# Calculated NMR Parameters (Chemical Shifts and Coupling Constants) of Cyclic $C_4H_2$ and $C_4H_4$ Molecules Containing Carbene Centers, and of Some of their Boron Analoga, Using Density Functional Theory (DFT)

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Singlet state structures of small, cyclic hydrocarbons which can result from the addition of molecular dicarbon ($C_2$) to ethyne (HC≡CH) or ethene ($H_2C=CH_2$) have been calculated (B3LYP/6-311+G(d,p) level of theory), and were found to contain carbene centres. Some structures of analogous boranes (replacement of the carbene centers by BH fragments) were also calculated. The computation of NMR parameters such as chemical shifts $\delta^{13}C$ and $\delta^{11}B$, and coupling constants $^1J(^{13}C,^1H)$, $^1J(^{11}B,^1H)$, $J(^{13}C,^{13}C)$ and $J(^{13}C,^{11}B)$ shows that these data can be used for the discussion of the bonding situation. The presence of inverted carbene centers is clearly indicated by the increased $^{13}C$ nuclear magnetic shielding. Scalar $^{13}C$-$^{13}C$ spin-spin coupling involving carbene centers are frequently dominated by spin-dipole and spin-orbital interactions.

*Key words:* Carbenes, Cyclic Hydrocarbons, Boranes, MO Calculations, NMR Parameters

## Introduction

Small, reactive cyclic hydrocarbon molecules are of considerable interest as intermediates in combustion chemistry [1] as well as in astrophysical processes [2]. An obvious entry into this field is the study of reactions of the dicarbon molecule $C_2$ in its singlet or triplet state with simple unsaturated hydrocarbons [3] such as ethyne or ethene [4]. This could afford cyclic species with the composition $C_4H_2$ (*e.g.*, **1a – 1c**) or $C_4H_4$ (*e.g.*, **2a** or **2b**), respectively, containing carbene- or alkyne-type carbon atoms (Scheme 1).
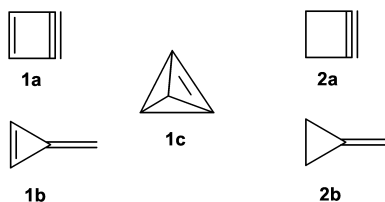


Scheme 1. Some examples of strained cyclic hydrocarbons which may result from the reaction of HC≡H or $H_2C=CH_2$ with molecular $C_2$.

Such compounds are extremely difficult to obtain by conventional techniques [5], in contrast to non-cyclic derivatives with the same composition. How-ever, the synthesis of long-lived kinetically stabilized cyclic derivatives may be feasible, if not with carbon possibly by isolobal replacement of one or more carbon atoms by one or more fragments B-R, where R is a bulky substituent. A typical example is the 1,2-diboretane-3-ylidene **3a**, of which several derivatives with bulky substituents at carbon and both boron atoms have been prepared [6,7] (**4** has been the first example [6]). The unique structure of **3** and **4**, predicted by theory [8], and confirmed for a derivative of **4** by single-crystal X-ray analysis in the solid state [9] as well as by NMR spectroscopy in solution [6,10], is particularly stimulating for discussing the bonding situation in carbon analoga. The three-coordinate carbon atom C(3) in **3a** or **4** can be regarded as an inverted carbene center [11 – 13], by which it supplies two electrons to a CBB 3c/2e $\pi$ bond (symbolized by the circle), and the two electrons in the B-B bond together with the now empty s orbital at C(3) form a 3c/2e $\sigma$ bond (dashed triangle). Thus, the C(3)BB unit is stabilized by double-aromatic delocalization, and the tetra-coordinate carbon atom C(4) makes **3a** and **4** a homoaromatic system [11].

The present work reports on the calculated structures of non-radical species related to **1** and **2**, and on similar molecules, in which carbon is replaced by
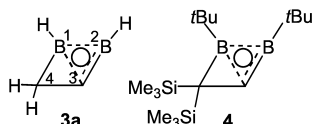
boron, using density functional theory methods (DFT). Since the NMR parameters of such molecules should mirror the electronic structure, DFT methods were used to calculate $^{11}B$ and $^{13}C$ chemical shifts and coupling constants $^1J(^{13}C,^1H)$, $^1J(^{11}B,^1H)$, $J(^{13}C,^{13}C)$, $J(^{13}C,^{11}B)$.

## Results and Discussion

### Selection of cyclic species 1 resulting from the equimolar reaction of HC≡CH and $C_2$

The calculations carried out in this work indicate that the structures **1a** (cyclobutenyne) and **1c** (tetrahedrene) do not represent minima on the potential energy surface (PES) for $C_4H_2$, in agreement with the literature [14]. The structure **1b** was already proposed previously to be stable [15]; its energy is 72.7 kcal/mol higher than that of HC≡C-C≡CH (B3LYP/6-311+G(d,p) level). The structure **1a** is a stationary point at the B3LYP/6-311+G(d,p) level, but possesses one imaginary frequency ($-901$ cm$^{-1}$); it collapses to **1d** (a strongly distorted tetrahedrene structure) when the $C_{2v}$ symmetry is relaxed. Minima for cyclic species were found for six structures, **1b**, **1d**, **1e** (see also [14]), and **1f**, all containing two CH fragments, and **1g** and **1h**, containing both a $CH_2$ fragment (Scheme 2). There are only small differences in energy between **1b**, **1d** and **1e**, whereas planar **1f**, the famous trialene [16, 17], is somewhat more stable. The isomer **1g** is of similar stability as **1f**, and **1h** is the least stable of all cyclic structures considered. With the exception of **1b**, the carbene centers in the other cyclic $C_4H_2$ structures have fully or partially inverted carbene character. Thus aromatic $\pi$ and $\sigma$ delocalization explains the relative stabilities of the apparently highly strained structures, in most of which the carbene centers are in close neighborhood.

A methyleneborane **5b** (vide infra for the pair **6b/2b**), directly comparable with **1b**, is not known. However, several examples of other substituted methyleneboranes with classical structures have been prepared [7]. Isolobal replacement of both carbene-type atoms in **1e** by BH fragments (Scheme 3) leads to the carborane **5e**, of which derivatives have been characterized, showing the prominent structural fea-
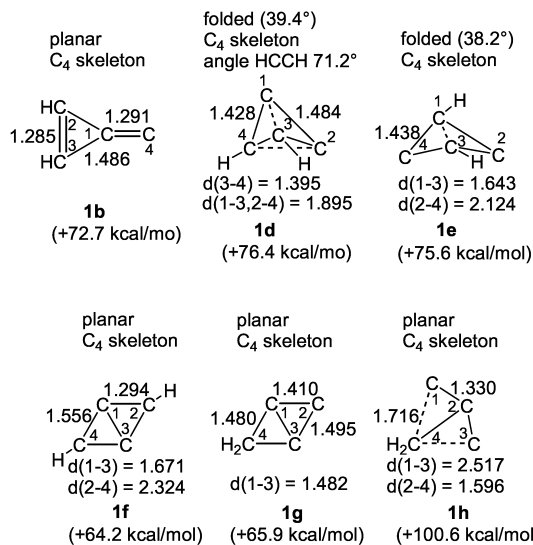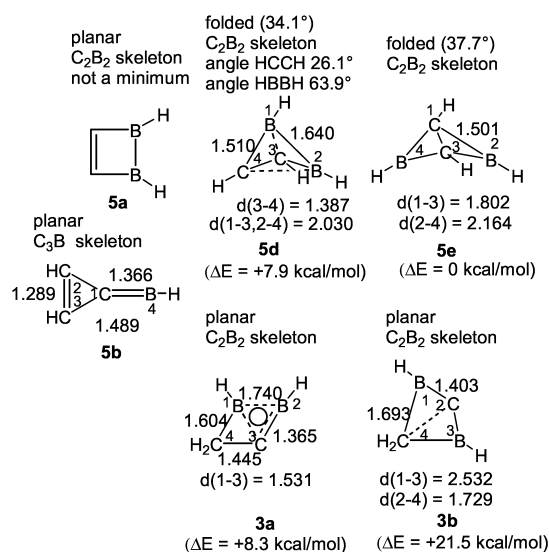
Scheme 2. Calculated cyclic structures $C_4H_2$ which were found to be minima on the PES (energies are given relative to 1,3-butadiene), Drawn or dashed lines do not necessarily represent 2c/2e bonds (distances in [Å]).

tures comparable with **1e** [18, 19]. Carboranes of the type **5d** [12b, 19], analogous to **1d**, have not been described so far. The search for a local minimum in the calculation of **5a** (B3LYP/6-311+G(d,p) level) led straightforwardly to the structure **5d**. A planar borane structure corresponding to trialene **1f** is not known. The optimization of the structure with a planar $B_2C_2$ skeleton with alternating B-C bonds converges to the folded structure of **5e** [19]. Isolobal replacement of two carbene-type atoms by BH fragments transforms the structure **1g** into that of 1,2-diboretane-3-ylidene **3a** [8], and **1h** into **3b**. Derivatives of **3a** are well known [6, 7], whereas derivatives of **3b** were proposed as reactive intermediates, *e.g.* in the reaction of **4** with heavy carbene homologues [20]. The structure **3b** may also explain the degenerate rearrangement which exchanges the boron atoms, observed in the case of compound **4** [6].

### Selection of cyclic species 2 resulting from the equimolar reaction of $H_2C=CH_2$ and $C_2$

The reaction of ethene with molecular $C_2$ has recently been carried out under single collision conditions using the crossed molecular beam method [4]. This makes it possible to limit the number of potential candidates for cyclic structures. In competition with the formation of radical species and final conversion

Scheme 3. Examples of calculated cyclic structures of the boranes **3** and **5** which are derived from the structures **1** in Scheme 2 (replacement of carbene centers by BH fragments). Drawn or dashed lines do not necessarily represent 2c/2e bonds (distances in [Å]).

Table 1. Calculated chemical shifts $\delta^{11}B$, $\delta^{13}C$ of the molecules **1 – 3, 5, 6**[a].

| | $\delta^{13}C(1)$ | $\delta^{13}C(2)$ | $\delta^{13}C(3)$ | $\delta^{13}C(4)$ |
|---|---|---|---|---|
| **1b** | 85.0 | 122.2 | 122.2 | *612.4* |
| **1d** | *219.6* | *219.6* | 106.2 | 106.2 |
| **1e** | 142.6 | *201.4* | 142.6 | *201.4* |
| **1f** | *155.2* | 88.3 | *155.2* | 88.3 |
| **1g** | *265.4* | *219.3* | *265.4* | 97.9 |
| **1h** | *345.5* | *123.6* | *345.5* | 29.8 |
| **2b** | 75.4 | 35.8 | 35.8 | *506.1* |
| **2c** | 75.5 | 33.7 | 30.0 | *311.4* |
| **3a** | 37.1 (B) | 9.4 (B) | 136.5 | 30.2 |
| **3b** | 48.7 (B) | *77.6* | 48.7 (B) | −14.8 |
| **5b** | 64.6 | 129.1 | 129.1 | 142.3 (B) |
| **5d** | 32.6 (B) | 32.6 (B) | 162.7 | 162.7 |
| **5e** | 96.5 | 34.3 (B) | 96.5 | 34.3 (B) |
| **6b** | 92.2 | 20.4 | 20.4 | 165.5 (B) |
| **6c** | 5.2 | 3.1 (B) | 54.8 | 32.3 |

[a] The numbering follows the patterns given in Schemes 2, 3 and 4; $\delta^{13}C$ value of carbene-type centers are given in italics.
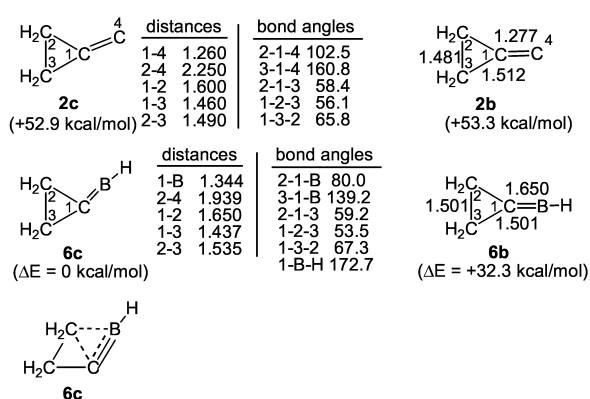


Scheme 4. Calculated structures **2b** and **2c** (energies are given relative to butatriene), together with the corresponding boranes **6b** and **6c** (distances in [Å]; bond angles in [°]).

into butatriene, an intermediate with the composition $C_4H_4$ has been identified for which the structure **2c** (Scheme 4) was assigned, supported by *ab initio* calculations [4]. The intriguing structural feature of **2c**, in contrast with **2b**, is the tilt of the exocyclic C=C bond towards one of the $CH_2$ groups, so that the molecular symmetry is only $C_s$. The calculations, carried out here, confirm this result; the structure of cyclobutyne **2a** was found as a stationary point (B3LYP/6-311+G(d,p) level) on the PES, not as a minimum, and converged to that of **2c**. The instability of the structure of **2a** with respect to ring contraction has been noted previously [21], however, the undistorted structure **2b** was given as the alternative. The structure **2b** is also a minimum on the PES, only 0.4 kcal/mol less stable than **2c**. The calculation of the structure of the corresponding borane **6c** shows an even stronger distortion, and **6c** is considerably more stable than **6b**. It appears that in both **2c** and **6c** hyperconjugation of the C(1)-C(2) bond with the respective empty C(4) or B $p_z$ orbital takes place. The strong tilt of the BH fragment towards one of the $CH_2$ units, found in the case of **6c**, suggests that the structure can be written in a different way (Scheme 4), invoking the concept of an inverted carbene center [11 – 13] which donates two electrons for C-B $\pi$ bonding, and a 3c/2e $\sigma$ bond (dashed triangle) is formed by one electron each from the $CH_2$ carbon and boron with the empty orbital at the carbene carbon atom. This view is supported by the calculated NMR data (vide infra).

*Calculated NMR data: chemical shifts $\delta^{13}C$ and $\delta^{11}B$ and coupling constants J*

The calculation of chemical shifts $\delta^{11}B$ or $\delta^{13}C$ by the IGLO or GIAO method, based on *ab initio* optimized geometries, has been very successful for structural assignments [22]. More recently, distinct progress has been made in the calculation of coupling constants $^nJ$ [22c, 23], using DFT methods, and experimental data have been reproduced remarkably well in the

Table 2. Selection of calculated coupling constants $J$ for the molecules **1 – 3**, **5**, **6**[a].

| | J(1,2) | J(2,3) | J(3,4) | J(1,4) | J(1,3) | J(2,4) | $^1J(^{13}C,^1H)$/ $^1J(^{11}B,^1H)$ |
|---|---|---|---|---|---|---|---|
| | +8.5 | +84.2 | −5.8 | +23.0 | +8.5 | −5.8 | 250.0 (C2,3) |
| **1b** | (−0.5;−1.5) | (+5.3;−3.4) | (+0.1;−2.5) | (−3.1;+4.8) | (−0.5;−1.5) | (+0.1;−2.5) | |
| | −13.0 | −9.1 | +31.8 | −9.1 | +15.7 | +15.7 | 211.8 (C3,4) |
| **1d** | (−1.0;−7.0) | (−0.3;−7.1) | (+0.8;−4.1) | (−0.3;−7.1) | (−0.5;+5.9) | (−0.5;+5.9) | |
| | −12.9 | −12.9 | −12.9 | −12.9 | −14.3 | +3.2 | 216.3 (C1,3) |
| **1e** | (−0.8;−7.3) | (+0.8;−7.3) | (+0.8;−7.3) | (+0.8;−7.3) | (−0.3;+1.4) | (−5.6;+15.7) | |
| **1f** | +67.1 | −6.6 | +67.1 | −6.6 | −8.2 | +9.6 | 265.3 (C2,4) |
| | (+6.4;−0.8) | (+0.2;−3.9) | (+6.4;−0.8) | (+0.2;−3.9) | (+0.7;−4.5) | (+2.7;+6.6) | |
| | −24.1 | −24.1 | −7.0 | −7.0 | +14.0 | −28.3 | 171.5 (C4) |
| **1g** | (1.0;−5.9) | (+1.0;−5.9) | (−0.3;−4.2) | (−0.3;−4.2) | (−1.2;−17.0) | (+0.2;−3.1) | |
| | +8.4 | +8.4 | −28.5 | −28.5 | +31.1 | −35.9 | 190.6 (C4) |
| **1h** | (+1.2;−6.6) | (+1.2;−6.6) | (+0.4;−2.1) | (+0.4;−2.1) | (+30.0;+11.5) | (+1.2;+1.7) | |
| | +10.6 | +17.3 | −3.9 | +32.7 | +10.6 | −3.9 | 164.4 (C2,3) |
| **2b** | (+0.1;−0.9) | (−0.3;−3.0) | (0.0;−1.1) | (+4.6;−5.9) | (+0.1;−0.9) | (0.0;−1.1) | |
| | −7.9 | +14.6 | −13.9 | +45.0 | +31.7 | −0.2 | 172.4 (C2) |
| **2c** | (+0.6;+0.3) | (−0.1;−2.6) | (+0.2;−1.0) | (+4.4;−4.9) | (−0.3;−1.7) | (+0.6;+1.0) | 160.7 (C3) |
| | +14.9 | +107.2 | +26.2 | +25.8 | −9.8 | +15.0 | 157.3 (C4)/ |
| **3a** | (+0.2;−2.2) | (+2.6;+0.9) | (−0.4;−3.6) | (−0.1;−1.4) | (+0.1;−4.0) | (+0.4;−0.4) | 200.0 (B1) |
| | | | | | | | 215.8 (B2) |
| | +79.1 | +79.1 | +14.1 | +14.1 | +18.0 | −17.6 | 158.8 (C4)/ |
| **3b** | (+1.2;−0.6) | (+1.2;−0.6) | (−0.1;−1.3) | (−0.1;−1.3) | (+0.3;−1.3) | (+1.6;+3.1) | 260.7 (B1,3) |
| | +11.4 | +76.3 | +0.3 | +194.1 | +11.4 | +0.3 | 237.0 (C2,3)/ |
| **5b** | (−0.6;−1.6) | (+5.5;−4.2) | (0.0;−1.3) | (+3.4;−2.0) | (−0.6;−1.6) | (0.0;−1.3) | 209.7 (B4) |
| | +46.0 | +41.8 | +26.0 | +41.8 | −12.1 | −12.1 | 165.4 (C3,4)/ |
| **5d** | (−0.2;−1.0) | (0.0;−3.1) | (+0.4;−8.0) | (0.0;−3.0) | (−0.5;+0.7) | (−0.5;+0.7) | 164.9 (B1,2) |
| | +39.2 | +39.2 | 39.2 | 39.2 | −21.1 | −5.1 | 167.5 (C1,3)/ |
| **5e** | (−0.5;−3.0) | (−0.5;−3.0) | (−0.5;−3.0) | (−0.5;−3.0) | (−0.3;+2.5) | (−0.2;+0.3) | 180.4 (B2,4) |
| | +20.1 | +14.2 | +2.8 | +197.9 | +20.1 | +2.8 | 158.9 (C2,3)/ |
| **6b** | (−0.2;−1.7) | (−0.1;−1.1) | (−0.1;−0.5) | (+12,5;−1.4) | (−0.5;−1.7) | (−0.1;−0.5) | 256.8 (B4) |
| | −5.5 | +144.4 | +37.1 | +13.0 | −20.6 | −5.0 | 166.3 (C1), |
| **6c** | (+0.6;+0.1) | (+3.8;+1.3) | (−0.4;−2.8) | (+0.2;−1.4) | (+0.6;+1.1) | (+0.3;−0.3) | 156.4 (C4)/ |
| | | | | | | | 214.6 (B2) |

[a] The numbering follows the patterns given in Schemes 2, 3 and 4; values are given in Hz. The data in parentheses are the calculated spin-dipole (first numer) and paramagnetic spin-orbital contributions (second number).

cases of non-classical carbocations [24], cyclic hydrocarbons [25], polyboranes and some carboranes [26], to name just a few examples. In connection with the present work, such calculations have already proved useful in the case of **3a** and derivatives, including the comparison with experimental data for **4** [10]. Calculated chemical shifts $\delta^{13}C$ and $\delta^{11}B$ of the compounds **1 – 6** are listed in Table 1. Calculated coupling constants $J$ are given in Table 2. Some calculated $^{13}C$ NMR parameters of typical carbenes **7 – 11** are given in Scheme 5 for comparison.

*Chemical shifts $\delta^{13}C$ and $\delta^{11}B$*

The $^{13}C$ nuclear magnetic shielding of carbene centers is very low if additional stabilization is absent, as in **1b**, **2b**, and **7 – 9**. This is due to the paramagnetic effect caused by $B_0$-induced circulation of charge between ground and excited states, where, in the case of carbenes, mainly the energetically low-lying empty $p_z$ orbital at the carbene center and $\sigma$ electrons of the lone pair at carbon and the C-C or C-N bonds are involved [27]. This reminds of $^{11}B$ nuclear shielding in trigonal boranes which has been analysed *e.g.* for trimesityl- or trimethylborane [28]. The $^{11}B$ nuclear shielding in **5b** is also rather low ($\delta^{11}B$ 142.3), in agreement with the finding for $^{13}C$ in the isostructural carbene **1b** [$\delta^{13}C$(carbene) 612.4]. $\pi$ Orbitals adjacent to the carbene center as in **1b** or **8** cause even stronger $^{13}C$(carbene) deshielding, opposite to the trend for $^{11}B$ nuclear shielding in trigonal boranes [29], which is due to the different polarity of C-C and B-C $\sigma$ bonds. The $p_z$-orbital of the carbene center in the $3\delta^2 - 1H$-pyridine **10** [30] is part of the aromatic $\pi$ system, and
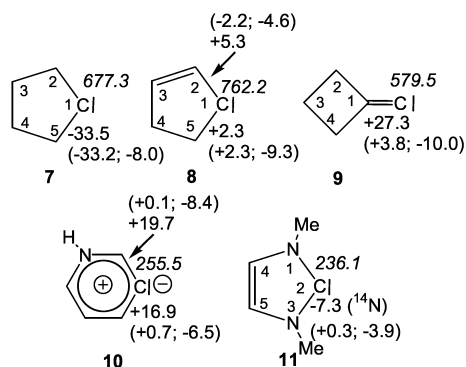
Scheme 5. Calculated structures and selected NMR parameters of carbenes **7 – 11**. Chemical shifts $\delta^{13}C$ of the carbene centers are given in italics; total coupling constants $^1J$ [Hz] are listed together with the spin-dipole and paramagnetic spin-orbital contributions (PSO) in parentheses.

therefore the gap between occupied and virtual orbitals is increased. Adjacent amino nitrogen atoms, as in **11**, lead to an increase in $^{13}C$(carbene) shielding (in agreement with experimental data [31]), and the same trend is observed for $^{11}B$ nuclear shielding in aminoboranes [compare *e.g.* $\delta^{11}B$ (Me$_3$B) 86.0, $\delta^{11}B$ (Me$_2$B-NMe$_2$) 44.6, and $\delta^{11}B$ (MeB(NMe$_2$)$_2$) 33.5 [29]]. The electronegative nature of the nitrogen atoms lowers the energy of electrons in the C(carbene)-N $\sigma$ bonds as well as of the lone pair at carbon. In addition, C(carbene)N-pp-$\pi$ bonding may cause an increase in the energy of relevant virtual orbitals.

The $^{13}C$ chemical shifts of carbene-type carbon atoms in **1d – h**, **2c** and **3a,b** (Table 1; entries in italics) are much more close to those of **10** or **11** than of **7**, **8** and **9**. In the case of inverted carbenes, the promotion of the lone pair of electrons at carbon into a p orbital for $\pi$ bonding and the presence of 3c/2e $\sigma$ bonding means that the energy difference between occupied ground states and low-lying excited states is larger than for "normal" carbene centers, and this is mirrored by less extreme $^{13}C$ nuclear magnetic deshielding. A striking case is the structure of trialene **1f**, where the shielding of carbene and olefinic carbon atoms is rather high, indicating the presence of an inverted carbene and a high degree of delocalization of $\sigma$ and $\pi$ electron density. Similarly, the calculated $^{13}C$ nuclear shielding of C(3) ($\delta$ 136.6) in **3a** is not typical at all for a normal carbene. In this case, the agreement, given for the different pattern of substituents, with the experimental value for **4** ($\delta^{13}C$(3) 116.9) should be noted [10]. In the case of **2c**, the apparently small change in the

structure (and in the energy), when compared with **2b**, causes an increase in $^{13}C$(carbene) shielding of almost 200 ppm. The structures of **1b** and **2b** are similar, and the difference in the $\delta^{13}C$ data for the carbene centers is similar as calculated for **7** amd **8**. Nuclear shielding of $^{11}B$ is affected by electron delocalization in a similar way as for $^{13}C$ of the inverted carbene centers. Deviations from a common trend are due to the different donor-acceptor properties of the two nuclei. This can be seen for example by comparing the structures and relevant chemical shifts of **2c** and **6c**. The $^{11}B$ nucleus is well shielded ($\delta^{11}B$ 3.1), in agreement with the calculated structure for significant $\sigma$ and $\pi$ delocalization, whereas the $^{13}C$(carbene) shielding in **2c** is still fairly low ($\delta^{13}C$ 311.4).

*Coupling constants J($^{13}C$,$^{13}C$), J($^{13}C$,$^{11}B$), J($^{11}B$,$^{11}B$), and $^1J$($^{13}C$,$^1H$), $^1J$($^{11}B$,$^1H$)*

Some experimental data for coupling constants $J$($^{13}C$,$^{13}C$) in strained hydrocarbons [25] or for $J$($^{13}C$,$^{11}B$) and $J$($^{11}B$,$^{11}B$) in carboranes and polyboranes [26] have been determined. However, such data are difficult to obtain for nuclei in chemically equivalent surroundings, and in particular for the quadrupolar $^{11}B$ nuclei, for which fast nuclear spin relaxation causes problems. In the case of carbenes, it is expected that the lone pair of electrons at carbon affects all coupling constants involving the carbene center in the usual way [32, 33], which means that there will be a markedly negative contribution to the Fermi contact term (FC) for one-bond couplings. Furthermore, other coupling mechanisms [33], the spin-dipole (SD) and the spin-orbit terms (SO), have to be considered If the electronic structure of the carbene center is inverted, the effect of the lone pair of electrons at carbon is less obvious. In most cases considered here, there are several coupling pathways, and therefore, it is not straightforward to relate the magnitude of $^1J$ or $^2J$ with the bonding situation. Usually, the SD and SO contributions to $^1J$ are assumed to increase if multiple bonding has to be considered. However, the physical picture behind these terms (in the case of SO, it is the paramagnetic part PSO) indicates that their contributions increase because of $B_0$-induced electron currents in energetically close lying occupied and virtual valence orbitals with p (or d) character. This situation applies to most of the structures containing a carbene center, in agreement with the calculated SD and PSO data. Since the PSO contribution is smaller in the boron

compounds, the lone pair of electrons at carbon plays an important role. These SD and PSO contributions can be of either sign, depending in a complex manner on the electronic structure (see data for **1b** and **2b** in Table 2, and **9** in Scheme 5; or **7** and **8** in Scheme 5).

The problems mentioned above are hardly relevant for $^1J(^{13}\text{C},^1\text{H})$ or $^1J(^{11}\text{B},^1\text{H})$, and the calculated data are in the expected ranges. The well documented correlations of the magnitude of $^1J(^{13}\text{C},^1\text{H})$ or $^1J(^{11}\text{B},^1\text{H})$ with the s-character of the respective C-H or B-H hybrid orbitals are clearly valid for the structures considered here.

## Conclusions

At least six small, cyclic hydrocarbons containing carbene centers were found as minima on the PES of the $C_4H_2$ system, and two energetically almost identical cyclopropylmethylidene structures, also containing carbene centers were discussed for the $C_4H_4$ system. Isolobal replacement of carbene-type carbon atoms by BH fragments leads to structures which are comparable, some of which, however, do not present minima. The most noteworthy quality of the carbene center, when compared with the BH fragment, is its ability to turn into an inverted carbene which means that it can act as a $\pi$ electron donor in 2c, 3c or multi-center bonds, and at the same time becomes an acceptor for $\sigma$ electrons, again in 3c or multi-center bonding. The calculated chemical shifts $\delta^{13}\text{C}$ are clearly different for carbene and inverted carbene centres. The calculated coupling constants $J(^{13}\text{C},^{13}\text{C})$ are frequently dominated by contributions arising from spin-dipole

and spin-orbital interactions. Therefore, many of these data cannot be used in a straightforward way to discuss the bonding situation.

## Experimental Section

*Computational*

All calculations were performed for the molecules in the gas phase, using the Gaussian 03 package [34]. Stationary points of the calculated geometries [B3LYP/6-311+G(d,p) [35]] were characterized as singlet ground states and as minima on the PES by examining the stability of the wave function and calculating the harmonic vibrational frequencies. Chemical shifts (GIAO) and coupling constants were calculated at the same level of theory. The diamagnetic spin-orbital contributions are not listed, since they are $< 0.1$ Hz in all cases. The B3LYP method was preferred here, since it has been shown to give the most reliable results for coupling constants in numerous boranes, polyboranes and carboranes [10, 26, 36]. Application of the MP2/6-311+G(d,p) method [37] gave the same principal structures when compared with the B3LYP method, with slight modifications of bond lengths and angles. Using these geometries for the calculation of the NMR parameters gave values which differ little from those in the Tables 1, 2 and Scheme 5. Chemical shifts $\delta^{13}\text{C}$ are given relative to $\text{Me}_4\text{Si}$ [$\delta^{13}\text{C} = \sigma(^{13}\text{C})(\text{Me}_4\text{Si}) - \sigma(^{13}\text{C})$; for $\sigma(^{13}\text{C})(\text{Me}_4\text{Si}) = 184.0$], and $\delta^{11}\text{B}$ relative to $\text{BF}_3\text{-OEt}_2$ [$\delta^{11}\text{B} = \sigma(^{11}\text{B})(\text{B}_2\text{H}_6) - \sigma(^{11}\text{B}) + 18.0$; for $\sigma(^{11}\text{B})(\text{B}_2\text{H}_6) = 84.2$].

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