.

Table 4. Redox potentials $E_{1/2}$ [V] versus SCE for **5a** and **5b**.

	Redox pair	$E_{1/2}$ [V]	ΔE [mV]
5a	2+/+	1.13	irrev.
	+/0	0.11	64 (rev.)
	0/−	−0.94	65 (rev.)
	−/2−	−2.12	65 (rev.)
5b	2+/+	not observed	
	+/0	+0.17	80 (semirev.)
	0/−	−0.85	137 (semirev.)
	−/2−	−2.09	103 (semirev.)

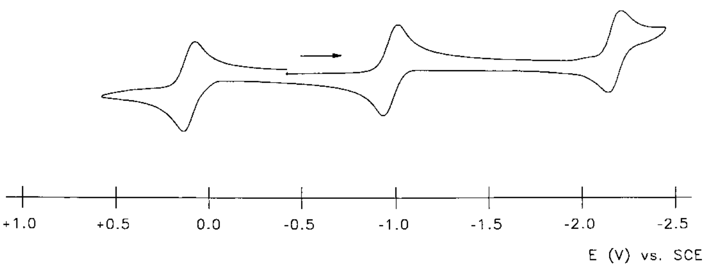


Figure 4. Cyclovoltammogram of **5a**.

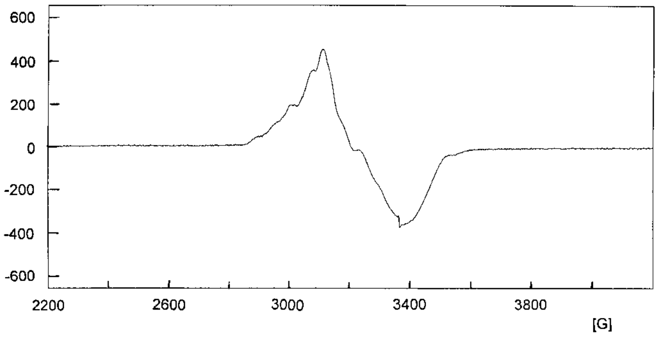


Figure 5. ESR spectrum of **5a**$^-$.

Conclusions

The nonclassical boriranylideneboranes **4** show interesting reactivity towards metal complex fragments. The reactions proceed with cleavage of the C–C bond in the three-membered ring and migration of substituents to result in very different dinuclear complexes of varying structure depending on electronic and steric effects. The dicobalt complexes **5a** and **5b**, which can be viewed as the first examples of complex-stabilized diborylcarbenes **6a** and **6b**, are stabilized by interactions of the central chain with the cobalt atoms and one aromatic ring. Reaction of the *tert*-butyl derivative **4c** with $[\mathrm{Co(C_5H_5)(C_2H_4)_2}]$ does not provide the analogous dinuclear complex but only the monocobalt complex **7c**, independent of reaction stoichiometry. The structure of **7** represents a possible intermediate in the formation of **5**. Reaction of diboretanylideneborane **8**, whose structure is similar to that of **7**, with $[\mathrm{Co(C_5H_5)(C_2H_4)_2}]$ does not provide another complex with a ptC, but instead the sandwich complex **10**. Completely different reactivity is shown by **4a** towards $[\mathrm{Pt(C_8H_{12})_2}]$. However, the diplatinum compound **11** can be viewed as a complex formed by oxidative addition of the two Pt(cod) moities onto the unknown diborylcarbene **12**.

Experimental Section

General: All experiments were carried out under nitrogen which had been dried and purified before use. Solvents were dried by conventional methods and saturated with nitrogen. NMR spectra were recorded on Bruker AC-200 (^{1}H: 200.13, ^{13}C: 50.32, ^{11}B: 64.21, ^{195}Pt: 43.0 MHz) and Bruker AC-500 instruments (^{1}H: 500.13, ^{13}C: 125.77 MHz). Chemical shifts are given relative to those of TMS and $\mathrm{BF_3 \cdot OEt_2}$. Mass spectra were recorded on a

Varian MAT CH7 and a Finnigan MAT8230. Alumina used for chromatography was dried and deactivated by addition of 5% water. Voltammetric experiments were conducted as described elsewhere.[40] Potentials are given in volts versus an SCE reference electrode. X-Band ESR spectra were obtained on a Bruker ESP300E spectrometer equipped with a liquid-N_2 variable-temperature unit. The field frequency was internally calibrated to 9.4500120 GHz. The procedure for the preparation of THF solutions of radical anions by stepwise reduction with a potassium mirror has been reported.[40]

***µ*-[Didurylborylbis(trimethylsilyl)methyleneborylcarbene]bis(μ^5-cyclopentadienyl)dicobalt (5a)**: A mixture of **4a** (0.310 g, 0.68 mmol) and $[Co(C_5H_5)(C_2H_4)_2]$ (0.380 g, 2.1 mmol) in hexane (15 mL) was stirred for 3 h. Chromatographic workup of the brown solution on Al_2O_3 with hexane provided an orange fraction with excess $[Co(C_5H_5)(C_2H_4)_2]$), a dark green fraction with **5a**, and a dark red fraction with traces of **7a**. Yield of **5a**: 230 mg (46%), m.p. = 183 °C (from hexane). ^{1}H NMR (500 MHz, $[D_8]$THF, −40 °C): $\delta = 0.21, 0.29$ (each s, 2×9H, $Si(CH_3)_3$), 0.57, 2.16, 2.20, 2.24, 2.25, 2.30, 2.32, 2.39 (each s, 8×3H, CCH_3), 4.07, 4.18 (each s, 2×5H, C_5H_5), 7.00, 7.12 (each s, 2×1H, *p*-H); ^{13}C NMR (125 MHz, $[D_8]$THF, −40 °C): $\delta = 5.4, 5.6$ (2q, $Si(CH_3)_3$), 20.0, 20.1, 20.6, 20.7, 20.9, 21.2, 22.4, 29.3 (8q, *o*- and *m*-CH_3), 28.9 (br, CSi_2), 80.1, 83.8 (2d, C_5H_5), 97.9 (br, *i*-*C*(B-Dur-Co)), 124.2 (br), 131.5, 132.9, 133.4, 135.5, 136.0, 140.4, 152.7 (8s, *o*- and *m*-C), 130.9, 134.9 (2d, *p*-C), 146.5 (br, *i*-C(B)), 194.5 (br, CB_2); ^{11}B NMR (96 MHz, $[D_8]$THF, 25 °C): $\delta = 41$; EI-MS: *m*/*z* (%) = 706 (M^+, 38.9), 632 ($M^+ - SiMe_3 - H$, 5.0), 582 ($M^+ - CoCp$, 100.0), 567 ($M^+ - CoCp - Me$, 3.5), 517 ($M^+ - Cp_2Co$, 8.6), 73 ($SiMe_3^+$, 88.9). No satisfactory C, H analysis could be obtained due to the high sensitivity of **5a**.

Compound 7a: EI-MS: *m*/*z* (%) = 610 (M^+, 94.0), 536 ($M^+ - SiMe_3 - H$, 6.3), 486 ($M^+ - CoCp$, 4.0), 73 ($SiMe_3^+$, 100.0), 28 ($C_2H_4^+$, 31.9).

***µ*-[Dimesitylborylbis(trimethylsilyl)methyleneborylcarbene]bis(η^5-cyclopentadienyl)dicobalt (5b)**: a) A mixture of **4b** (0.200 g, 0.47 mmol) and $[Co(C_5H_5)(C_2H_4)_2]$ (0.170 g, 0.94 mmol) in hexane (2 mL) was placed in a quartz NMR tube and irradiated for 6.5 h with a mercury vapor lamp. Chromatographic workup of the brown solution on Al_2O_3 with hexane provided an orange fraction (excess $[Co(C_5H_5)(C_2H_4)_2]$) and dark green **5b** (0.060 g, 19%). b) A mixture of **4b** (0.270 g, 0.63 mmol) and $[Co(C_5H_5)(C_6Me_6)]$ (0.360 g, 1.26 mmol) in hexane (15 mL) was heated at reflux for 0.5 h. Chromatographic workup of the brown solution on Al_2O_3 with hexane provided an orange boron-free fraction and dark green **5b** (0.050 g, 12%); m.p. = 155 °C (from hexane). ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 0.46, 0.52$ (each s, 2×9H, $Si(CH_3)_3$), 1.58, 2.18, 2.40, 2.44, 3.27, 3.48 (each s, 6×3H, CCH_3), 3.06, 3.90 (each s, 2×5H, C_5H_5),6.80, 6.84, 6.90, 7.26 (each s, 4×1H, *m*-H); ^{11}B NMR (96 MHz, $[D_8]$THF, 25 °C): $\delta = 46$; EI-MS: *m*/*z* (%) = 678 (M^+, 8.9), 604 ($M^+ - SiMe_3 - H$, 0.8), 554 ($M^+ - CoCp$, 100.0), 539 ($M^+ - CoCp - Me$, 2.2), 73 ($SiMe_3^+$, 82.8).

1-(η^5-Pentamethylcyclopentadienyl)-(η^2-ethene)-2,2-bis(trimethylsilyl)-3-duryl-4-durylborylidene-1-cobalta-3-boracyclobutane (7b): A solution of **4a** (0.350 g, 0.76 mmol) in toluene (25 mL) was added to $[Co(C_5Me_5)(C_2H_4)_2]$ (0.190 g, 0.76 mmol) at room temperature and heated at reflux for 2 h. Chromatographic workup on Al_2O_3 with hexane provided a red brown fraction, from which traces of black, insoluble **7b** were isolated. EI-MS: *m*/*z* (%) = 680 (M^+, 15.1), 652 ($M^+ - C_2H_4$, 1.2), 534 ($M^+ - 2\ SiMe_3$, 1.2), 486 ($M^+ - Cp^*Co$, 1.9), 413 ($M^+ - Cp^*Co - SiMe_3$, 2.9), 73 ($SiMe_3^+$, 100.0), 28 ($C_2H_4^+$, 11.0)

1-(η^5-Cyclopentadienyl)(η^2-ethene)-2,2-bis(trimethylsilyl)-3-*tert*-butyl-4-*tert*-butylborylidene-1-cobalta-3-boracyclobutane (7c): A solution of $[Co(C_5Me_5)(C_2H_4)_2]$ (0.300 g, 1.66 mmol) in hexane (20 mL) was treated with **4c** (0.255 g, 0.83 mmol) at room temperature, and the resulting mixture heated at reflux for 0.5 h. Chromatographic workup on Al_2O_3 with hexane provided a green fraction, from which traces of brown, insoluble **7c** were isolated. EI-MS: *m*/*z* (%) = 458 (M^+, 23.8), 443 ($M^+ - Me$, 1.2), 400 ($M^+ - tBu - H$, 1.4), 385 ($M^+ - SiMe_3$, 1.8), 73 ($SiMe_3^+$, 100.0), 57 (tBu^+, 15.1), 28 ($C_2H_4^+$, 56.1).

1-(η^5-Cyclopentadienyl)(carbonyl)-2,2-bis(trimethylsilyl)-3-*tert*-butyl-4-*tert*-butylborylidene-1-cobalta-3-boracyclobutane (7d): Complex **7c** was prepared in situ as described above from **4c** (0.530 g, 1.73 mmol) and $[Co(C_5Me_5)(C_2H_4)_2]$ (0.300 g, 1.67 mmol), and CO gas was bubbled through the solution for 10 min. Chromatographic workup on Al_2O_3 with hexane provided an orange red fraction with the red oil **7d** (0.043 g, 11%); b. p. = 90 °C/3 × 10^{-2} Torr. ^{11}B NMR (64.2 MHz, C_6D_6): $\delta = 55, 80$; FT-IR (hexane): $\tilde{\nu}_{CO} = 1979\ cm^{-1}$; EI-MS: *m*/*z* (%) = 458 (M^+, 10.9), 443 ($M^+ - Me$, 0.5), 400 ($M^+ - tBu - H$, 1.3), 385 ($M^+ - SiMe_3$, 1.9), 73 ($SiMe_3^+$, 100.0), 57 (tBu^+, 6.8), 28 (CO^+, 6.1)

1-(η^5-Cyclopentadienyl)(*tert*-butylisocyano)-2,2-bis(trimethylsilyl)-3-*tert*-butyl-4-*tert*-butylborylidene-1-cobalta-3-boracyclobutane (7e): Complex **7c** was prepared in situ as described above from **4c** (0.360 g, 1.18 mmol) and $[Co(C_5Me_5)(C_2H_4)_2]$ (0.230 g, 1.28 mmol), and then treated with *t*BuNC (0.106 g, 1.28 mmol). Chromatographic workup on Al_2O_3 with hexane provided an orange red fraction with **7e** (0.050 g, 10%); m.p. = 105 °C (decomp). ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 0.27, 0.43$ (each s, 2×9H, $Si(CH_3)_3$), 0.92, 1.31, 1.34 (each s, 3×9H, $C(CH_3)_3$), 4.72 (s, 5H, C_5H_5); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 2.2, 4.4$ ($Si(CH_3)_3$), 30.1, 31.3, 32.8 ($C(CH_3)_3$), 85.4 (C_5H_5), signals for carbon atoms adjacent to boron atoms were not observed; ^{11}B NMR (64.2 MHz, C_6D_6): $\delta = 50, 72$; FT-IR (hexane): $\tilde{\nu}_{CN} = 2107\ cm^{-1}$; EI-MS: *m*/*z* (%) = 513 (M^+, 1.2), 483 ($M^+ - 2Me$, 0.1), 456 ($M^+ - tBu$, 0.2), 73 ($SiMe_3^+$, 100.0), 57 (tBu^+, 26.9).

(η^5-1,3-Diduryl-2-durylmethylboryl-4-trimethylsilyl-5-dimethyl-1,3-dibora-5-silapenta-1,4-diene)(η^5-cyclopentadienyl)cobalt (10): Diboretanylideneborane **8** (1.030 g, 1.52 mmol) in hexane (25 mL) and toluene (5 mL) was added to $[Co(C_5Me_5)(C_2H_4)_2]$ (0.350 g, 1.94 mmol) at 0 °C. The solution was stirred for 5 h at room temperature and then filtered. The solvent was removed in vacuo, and the residue dissolved in hexane (25 mL). After stirring for one hour at room temperature the solution was again filtered, and the filtrate stored at 4 °C to provide dark red crystals of **29** (0.030 g, 3%); m.p. = 158 °C (decomp). ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 0.25$ (s, 9H, $Si(CH_3)_3$), −0.59, 0.51 (2s, 2×3H, $Si(CH_3)_2$), 1.11, 1.20, 1.48, (3s, 3×3H, *o*- and *m*-CH_3), 1.68 (s, 3H, BCH_3), 1.84 (s, 6H, *o*- and *m*-CH_3), 2.01, 2.08, 2.23, 2.24, 2.31, 2.90, 3.10 (7s, 7×3H, *o*- and *m*-CH_3), 4.94 (s, 5H; C_5H_5), 6.70 (s, 1H, *p*-H), 6.98 (s, 2H, *p*-H); ^{11}B NMR (64.2 MHz, C_6D_6): $\delta = 29$ (2B), 70 (1B); EI-MS: *m*/*z* (%) = 726 (M^+, 0.2), 602 ($M^+ - CoCp$,

Table 5. Crystal and data-collection parameters for **5a**, **10**, and **11**.

	5a	**10**	**11**
formula	$C_{38}H_{54}B_2Co_2Si_2$	$C_{43}H_{62}B_3CoSi_2$	$C_{45}H_{68}B_2Cl_2Pt_2Si_2$
M_r	706.47	726.47	1147.87
crystal system	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a [Å]	8.960(6)	12.719(6)	11.650(6)
b [Å]	17.187(10)	16.928(8)	13.020(6)
c [Å]	24.08(2)	19.319(10)	15.921(8)
α [°]	90	90	102.83(4)
β [°]	90	90	97.91(3)
γ [°]	90	90	96.04(4)
V [Å^3]	3708	4160	2309
Z	4	4	2
ρ_{calcd} [g cm^{-3}]	1.27	1.16	1.65
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.98	0.50	6.25
crystal size (mm)	0.10 × 0.15 × 0.45	0.6 × 0.7 × 0.8	0.08 × 0.23 × 0.35
T [°C]	−55	−70	−55
$2\theta_{max}$ [°]	50	53	48
h, k, l range	−3/10, −16/20, −23/28	0/15, 0/21, 0/24	−13/12, −14/14, 0/18
reflns collected	4713	5187	6938
unique	4327	4784	6938
observed ($I > 2\sigma I$)	3036	4215	4725
abs. corr. transmission	0.91–1.00	0.93–1.00	0.58–1.00
parameters refined	395	468	507
$R1 = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$ (observed reflns)	0.047	0.033	0.045
$wR2$	0.102	0.084	0.102

0.1), 468 (M^+ – CoCp – DurH, 1.8), 453 (M^+ – CoCp – DurH – Me, 0.7), 119 ($DurH^+$ – Me, 100.0), 73 ($SiMe_3^+$, 7.6).

***µ*-[(Dimethylsilyltrimethylsilylmethyene)durylborylene](methyldurylboryl)carbene(η^2-1,5-cyclooctadiene)(η^4-1,5-cyclooctadiene)diplatinum (11)**: A solution of **4a** (0.225 g, 0.49 mmol) in a mixture of hexane (6 mL) and toluene (1 mL) was added at 0 °C to $[Pt(C_8H_{12})_2]$ (0.405 g, 0.98 mmol) and stirred for 3 h at 20 °C. Chromatographic workup on Al_2O_3 with hexane eluent provided a yellow fraction (**4a** and uncharacterized side products). Further elution with hexane/toluene (1/1) provided red-orange **11** (330 mg, 63 %); m.p. = 165 °C (decomp). ^{1}H NMR (200.1 MHz, CD_2Cl_2): $\delta = -0.12$ (s, 9H, $Si(CH_3)_3$), 0.37, 0.48 (2s, 2 × 3H, $^3J(Pt,H) = 42$ Hz, $Si(CH_3)_2$), 0.81 (s, 3H, BCH_3), 1.56, 1.66, 1.72, 1.75, 2.03, 2.08, 2.28, 2.35 (8s, 8 × 3H, *o*- and *m*-CH_3), 1.95 – 2.70 (m, br, 16H, CH_2), 4.05 – 4.35 (m, br, 2H, –CH=), 5.10 – 6.10 (m, br, 6H, –CH=), 6.41 (s, 2H, *p*-H); ^{13}C NMR (50.3 MHz, CD_2Cl_2): $\delta = 2.9$ ($^1J(Si,C) = 14$ Hz, $Si(CH_3)_3$), 5.4, 5.7 ($Si(CH_3)_2$), 18.7, 19.3, 19.4, 19.5, 19.8, 20.9, 21.5, 22.4 (CCH_3), 27.9, 29.0, 29.2, 29.5, 29.6, 30.8, 31.1, 33.2 (CH_2), 80.8, 81.8, 88.2, 89.1, 89.3, 93.5 (Pt-coordinated –CH=), 128.0, 128.5, 129.2, 130.0 (uncoordinated –CH= and *p*-C), 130.9, 131.0, 131.1, 131.2, 131.4, 131.6, 133.8, 134.5 (*C*CH_3), signals for carbon atoms adjacent to boron atoms were not observed; ^{11}B NMR (96 MHz, CD_2Cl_2): $\delta = 41, 65$; ^{195}Pt NMR (43.0 MHz, CD_2Cl_2): $\delta = -4429, -3882$; EI-MS: *m/z* (%) = 761 (M^+ – Pt(cod), 0.2), 746 (M^+–Pt(cod) – CH_3, 0.7), 703 (M^+ – Pt(cod) – $SiMe_2$, 0.2), 653 (M^+ – $Pt(cod)_2$, 0.9), 134 ($DurH^+$, 64.7), 119 ($DurH^+$ – Me 100.0), 108 (cod^+, 37.2), 73 ($SiMe_3^+$, 99.6), elemental analysis calcd for $C_{44}H_{68}B_2Pt_2Si_2$(1065.0): C 49.62, H 6.44; found: C 49.39, H 6.40.

Crystal structure determinations for 5a, 10, and 11:[41] Diffraction data were collected on a Siemens-Stoe AED 2 diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator) in the ω-scan mode. Crystal data and details of the measurements are summarized in Table 5. The structures were solved by direct methods (SHELXS86) and refined by full-matrix least squares (SHELXL93) based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added in calculated positions. In **5a** one of the Cp rings is disordered.

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft (SFB 247) and the Fonds der Chemischen Industrie. We thank Prof. Dr. R. Gleiter and Dr. I. Hyla-Kryspin (Heidelberg, Germany) for the theoretical calculations, and Prof. Dr. D. Fenske (Karlsruhe, Germany) for the structural analysis of **5b**.

Received: May 16, 1997 [F696]

---

[1] a) R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr., *J. Am. Chem. Soc.* **1970**, *92*, 4992; b) R. Hoffmann, *Pure Appl. Chem.* **1971**, *28*, 181.

[2] a) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. von R. Schleyer, R. Seeger, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419; b) J. Chandrasekhar, P. von R. Schleyer, *J. Chem. Soc. Chem. Commun.* **1981**, 260; c) K. Sorger, P. von R. Schleyer, *J. Mol. Struct.* (*Theochem*) **1995**, *338*, 317; d) K. Sorger, P. von R. Schleyer, R. Fleischer, D. Stalke, *J. Am. Chem. Soc.* **1996**, *118*, 6924.

[3] D. Röttger, G. Erker, *Angew. Chem.* **1997**, *109*, 840; *Angew. Chem. Int. Ed. Engl.* **1997**, and references therein.

[4] V. Sernau, G. Huttner, J. Scherer, O. Walter, *Chem. Ber.* **1996**, *129*, 243.

[5] C. Oldham in *Comprehensive Coordination Chemistry Vol. 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, p. 435 ff.

[6] T. Beringhelli, G. Ciani, G. D'Alfonso, A. Sironi, M. Freni, *J. Chem. Soc. Chem. Commun.* **1985**, 978.

[7] A. Gunale, A. Bethäuser, W. Siebert, unpublished results.

[8] a) W. Siebert, *Angew. Chem.* **1985**, *97*, 924; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 943; b) *Pure Appl. Chem.* **1987**, *59*, 947; c) **1988**, *60*, 1345.

[9] a) M. Hildenbrand, H. Pritzkow, U. Zenneck, W. Siebert, *Angew. Chem.* **1984**, *96*, 371; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 372; b) M. Hildenbrand, Dissertation, Universität Heidelberg, **1986**.

[10] R. Wehrmann, C. Pues, H. Klusik, A. Berndt, *Angew. Chem.* **1984**, *96*, 372; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 372.

[11] M. Pilz, J. Allwohn, M. Bühl, P. von R. Schleyer, A. Berndt, *Z. Naturforsch. B* **1991**, *46*, 1085.

[12] a) M. Hildenbrand, H. Pritzkow, W. Siebert, *Angew. Chem.* **1985**, *97*, 769; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 759; b) D. Kaufmann, R. Boese, A. Scheer, *Chem. Ber.* **1994**, *127*, 2349.

[13] K. Krogh-Jespersen, D. Cremer, J. D. Dill, J. A. Pople, P. von R. Schleyer, *J. Am. Chem. Soc.* **1981**, *103*, 2589.

[14] A. Krämer, H. Pritzkow, W. Siebert, *Z. Naturforsch. B* **1989**, *44*, 96.

[15] A. Gunale, Dissertation, Universität Heidelberg, **1997**.

[16] a) H. Klusik, A. Berndt, *Angew. Chem.* **1983**, *95*, 895; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 877; b) A. Berndt, *ibid.* **1993**, *105*, 1034 and **1993**, *32*, 985; c) M. Menzel, H.-J. Winkler, T. Ablelom, D. Steiner, S. Fau, G. Frenking, W. Massa, A. Berndt, *ibid.* **1995**, *107*, 1476 and **1995**, *34*, 1110; d) A. Berndt, D. Steiner, D. Schweikart, C. Balzereit, M. Menzel, H.-J. Winkler, S. Mehle, M. Unverzagt, T. Happel, P. von R. Schleyer, G. Subramanian, M. Hofmann, in *Advances in Boron Chemistry* (Ed.: W. Siebert), Special Publication No. 201, The Royal Society of Chemistry, Cambridge, **1997**, pp. 61; M. Unverzagt, G. Subramanian, M. Hofmann, P. von R. Schleyer, S. Berger, K. Harms, W. Massa, A. Berndt, *Angew. Chem.* **1997**, *109*, 1567; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1469.

[17] P. H. M. Budzelaar, P. von R. Schleyer, K. Krogh-Jespersen, *Angew. Chem.* **1984**, *96*, 809; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 825.

[18] G. Frenking, H. F. Schaefer III, *Chem. Phys. Lett.* **1984**, *109*, 521.

[19] C. Wieczorek, J. Allwohn, G. Schmidt-Lukasch, R. Hunold, W. Massa, A. Berndt, *Angew. Chem.* **1990**, *102*, 435; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 398.

[20] A. Gunale, H. Pritzkow, W. Siebert, D. Steiner, A. Berndt, *Angew. Chem.* **1995**, *107*, 1194; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1111.

[21] I. Hyla-Kryspin, R. Gleiter, M.-M. Rohmer, J. Devemy, A. Gunale, H. Pritzkow, W. Siebert, *Chem. Eur. J.* **1997**, *3*, 294.

[22] a) K. Jonas, C. Krüger, *Angew. Chem.* **1980**, *92*, 513; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 520; b) K. Jonas, E. Deffense, D. Habermann, *ibid.* **1983**, *95*, 729 and **1983**, *22*, 716.

[23] K. Jonas, E. Deffense, D. Habermann, *Angew. Chem. Suppl.* **1983**, 1005; *Angew. Chem. Int. Ed. Engl.* **1983**, 1005.

[24] R. D. Adams, *Chem. Rev.* **1989**, *89*, 1703.

[25] a) U. Kölle, R. Khouzami, B. Fuss, *Angew. Chem.* **1982**, *94*, 132; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 131; b) U. Kölle, R. Khouzami, B. Fuss, *Angew. Chem. Suppl.* **1982**, 230; *Angew. Chem. Int. Ed. Engl.* **1982**, 230.

[26] N. E. Schore, *J. Organomet. Chem.* **1979**, *173*, 301.

[27] R. Hunold, M. Pilz, J. Allwohn, M Stadler, W. Massa, P. von R. Schleyer, A. Berndt, *Angew. Chem.* **1989**, *101*, 759; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 781.

[28] Y. Yamamoto, T. Mise, H. Yamazaki, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2743.

[29] A. Salzer, H. Werner, *Angew. Chem.* **1972**, *84*, 949; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 930.

[30] a) B. Bogdanovic, M. Kröner, G. Wilke, *Liebigs Ann. Chem.* **1966**, *699*, 1; b) K. Jonas, R. Mugnott, C. Krüger, J. C. Sekutowski, Y. H. Tsay, *Angew. Chem.* **1976**, *88*, 808; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 767.

[31] H. Fleckner, F.-W. Grevels, D. Hess, *J. Am. Chem. Soc.* **1984**, *106*, 2027.

[32] J. L. Spencer, *Inorg. Synth.* **1979**, *19*, 213.

[33] G. E. Herberich, B. Hessner, *Z. Naturforsch. B* **1979**, *34*, 638.

[34] H. Wadepohl, H. Pritzkow, *Angew. Chem.* **1987**, *99*, 132; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 127.

[35] a) L. G. Sneddon, D. Voet, *J. Chem. Soc. Chem. Commun.* **1976**, 118; b) J. R. Pipal, R. N. Grimes, *Inorg. Chem.* **1977**, *16*, 3255.

[36] S. W. Helm, G. Linti, H. Nöth, S. Channareddy, P. Hofmann, *Chem. Ber.* **1992**, *125*, 73.

[37] See, for example, P. Paetzold, D. Hahnfeld, U. Englert, W. Wojnowski, B. Dreczewski, Z. Pawelek, L. Walz, *Chem. Ber.* **1992**, *125*, 1073.

[38] K. M. Mackay, B. K. Nicholson *Comprehensive Organometallic Chemistry*, *Vol. 6* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**, p. 1043.

[39] R. J. Puddephatt, *Polyhedron*, **1988**, *7*, 767.

[40] M. Stefan, J. H. Davis, Jr., X. Meng, K. P. Chase, J. Hauss, U. Zenneck, H. Pritzkow, W. Siebert, R. N. Grimes, *J. Am. Chem. Soc.* **1992**, *114*, 5214.

[41] Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-401 952 (**5a**), CSD-380 135 (**10**), and CSD-401 953 (**11**).

0947-6539/98/0401-0052 $ 17.50+.50/0