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1,2-, 1,7- and 1,12-Dicarba-*closo*-dodecaborane(12) Derivatives Revisited by ^{13}C NMR Spectroscopy and DFT Calculations. First Observation of Isotope-Induced Chemical Shifts $^{1}\Delta^{10/11}$B(^{13}C), and the Signs and Magnitudes of Coupling Constants $^{1}J(^{13}C,^{13}C)$ and $^{1}J(^{13}C,^{11}B)$

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Dedicated to Professor Wilhelm Preetz on the Occasion of His 75th Birthday

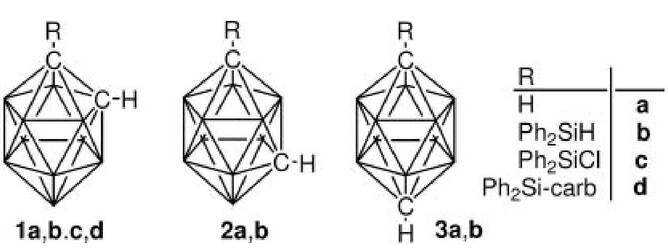
Keywords: Carboranes; NMR spectroscopy; Isotope-induced chemical shifts; Coupling constants; Density functional calculations

Abstract. The origin of broadening of ^{13}C(carborane) NMR signals of 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes(12) and several diphenylsilyl derivatives has been examined in detail and could be traced only partially to unresolved $^{13}C-^{11}B$ spin-spin coupling. Other contributions to the line widths arise from $^{13}C-^{1}H$ dipole-dipole interactions and, in particular, from isotope-induced chemical shifts $^{1}\Delta^{10/11}$B(^{13}C), observed here for carboranes for the first time. In the case of 1-diphenylsilyl-1,2-dicarba-*closo*-dodecaborane-(12), the coupling constant $^{1}J(^{13}C,^{13}C) = 9.3$ Hz was measured in natural abundance of ^{13}C. The small value of this coupling constant and its negative sign is predicted by calculations based on optimised structures [B3LYP/6-311+G(d,p) level of theory] of the parent carboranes and 1-silyl-1,2-dicarba-*closo*-dodecaborane(12) as a model compound [calcd. $^{1}J(^{13}C,^{13}C) = -10.5$ Hz]. Calculated coupling constants $^{1}J(^{13}C,^{11}B)$ are small (<7 Hz), in contrast to published assumptions, and of either sign, whereas $^{1}J(^{11}B,^{11}B)$ are all positive and range up to 15 Hz.

Introduction

There is a wealth of derivatives of the three isomers of dicarba-*closo*-dodecaboranes(12) („*ortho*-" **1a**, "*meta*-" **2a** and "*para*-carborane" **3a**) bearing substituents at one or both carbon atoms [1−11], and many of these compounds were characterised by NMR spectroscopic methods. From the beginning of carborane chemistry, ^{11}B NMR played an important role [12−17] accompanied by routine ^{1}H NMR spectra, mainly focusing on the organic moieties of substituents at the carbon atoms. In contrast, ^{13}C NMR spectroscopy dealing with the carbon atoms in the carborane cage has received less attention [18−22]. The substantial broadening observed for the ^{13}C NMR signals of the parent carboranes $C_2B_{10}H_{12}$ [18−22] has been interpreted as a result of scalar relaxation of the second kind [23], owing to partially relaxed $^{13}C-^{11}B$ spin-spin coupling (^{11}B: I = 3/2) [24] and might have been somewhat discouraging for more detailed studies. Thus, indirect nuclear $^{13}C-^{13}C$ spin-spin coupling [$^{1}J(^{13}C,^{13}C)$] in **1** or its derivatives has not been measured so far. However, in substituted carboranes, the broadening appears to be less serious [11, 25−27] as a result of relatively fast quadrupole-induced ^{11}B nuclear spin relaxation. Therefore, the ^{13}C(carborane) NMR signals are readily observed and deserve attention with respect to structural assignments. Moreover, they offer an almost unique opportunity to observe isotope-induced chemical shifts [28] $^{1}\Delta^{10/11}$B(^{13}C) which are difficult to determine for most other boron−carbon compounds.

Here we report the first example of $^{1}J(^{13}C,^{13}C)$ for a 1-silyl derivative of **1a**, and also the first examples of $^{1}\Delta^{10/11}$B(^{13}C) for *ortho*-, *meta*- and *para*-carboranes bearing silyl groups at the carbon atoms (Scheme 1). We also point out that these effects are most likely observable for many other similar carborane derivatives.



Scheme 1. Dicarba-*closo*-dodecacarboranes(12) and derivatives studied here by ^{13}C NMR spectroscopy.

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Results and Discussion

The carborane derivatives **1**−**3** (Scheme 1) were prepared by mono-lithiation of the parent carboranes, using butyllithium, followed by reaction with the corresponding chlorosilanes. Because the lithiation affords mixtures containing mainly the desired C mono-lithiated carborane along with the dilithiated carborane and the respective parent carborane [29, 30], the reaction mixture, in general, also contains the parent carboranes and small amount of disubstituted carboranes, When dichloro(diphenyl)silane was used, in order to prepare **1d**, the mixture of soluble materials also contained **1a** and **1c**. All carborane derivatives **1**−**3** are fairly soluble and stable in C_6D_6 or $CDCl_3$, and their composition is readily established by ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR spectroscopy.

The literature on ^{13}C NMR studies of the parent carboranes [18−22] points out the particular feature of broad ^{13}C NMR signals which, at a first glance, is not surprising considering the neighbourhood of the ^{13}C nuclei to the quadrupolar ^{11}B and/or ^{10}B nuclei. The ^{11}B NMR signals of the parent carboranes are rather sharp, indicating only moderately fast ^{11}B quadrupole-induced relaxation, confirmed by measurements of the relaxation times $T_1(^{11}B)$ [22]. Unresolved ^{11}B-^{11}B and ^{11}B-^{10}B spin-spin coupling will also contribute significantly to the line widths of the ^{11}B NMR signals [13]. A two-dimensional (2D) heteronuclear shift correlation $^{13}C/^{11}B$ has been carried out in order to explore the potential of this experiment for establishing $^{13}C-^{11}B$ connectivities [22]. The experiment seemed to be successful, although some cross peaks were not observed. In these experiments, it was assumed that the magnitude of $^1J(^{13}C,^{11}B)$ was in the order of 70 Hz [22]. This assumption is in contrast with the appearance of the one-dimensional (1D) $^{13}C\{^1H\}$ NMR spectra, for which one would then expect to observe a fine structure owing to partially resolved $^{13}C-^{11}B$ spin-spin coupling, taking into account the $T_1(^{11}B)$ values determined by the same authors [22]. We have approached this problem in two ways: (i) In the case of boranes, the NMR parameters such as ^{11}B chemical shifts [31] and coupling constants [32−34], can be calculated reasonably well by using various ab-initio methods and also by DFT methods (vide infra); (ii) the origin of the broadening of the ^{13}C(carborane) NMR signals needs to be elucidated more precisely.

Broadening of ^{13}C(Carborane) NMR Signals

In principle, ^{11}B decoupling should remove the broadening effect of ^{11}B nuclei on the line widths of ^{13}C NMR signals [35]. In the cases of **1a**−**3a**, this leads to significant sharpening of the ^{13}C NMR signals, as expected. However, the line widths of the signals are still in the order of 2 to 5 Hz, depending on the field strength (B_0 = 4.6 or 11.5 T) of the spectrometer, the signals being slightly sharper at lower field strength. Since the molecular shape of the parent carboranes rules out anisotropic behaviour in solution, there must be other reasons. One reason for residual broadening could be efficient relaxation by $^{13}C-^{1}H$ dipole-dipole

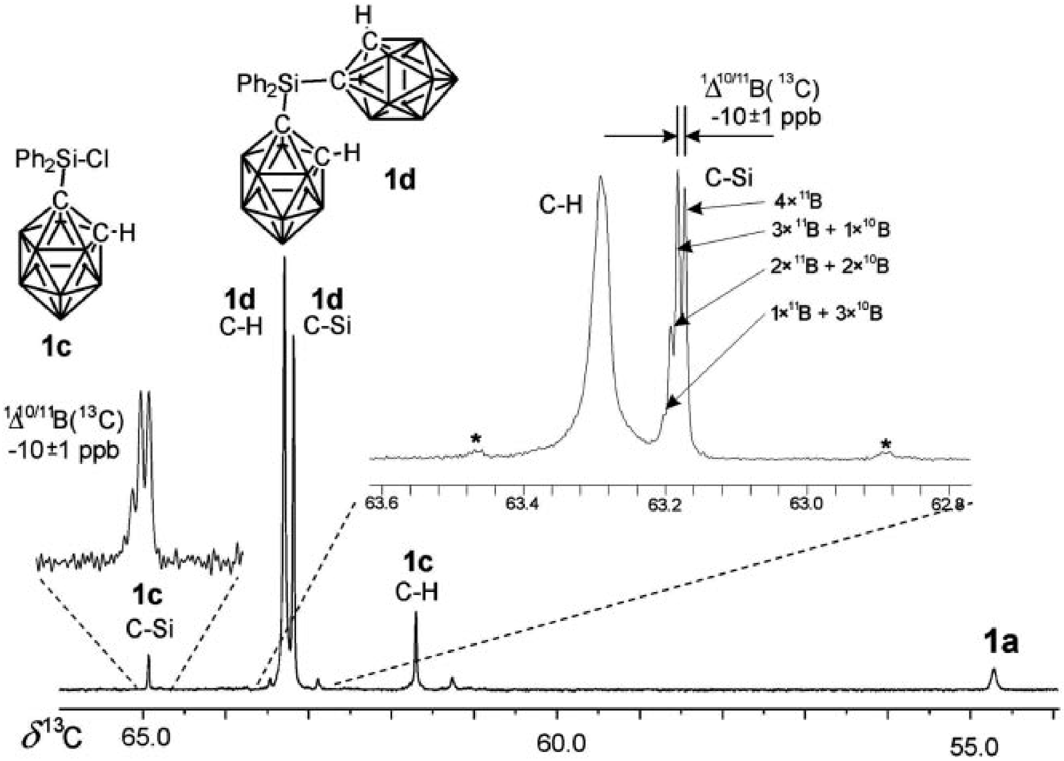

Figure 1. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of a mixture containing **1d** along with **1a** and **1c**, ^{29}Si satellites for $^1J(^{29}Si,^{13}C)$ = 59.1 Hz are marked by asterisks (expansion for **1d**).

interactions. This question can be answered by studying mono-substituted carboranes. In such compounds, the relaxation behaviour of the boron nuclei should have the same effects on both the substituted and unsubstituted ^{13}C nuclei. At the same time, the increasing molecular size of the carborane derivative causes faster ^{11}B nuclear spin relaxation, and $^{13}C\{^{11}B,^{1}H\}$ experiments become unnecessary. Figure 1 shows the ^{13}C(carborane) NMR signals of a mixture containing **1a**, **1c** and **1d**. The ^{13}C(CH) NMR signals of **1c** and **1d** are somewhat broad, whereas the ^{13}C(SiC) NMR signals are sharper and split into several lines. An inspection of the relative intensities of these lines clearly indicates additive isotope-induced chemical shifts $^{1}\Delta^{10/11}B(^{13}C)$, and their positions are a function of the number of ^{10}B atoms adjacent to the ^{13}C nucleus in question. In Figure 2, a comparison of these patterns is shown for the different isomers **1b**, **2b** and **3b**. There are four boron atoms adjacent to each carbon atom in *ortho*-carboranes, and five boron atoms are adjacent to the carbon atoms in both *meta*- and *para*-carboranes, leading to characteristic calculated intensity patterns, very close to those observed experimentally. Apparently, the influence stemming from boron atoms non-adjacent to carbon atoms is extremely small.

The isotope effects are resolved solely for the ^{13}C NMR signals of the substituted carbon atoms, because residual broadening owing to strong $^{13}C-^{1}H$ dipolar interactions is absent. This is in contrast to the $^{13}C-^{1}H$ unit, where the splitting due to isotope effects is hidden in the broadened signal. It is likely that the isotope effects can be detected for many carborane derivatives, if ^{13}C NMR spectra are carefully measured observing conditions for best field homogeneity and sufficient digital resolution. This is shown in Figure 3 for two examples of 1,2-disubstuted *ortho*-carborane derivatives which have previously been measured under routine conditions [36]. Improved conditions clearly reveal the isotope effects.

$^{13}C-^{11}B$ and $^{13}C-^{13}C$ Spin-Spin Coupling in Carboranes

The qualitative analysis of the origin of broad lines of ^{13}C(carborane) NMR signals has shown that partially relaxed ^{13}C-^{11}B spin-spin coupling plays a role which however, is not in agreement with the proposed [22] large magnitudes (≈ 70 Hz) of these coupling constants. Although it is difficult to obtain the accurate line widths of the ^{13}C(carborane) NMR signals, as outlined above, one can estimate [37] that a magnitude of $^{1}J(^{13}C,^{11}B)| < 10$ Hz is much more correct. This is in reasonable agreement with calculated data (vide infra).

A major challenge in carbon compounds is the determination of coupling constants $^{1}J(^{13}C,^{13}C)$ at natural abundance of ^{13}C [38, 39]. In the case of the *ortho*-carborane derivatives, this task is even more difficult, considering the broadening of the ^{13}C NMR signals. Nevertheless, it should be possible to overcome this problem by using more time

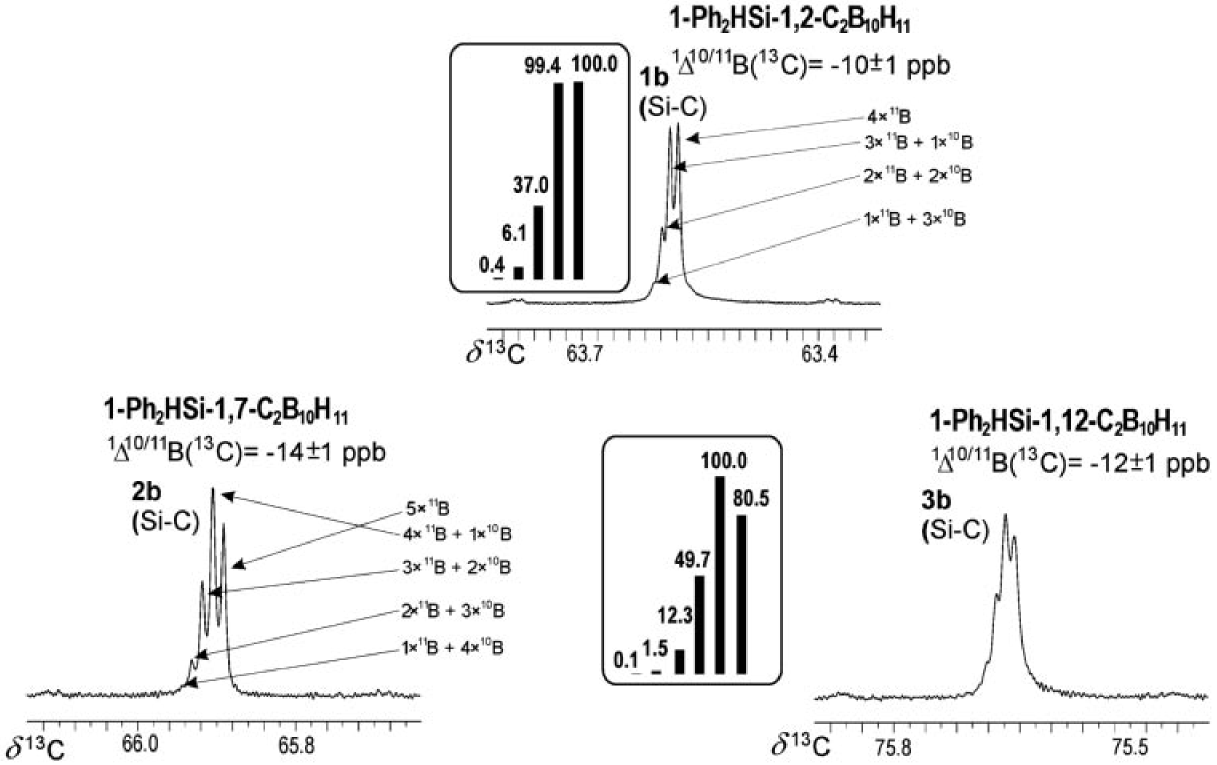

Figure 2. 125.8 MHz $^{13}C\{^{1}H\}$ NMR spectra of the Si$-C_{carb}$ resonances of the carborane isomers **1b**, **2b** and **3b**, showing the pattern due to the isotope-induced chemical shifts $^{1}\Delta^{10/11}B(^{13}C)$ together with the calculated intensity distributions for the neighbourhood of carbon to four (**1b**) and five boron atoms (**2b**, **3b**).

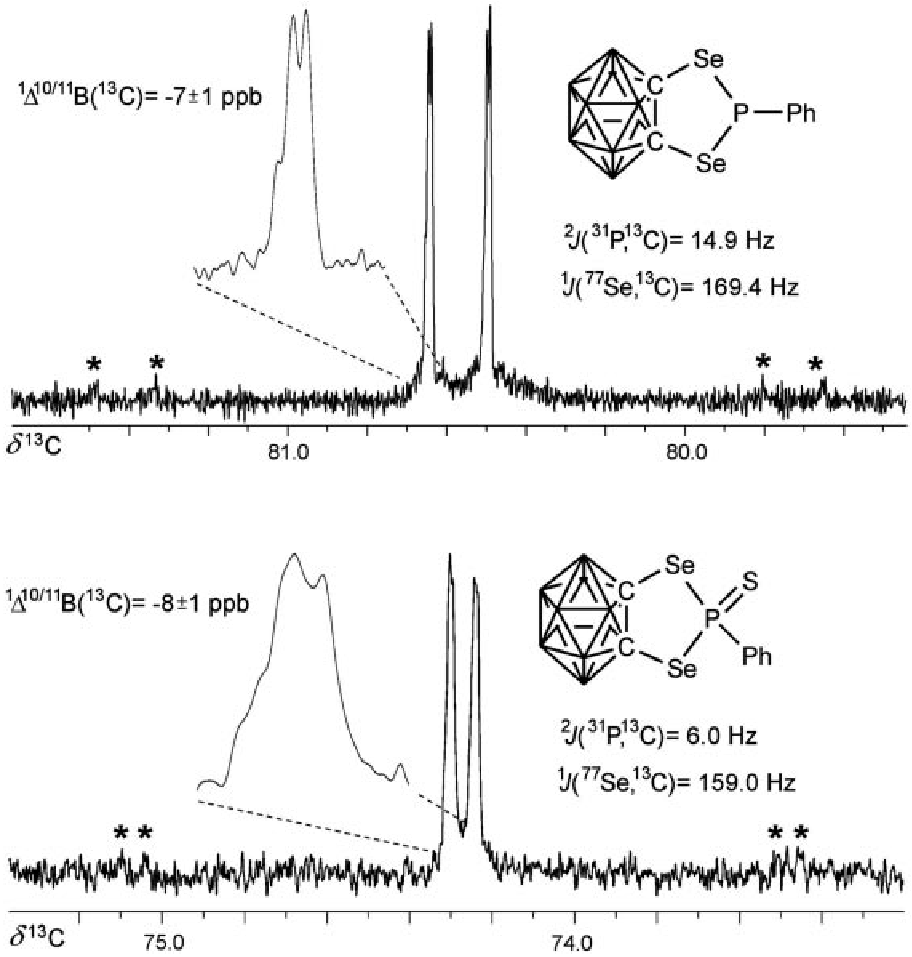

Figure 3. 125.8 MHz ^{13}C{^{1}H} NMR spectra of two examples of 1,2-disubstituted *ortho*-carboranes [36] recorded and processed in order to show the isotope-induced chemical shifts $^1\Delta^{10/11}$B(^{13}C) typical of *ortho*-carboranes. ^{77}Se satellites for ^1J(^{77}Se,^{13}C) are marked by asterisks.

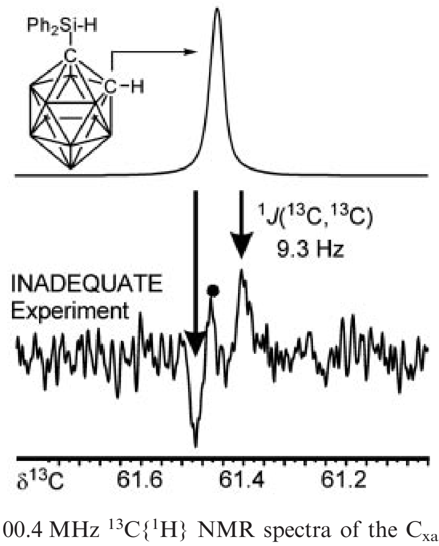

Figure 4. 100.4 MHz ^{13}C{^{1}H} NMR spectra of the C$_{xarb}$-H signal of **1b**. The upper trace shows the result of the normal single pulse experiments after 4000 transients, and the lower trace shows the ^{13}C satellites as the result of an INADEQUATE experiment [40], assuming ^1J(^{13}C,^{13}C) ≈10 Hz (relaxation delay 5 s, after 12 h, 5000 transients). The residual intensity of the central line is marked by a filled circle.

for the measurement. The next problem however, concerns the approximate magnitude of this coupling constant. Thus, "normal" single pulse 1D ^{13}C{^{1}H} NMR spectra of the compounds **1b** and **1c** did not give useful results in spite of excellent signal-to-noise ratios. In the case of **1d**, the difference in chemical shifts $\Delta\delta^{13}$C(1,2) was too small. Different experiments with the shortest INADEQUATE pulse sequence [40], in order to suppress the central line, using various delays according to assumed values of ^1J(^{13}C,^{13}C) finally gave the desired result for **1b** (Figure 4). The coupling constant ^1J(^{13}C,^{13}C) = 9.3 Hz is rather small and therefore, satellite signals would be invisible, covered by the central line, using single pulse ^{13}C{^{1}H} experiments.

DFT Calculations

The gas-phase geometries of the parent carboranes **1a**, **2a**, **3a** and of the model compound 1-H$_3$Si-1,2-C$_2$B$_{a0}$H$_{11}$ (**1M**) were optimised at the B3LYP/6-311+G(d,p) level of theory [41, 42], and the coupling constants ^1J(^{11}B,^{11}B), ^1J(^{13}C,^{11}B) and ^1J(^{13}C,^{13}C) were calculated [43−45] at the same level of theory. Selected data are given in Table 1. The calculated values for ^1J(^{13}C,^{11}B) are small and of either

Table 1. Selected calculated coupling constants /Hz for the carboranes **1a**, **1M**, **2a**, and **3a**.

	$J(^{13}C,^{11}B)$	$J(^{13}C,^{13}C)$	$^{1}J(^{11}B,^{11}B)$
1,2-$C_2B_{10}H_{12}$ (**1a**)	−0.4 (1−3)	−5.0 (1−2)	+9.5 (3−4)
	+2.9 (1−4)		+8.5 (4−5)
	+0.1 (1−12)		+14.5 (7−12)
1-SiH_3-1,2-$C_2B_{10}H_{11}$ (**1M**)	−1.7 (1−3)	−10.5 (1−2)	+10.3 (3−4)
	−0.6 (1−4)	[exp. 9.3 (**1b**)]	+9.3 (4−5)
	+1.2 (2−3)		+13.8 (7−12)
	+2.1 (2−7)		
1,7-$C_2B_{10}H_{12}$ (**2a**)	+6.2 (1−2)	+0.2 (1−7)	+2.5 (2−3)
	+1.1 (1−4)		+9.5 (3−4)
	+2.3 (1−6)		+8.2 (4−5)
			+2.1 (8−12)
			+14.2 (9−12)
1,12-$C_2B_{10}H_{12}$ (**3a**)	+4.2 (1−2)	−0.2 (1−12)	+7.3 (2−3)
			+16.6 (2−7)

sign. In organoboranes or organoborates with 2e/2c B−C bonds, the coupling constants $^{1}J(^{13}C,^{11}B)$ are generally >40 Hz and possess a positive sign [24], and the agreement between experimental and calculated data is excellent [33, 34d]. Thus, multi centre bonding reduces expectedly the B−C s orbital overlap integral and gives negative contributions to the dominant Fermi contact term in the spin-spin coupling mechanism. This is more pronounced for electronegative elements such as nitrogen in aza-*closo*-dodecaborane $NB_{11}H_{12}$ [46] or carbon in the carboranes discussed here than for the electropositive boron, where all coupling constants $^{1}J(^{11}B,^{11}B)$ possess positive signs and their calculated magnitudes are in the order expected and experimentally determined for B−B−B multicentre bonding [13, 16, 46].

The huge data set known for coupling constants $^{1}J(^{13}C,^{13}C)$ [38, 39] contains very few examples with a negative sign. Again, the small C−C s orbital overlap integral and negative contributions to the Fermi contact term are responsible in the case of the *ortho*-carboranes. Electropositive substtuents such as a silyl group at the carbon atom apparently enhance these negative contributions. The calculated value $^{1}J(^{13}C,^{13}C)$ = −10.5 Hz for 1-H_3Si-1,2-$C_2B_{19}H_{11}$ (**1M**) is numerically very close to the experimental value of 9.3 Hz for 1-$Ph_2(H)Si$-1,2-$C_2B_{10}H_{11}$ (**1b**) and therefore, we propose a negative sign for this coupling constant.

Conclusions

Isotope-induced chemical shifts $^{1}\Delta^{10/11}B(^{13}C)$ in derivatives of *ortho*-, *meta*- and *para*-carboranes $C_2B_{10}H_{12}$ have been observed for the first time. This type of NMR parameter depends in a complex manner on dynamic and electronic effects of molecular structures. Although the main body of data [28] refers to the effects by exchanging hydrogen against deuterium [$^{1}\Delta^{1/2}H(X)$], the availability of more powerful NMR instruments with ever higher field strengths opens a more convenient access to isotope-induced chemical shifts in general. The unique electronic structure of icosahedral carboranes is reflected by spin-spin coupling involving those nuclei forming the polyhedral frame. This is a first attempt in this field to combine the knowledge about coupling constants $^{1}J(^{11}B,^{11}B)$, $^{1}J(^{13}C,^{11}B)$ and $^{1}J(^{13}C,^{13}C)$ both by experiment and calculations, and this may well be extended to other nuclei being part of polyhedral clusters.

Experimental Section

The preparative work required at various stages exclusion of oxygen and moisture, and the handling of the compounds was done with great care to prepare samples of high quality for the NMR experiments. The parent carboranes **1a**, **2a** and **3a** (Katchem), butyllithium in hexane (1.6 M) and the chlorosilanes (Aldrich) were used as commercial products. NMR spectra were recorded at 23 °C with Bruker WP 200, Bruker ARX 250, Bruker DRX 500 and Varian Inova 400 spectrometers, all equipped with multinuclear units, using C_6D_6 solutions (ca. 5−10 % v/v) in 5 mm tubes. The instruments Bruker WP 200 and Bruker DRX 500 were equipped with hardware for performing the $^{13}C\{^{1}H,^{11}B\}$ heteronuclear triple resonance experiments. Chemical shifts are given relative to $SiMe_4$ [$\delta^{1}H$ (C_6D_5H) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz], BF_3-OEt_2 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz]. ^{29}Si NMR spectra were measured using the refocused INEPT pulse sequence [based on $^{1}J(^{29}Si,^{1}H) \approx 250$ Hz (**1b**, **2b**, **3b**) or $^{3}J(^{29}Si,^{1}H_{Ph}) \approx 8$ Hz (**1c**, **d**)] with ^{1}H decoupling [47]. Isotope-induced chemical shifts $^{1}\Delta^{10/11}B(^{13}C)$ are given in ppb with a negative sign indicating a shift of the ^{13}C NMR signal of the more heavy isotopomer to lower frequency.

The calculations were performed using the Gaussian 03 program package [48]. Frequencies were calculated analytically to characterise the stationary points of the optimised geometries as minima by the absence of imaginary frequencies. The Fermi contact term is dominant in the spin-spin coupling mechanism. Rather small contributions were calculated for the paramagnetic spin-orbital term (PSO) with less than 3 % to the coupling constants $^{1}J(^{11}B,^{11}B)$, $^{1}J(^{13}C,^{11}B)$ and $^{1}J(^{13}C,^{13}C)$. The contributions from the spin-dipole term (SD) and the diamagnetic spin-orbital term (DSO) were small (<< 1 Hz) in all cases studied.

1-Diphenylsilyl-closo-1,2-dicarbadecaborane (1b): *ortho*-Carborane **1a** (0.35 g, 2.39 mmol) was dissolved in THF (40 mL), and the solution was cooled to −78 °C and kept stirring. After addition of BuLi in hexane (1.49 mL, 2.39 mmol), the mixture was warmed to room temperature, cooled again to −78 °C, and the chloro(diphenyl)silane (0.53 g, 1.39 mmol) was added in one portion. Then the mixture was stirred for 2 h at room temperature. All volatiles were removed, the solid residue was taken up in hexane (20 mL), insoluble materials were filtered off, hexane was removed, and the product was characterised by NMR spectroscopy. **^{1}H NMR** (400 MHz): δ = 1.6−3.4 (m, 10 H, BH), 3.04 (s, 1 H, CH), 5.11 [s, $^{1}J(^{29}Si,^{1}H)$ = 219.9 Hz, 1 H, SiH], 7.2−7.4 (m, 6 H, Ph), 7.65 (m, 4 H, Ph). **^{13}C NMR** (125.8 MHz): δ = 58.1 (C_{carb}-H), 61.4 [$^{1}J(^{29}Si,^{13}C)$ = 50.1 Hz, C_{carb}-Si], 128.3 (*p*-Ph), 128.9 (m-Ph), 131.8 [*i*-Ph, $^{1}J(^{29}Si,^{13}C)$ = 54.8 Hz], 135.8 (*o*-Ph). **^{11}B NMR** (128.3 MHz): δ = −13.4 (2 B), −11.2 (4 B), −6.5 (2 B), −0.5 (2 B). **^{29}Si NMR** (99.4 MHz): δ = −7.1.

Bis(closo-1,2-dicarbadecaboran-1-yl)diphenylsilane (1d): The same procedure as for **1b** was applied, starting from **1a** (0.35 g, 2.43 mmol) and dichloro(diphenyl)silane (0.154 g, 1.215 mmol).

The soluble product obtained contained also a small amount of **1c** (see Figure 1). **1d:** **^{1}H NMR** (400 MHz): δ = 1.6−3.6 (br., 20 H, BH), 3.03 (s, 2 H, CH), 7.1−7.7 (m, 10 H, Ph). **^{13}C NMR** (100.5 MHz, C_6D_6): δ = 63.3 (C-H), 63.2 [$^1J(^{29}Si,^{13}C)$ = 58.1 Hz, C_{carb}-Si], 126.0 [$^1J(^{29}Si,^{13}C)$ = 80.6 Hz, *i*-Ph], 129.2 (*m*-Ph), 133.1 (*p*-Ph), 137.9 (*o*-Ph).

1c: **^{1}H NMR** (400 MHz): δ = 1.6−3.6 (br., 10 H, BH), 3.11 (s, 1 H, CH), 7.1−7.6 (m, 10 H, Ph). **^{13}C NMR** (100.5 MHz): δ = 61.8 (C_{carb}-H), 65.0 (C_{carb}-Si).

1-Diphenylsilyl-1,7- and -1,12-dicarba-closo-dodecaboranes(12) (2b) and (3b): The carborane derivatives **2b** and **3b** were prepared in the same way as **1b**, only at a smaller scale, starting from the respective parent carborane (70 mg), sufficient to run the NMR spectra. **2b:** **^{1}H NMR** (500 MHz): δ = 1.6−3.7 (m, 10 H, BH), 2.67 (s, 1 H, C-H), 5.03 [s, $^1J(^{29}Si,^1H)$ = 216.8 Hz, 1 H, Si-H], 7.4 (m, 6 H, Ph), 7.7 (m, 4 H, Ph). **^{13}C NMR** (100.5 MHz): δ = 59.0 (C-H), 66.2 [$^1J(^{29}Si,^{13}C)$ = 52.6 Hz, C_{carb}-Si], 129.0 (*m*-Ph), 131.1 [$^1J(^{29}Si,^{13}C)$ = 74.5 Hz, *i*-Ph], 131.5 (*p*-Ph), 136.4 (*o*-Ph). **^{29}Si NMR** (99.4 MHz): δ = −6.6. **3b:** **^{1}H NMR** (500 MHz): δ = 1.7−3.4 (m, 10 H, BH), 2.35 (s, 1 H, C-H), 4.91 [s$^1J(^{29}Si,^1H)$ = 214.3 Hz, 1 H, Si-H], 7.2 (m, 6 H, Ph), 7.6 (m, 4 H, Ph). **^{13}C NMR** (100.5 MHz): δ = 68.3 (C-H), 76.0 [$^1J(^{29}Si,^{13}C)$ = 53.1 Hz, C_{carb}-Si], 128.8 (*m*-Ph), 131.1 [$^1J(^{29}Si,^{13}C)$ = 73.9 Hz, *i*-Ph], 131.3 (*p*-Ph), 136.4 (*o*-Ph). **^{29}Si NMR** (99.6 MHz): δ = −5.9.

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