



# First example of the formation of a Si–C bond from an intramolecular Si–H···H–C dihydrogen interaction in a metallacarborane: A theoretical study

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## ABSTRACT

The recently reported crystal structure of  $[\text{NMe}_4][1\text{-SiMe}_2\text{H-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$  shows short contacts between the Si–H proton acceptor group and the C<sub>c</sub>–H proton donor moiety in the dicarbollide ligand. These short contacts were studied within the framework of the Quantum Theory of Atoms in Molecules (QTAIM) at different levels of DFT theory (B3LYP/6-311(d,p) and BP86/TZ2P(+)) that shows the existence of a bifurcated Si–H···H–C<sub>c</sub> dihydrogen bond. This paper presents the study of an experimental uncommon Si–H group playing as proton acceptor bond in a dihydrogen bond where hydrides like M–H (M, as metal transition), B–H or Al–H usually perform this role. Furthermore, this paper accounts with a new simple method to estimate bonding energies for closed-shell intramolecular interactions in the scheme of Voronoi charge population analysis and Coulomb's Law.

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## 1. Introduction

In the course of our investigations to incorporate silane groups on the cluster carbon of the sandwich complex  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  we observed an unexpected reaction [1]. By mixing 1 equiv. of  $\text{Me}_2\text{SiHCl}$  with 1 equiv. of  $[1\text{-Li-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^-$ , at  $-40^\circ\text{C}$  that expectedly should have produced  $[1\text{-Me}_2\text{SiH-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^-$ , it was obtained instead  $[1,1'\text{-}\mu\text{-Me}_2\text{Si-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ . The reaction conditions implied that an intramolecular hydride–protonic reaction had taken place. This was unanticipated because the charges on both hydrogen atoms had to be very weak. The reaction is shown in Scheme 1. Our hypothesis was that a dihydrogen bond develops as a result of the favorable geometric characteristics of the cobaltabisdicarbollide anion, that weakens both the C<sub>c</sub>–H and Si–H bonds producing a Si–C<sub>c</sub>. The C<sub>c</sub>–H stands for the hydrogen bonded to the cluster carbon. It is well established that agostic C–H interactions can significantly weaken the C–H bond, thereby rendering it susceptible to a wide range of inter- and intramolecular reactions. Likewise dihydrogen interactions may play an important role in lowering the activation energy for dihydrogen evolution and in influencing the generation of new covalent bonds. We could not find, however, any example in the literature of a Si–H and C–H interacting groups that at low temperatures evolved to a Si–C

bond. Thus we wanted to confirm first, the existence of a C<sub>c</sub>–H···H–Si dihydrogen bond in  $[1\text{-Me}_2\text{SiH-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^-$  and, second, its particular characteristics that made it to react so uniquely.

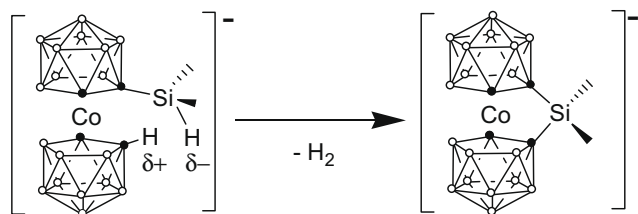
The dihydrogen bond (DHB) is a type of unconventional hydrogen bond in which a proton donating moiety D–H interacts with a proton acceptor A–H, see Scheme 2. They display characteristics similar to conventional hydrogen bonding [2].

The usual functional groups performing proton donating characteristics are F–H, O–H, N–H or C–H with a remarkable excess of positive charge on the hydrogen atom, and the usual proton acceptor groups contain hydridic atoms connected to Al, B, Ga, Ir, Mo, Mn, Os, Re, Ru or W atoms. Other systems have been described where two interacting hydrogen atoms do not show a clear protic and hydridic character [3]; it is the case of the H–H bonding interaction. The latter results from the close approach of two bonded hydrogen atoms bearing the same or similar net charges that stabilize the whole system. While it is also a closed shell interaction, the H–H bonding is distinct from DHB in its atomic and geometric characteristics [4]. Since the first DHB was found [5] until present, the DHB has been extensively studied in theoretical and experimental aspects [6]. The Quantum Theory of Atoms in Molecules of Bader [7] (QTAIM) is an important tool often applied to study DHB; Popelier established a sort of criteria based on the QTAIM to characterize DHB [8], and recently, Alkorta and co-workers [6b] have applied natural bond orbital methods (NBO) to determine whether intramolecular H···H interactions can be classified as DHB.

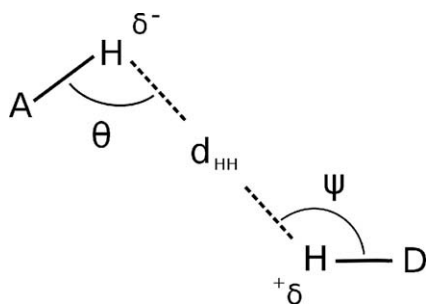
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**Scheme 1.** Suggested pathway for the intramolecular reaction that causes the clusters' bridge in anions [1].



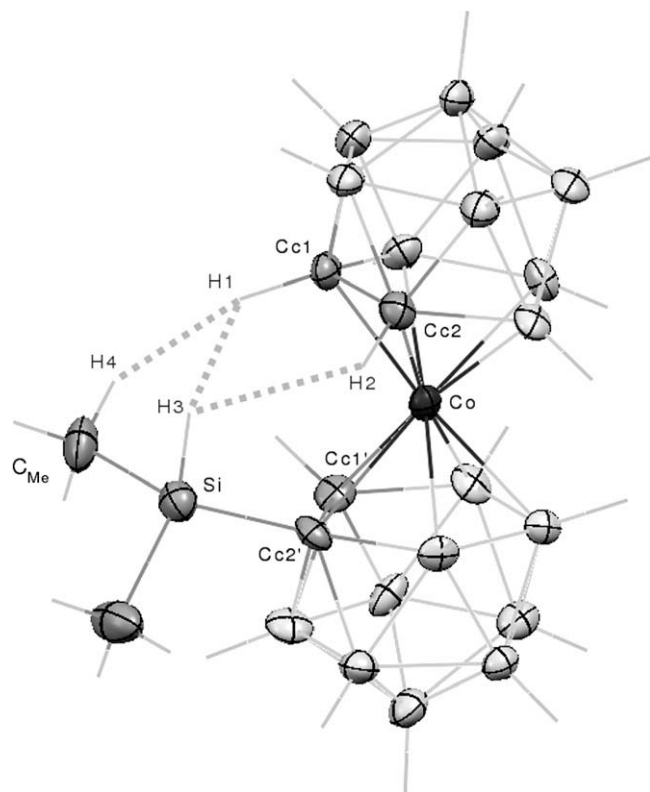
**Scheme 2.** Geometrical representation of the parameters of the DHB. A (Si or C<sub>Me</sub>), D (C<sub>c</sub>).

In this study, we will analyze the factors that have led to this intramolecular reaction shown in [Scheme 1](#), by using QTAIM at different levels of DFT theory (B3LYP/6-311(d,p) and BP86/TZ2P(+)). For this purpose the H...H interactions in the crystal structure of [NMe<sub>4</sub>][1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup> have been studied. Three intramolecular H...H interactions that might be treated as dihydrogen bonds, H-H bonding interactions or Van der Waals complexes are observed there. In addition, bonding energies for closed-shell intramolecular interactions in the scheme of Voronoi charge population analysis and Coulomb's Law have also been calculated.

## 2. Results and discussion

### 2.1. Experimental evidences for DHB in the [NMe<sub>4</sub>][1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] salt

Atomic distances are one of the main indicators for the existence of a bond. This is also valid for hydrogen and dihydrogen bonding [9]. Distances shorter than the Van der Waals radii point to a some type of interaction. Therefore distances shorter than 2.4 Å are indicative of a H...H interaction. The crystal structure of [NMe<sub>4</sub>][1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] is the first example of C<sub>c</sub>-monosubstituted cobaltabisdicarbollide anion reported in literature [1]. This unique molecular structure presents an anion with three intramolecular short contacts with distances at 2.409, 2.212 and 2.059 Å between the H atoms. Two are clearly below the Van der Waals cut-off while one is slightly longer than 2.4 Å. First two short contacts are involving the hydridic hydrogen atom of the Si-H function and the protonic hydrogen atoms of the carbon cluster atoms (C<sub>c</sub>-H) of the dicarbollide ligand. The third short contact (2.059 Å) is established between the hydrogen atom of a methyl moiety in the silane function (C<sub>Me</sub>-H) and the hydrogen atom of one C<sub>c</sub>-H function. [Fig. 1](#) shows the spatial disposition of these three short contacts. Are all of them true DHBs? According to the crystal data these with 2.212 and 2.059 Å should, but what about the 2.409 Å distance?



**Fig. 1.** XRD molecular structure of the anion [1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup> shows intramolecular short contacts Si-H3...H1-C<sub>c</sub>, Si-H3...H2-C<sub>c</sub> and C<sub>Me</sub>-H4...H1-C<sub>c</sub>. The non hydrogen atoms are represented at 40% probability level thermal ellipsoids.

Furthermore, the shortest contact corresponds to (Si-CH<sub>2</sub>)H...H-C. This is surprising due to the equal nature of the donor and acceptor atoms C<sub>Me</sub>-H and C<sub>c</sub>-H. The two other interactions are Si-H...H-C<sub>c</sub> contacts. The difference in electronegativity between Si and C, 1.90 versus 2.55 suggests that DHB could be formed. If this was the case it would imply a shift of the interacting C<sub>c</sub>-H resonance in the <sup>1</sup>H NMR. Solution NMR data of weak intermolecular dihydrogen bonds is scarce due to the perturbing effect of the solvent, however, the intramolecular interaction reported here could afford first details on the C<sub>c</sub>-H...H-Si interaction. Fortunately, the C<sub>c</sub>-H chemical shift in the <sup>1</sup>H NMR can be informative because few other types of protons resonate in its region, 3.94 ppm in pristine [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>. For an adequate comparison of the chemical shifts involved, [1-SiMe<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup> was taken as a reference. This anion has been recently described in our group [1] and its <sup>1</sup>H NMR spectrum shows three resonances at 4.02, 3.83, and 3.72 ppm due to the three C<sub>c</sub>-H bonds. Conversely, in [1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup>, only two resonances are observed at 3.85 and 3.69 ppm, with relative areas 1:2. Therefore, the resonance at 4.02 ppm in [1-SiMe<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup> has been shifted to 3.69 ppm in [1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup>, see [Fig. 2](#). It can be interpreted as if H<sup>+</sup> in C<sub>c</sub>-H has received electron density from H<sup>-</sup> in Si-H to become more shielded, or more electron-rich. These experimental data are fully consistent with the formation of a H...H interaction, and were supportive of a more thorough investigation by using computational methods.

After a thorough search at the Cambridge Structural Database (CSD), it appears that the crystal structures of [NMe<sub>4</sub>][1-SiMe<sub>2</sub>H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] and [1,1'-μ-Me<sub>2</sub>Si-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> are the only pair of related X-ray determined com-

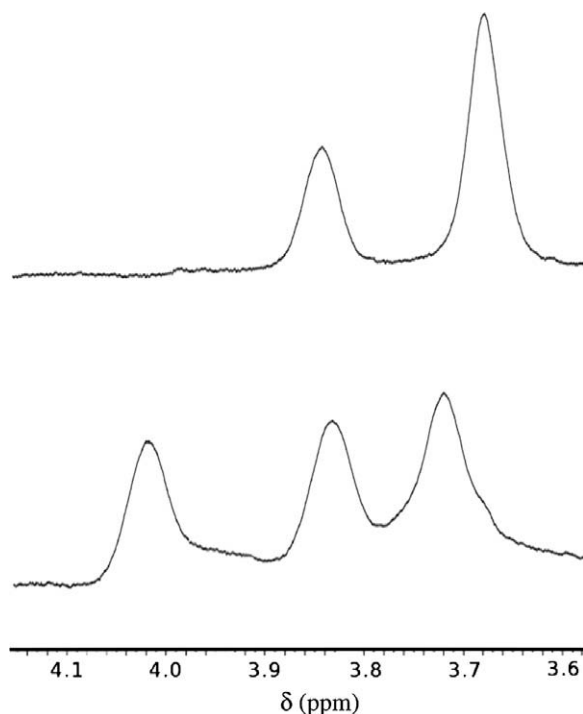


Fig. 2.  $^1\text{H}$  NMR spectra of  $[1\text{-SiMe}_2\text{H-3,3'-Co(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$  (up) and  $[1\text{-SiMe}_3\text{-3,3'-Co(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$  (down).

pounds, one with a Si–H···H–C DHB bond and the second with a Si–C bond, all other elements being equal. In fact, few examples of crystal structures with Si–H···H–C contacts in which the Si–H has an environment comparable to carborane-Si(alkyl)<sub>2</sub>–H are very scarce. For similar environment we understand aryl-Si(alkyl)<sub>2</sub>–H or even alkyl-Si(alkyl)<sub>2</sub>–H. In none of these cases the intramolecular reaction was ever observed [10]. This evidences the difficulty of dihydrogen evolution to generate a Si–C bond.

A possible explanation for the uniqueness of the Si–H···H–C to Si–C transformation may arise from the geometric disposition of substituents on the C<sub>2</sub>B<sub>3</sub> faces. Whereas in the chemical sandwich complex ferrocene, substituents are coplanar to the C<sub>5</sub> framework, in  $[3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$  the substituents are tilted regarding the C<sub>2</sub>B<sub>3</sub> plane. This is visualized in Fig. 1, in which the Si atom is closer to the C<sub>c</sub>–H proton than would be in ferrocene. Because of the tilted disposition of the substituents in dicarbollide derivatives, the formation of the bridging silane does not distort as much the geometric characteristics of  $[3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$ , as would

have been the case in other arrangements, this perhaps facilitating the Si–H···H–C to Si–C transformation.

## 2.2. DFT geometry optimization of the crystal structure and charge population analysis

Two levels of theory, B3LYP/6-311(d,p) and BP86/TZ2P(+), have been used for the geometry optimization in gas phase of  $[1\text{-SiMe}_2\text{H-3,3'-Co(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ . Comparison between calculated and experimental averaged bond lengths in each type of bond with their standard deviation is shown in Table 1. It can there be observed that the optimized structure of the anion at BP86/TZ2P(+) matches better the crystal structure than B3LYP/6-311(d,p).

As it is well-known X-ray diffraction methods do not reflect properly the X–H bond lengths, where X in the case studied here indicates B, C<sub>Me</sub>, C<sub>c</sub> and Si atoms. The DFT calculations are used to correct these H atom position. In Table 2 the geometrical parameters of the three intramolecular short contacts and the bond lengths of the Si–H, C<sub>c</sub>–H and C<sub>Me</sub>–H moieties at the different levels of theory and for the crystal structure are shown. An important X–H length correction can be seen, mainly with the two stronger H···H interactions.

Table 2 shows that H···H distances are below 2.4 Å for the short contacts C<sub>Me</sub>–H4···H1–C<sub>c</sub> and Si–H3···H2–C<sub>c</sub> in all theory levels and in the crystal structure. However, the H···H distance for the Si–H3···H1–C<sub>c</sub> short contact is in the range 2.409–2.440 Å; the closest value to 2.4 Å is found in the crystal structure whereas the farthest is in the geometry optimization at B3LYP/6-311(d,p) level. The angles  $\theta$  and  $\psi$  are important geometrical parameters of a DHB. A Cambridge Structural Database (CSD) investigation [11] evidenced that the experimental range for the B–H···H angle ( $\theta$ ) is in a range of 95–120° and for the N–H···H angle ( $\psi$ ) 150–170°. It is characteristic of DHB the strong bent in the  $\theta$  angle, more than a linear arrangement that usually is a exception [2b,6e,11]. Our values for  $\theta$  are in the range for normal DHBs but  $\psi$  values are smaller possibly due to the constrained geometry of the intramolecular interactions.

Atomic charges and population analysis were computed with the Natural Population Analysis (NPA) and Voronoi Deformation Density methods (VDD) at B3LYP/6-311(d,p) and BP86/TZ2P(+) level of theory, respectively (Table 3).

NPA and VDD are adequate basis set independent methods to compute atomic charges. Care should be taken, however, with this data as it is accepted that in general NPA tends to give a too ionic view of the bonds [12] and more reliable methods already have already been used to compute atomic charges in heteroboranes [6y,6z]. In this regard, the NPA charge in the hydrogen atom in the C<sub>Me</sub>–H4 bond seems to be too positive (+0.224) for a methylen-

Table 1  
Average bond lengths for each type of bond in the C-substituted cobaltabisdicarbollide anion (Å). In parenthesis standard deviation (Å X1000).

	Co–C <sub>c</sub>	Co–B	C <sub>c</sub> –C <sub>c</sub>	C–B	B–B	Si–C <sub>c</sub>	Si–C <sub>Me</sub>
<i>B3LYP/6-311G(d,p)</i>							
C-substituted <sup>a</sup>	2.114(31)	2.120(12)	1.623(0)	1.715(13)	1.780(14)	1.914(0)	1.889(4)
Unsubstituted <sup>b</sup>	2.078(4)	2.129(10)	1.604(0)	1.703(17)	1.782(13)	–	–
<i>BP86/TZ2P(+)</i>							
C-substituted	2.081(28)	2.102(12)	1.639(0)	1.715(11)	1.783(15)	1.909(0)	1.891(4)
Unsubstituted	2.056(5)	2.112(12)	1.615(0)	1.704(14)	1.781(16)	–	–
<i>Crystal structure</i>							
C-substituted	2.081(25)	2.099(8)	1.627(0)	1.728(14)	1.778(16)	1.906(0)	1.864(1)
Unsubstituted	2.054(4)	2.107(15)	1.608(0)	1.707(14)	1.785(18)	–	–

<sup>a</sup> C-substituted dicarbollide ligand with SiMe<sub>2</sub>H function.

<sup>b</sup> Unsubstituted dicarbollide ligand.

**Table 2**

Geometrical parameters of the H...H short contacts and X–H bond distances for the crystal structure and optimized geometries. Distances in Å, angles in degrees.

	Crystal structure			B3LYP/6-311G (d,p)			BP86/TZ2P(+)		
	$d_{HH}$	$\theta$	$\psi$	$d_{HH}$	$\theta$	$\psi$	$d_{HH}$	$\theta$	$\psi$
<i>Short contacts interactions<sup>a</sup></i>									
H3...H1	2.409	83.1	108.7	2.440	87.7	112.9	2.413	86.1	112.7
H3...H2	2.212	111.4	115.2	2.167	119.1	122.8	2.154	117.7	122.0
H4...H1	2.059	119.5	155.7	2.224	113.0	150.0	2.157	112.1	148.8
	$d$			$d$			$d$		
<i>Bond distances<sup>b</sup></i>									
C <sub>c</sub> –H1		1.121			1.079			1.086	
C <sub>c</sub> –H2		1.121			1.080			1.086	
Si–H3		1.541			1.488			1.498	
C <sub>Me</sub> –H4		0.980			1.092			1.099	

<sup>a</sup> See Fig. 1 and Scheme 1.<sup>b</sup> See Fig. 1.**Table 3**

Atomic charges on H atoms (au).

	NPA <sup>a</sup>			VDD <sup>b</sup>		
	Hydride	Proton	Difference	Hydride	Proton	Difference
H3...H1	–0.195	+0.267	0.462	–0.085	+0.130	0.215
H3...H2	–0.195	+0.282	0.477	–0.085	+0.122	0.207
H4...H1	+0.224	+0.267	0.043	+0.025	+0.130	0.105

<sup>a</sup> Optimized anion at B3LYP/6-311G(d,p).<sup>b</sup> Optimized anion at BP86/TZ2P(+).**Table 4**

VDD charges on hydrogen atoms (au).

	BP86/TZ2P(+)
Methane	+0.022
Ethene	+0.037
Benzene	+0.046
Ethyne	+0.098
C <sub>c</sub> –H <sup>a</sup>	+0.125
SiH <sub>4</sub>	–0.063
SiMe <sub>3</sub> H <sup>b</sup>	–0.090

<sup>a</sup> Protonic hydrogen in [3,3'-Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>–</sup>.<sup>b</sup> Hydridic hydrogen in Si–H.

ic hydrogen atom. It is known that the acidity of the C–H bond in hydrogen bonds increases in the order C(sp<sup>3</sup>)–H < C(sp<sup>2</sup>)–H < C(sp)–H that corresponds with the strength of the C–H...Y hydrogen bonds. With the aim to compare the possibilities of C<sub>c</sub>–H as a proton-donating bond, a VDD population analysis over methane, ethene, ethyne and benzene along with the hydridic hydrogens of two generic silanes has been calculated and compared with C<sub>c</sub>–H in [3,3'-Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>–</sup>. The results are shown in Table 4. It is to be noticed that the positive VDD charge of the hydrogen atom in C<sub>c</sub>–H is even larger than C–H in ethyne. It is then clear the importance of the C<sub>c</sub>–H moiety to generate a DHB with the appropriate H acceptor.

According to the calculated charges and the adopted geometry of the H3, H2, H1 and H4 hydrogen atoms, it can be stated that Si–H3...H1–C<sub>c</sub> and Si–H3...H2–C<sub>c</sub> short contacts are candidates to an asymmetric bifurcated Si–H3...H(H–C<sub>c</sub>)<sub>2</sub> DHB [6] and C<sub>Me</sub>–H4...H1–C<sub>c</sub> for H–H bonding [2b,4]. Next section offers more insight in the nature of these interactions.

### 3. QTAIM calculations

The above mentioned dihydrogen short contacts were analyzed in terms of their calculated electron density with DFT methods. For the two optimized geometries at different levels of theory, bond

critical points (BCP) are found for Si–H3...H1–C<sub>c</sub> and Si–H3...H2–C<sub>c</sub>. The electron density at the BCP ( $\rho_{cp}$ ) is in a range between 0.0088 and 0.0106 au, whereas for the C<sub>Me</sub>–H4...H1–C<sub>c</sub> hydrogen interaction, the BCP is found only in the optimized structure at B3LYP/6-311(d,p) level with a value of  $\rho_{cp}$  equal to 0.0077 au. We have been unable to find a BCP for C<sub>Me</sub>–H4...H1–C<sub>c</sub> at BP86/TZ2P(+) level of theory, even when the length is clearly lower than the sum of the Van der Waals radii see Table 5.

The corresponding electronic density Laplacian in the BCP ( $\nabla^2\rho_{cp}$ ) is positive for all contacts. It indicates that all interactions are closed-shell type and their nature is mostly electrostatic [13]. The  $\nabla^2\rho_{cp}$  for Si–H3...H1–C<sub>c</sub> and Si–H3...H2–C<sub>c</sub> are in the range 0.0316–0.0269 au for all calculation levels. For C<sub>Me</sub>–H4...H1–C<sub>c</sub> at B3LYP/6-311(d,p) level,  $\nabla^2\rho_{cp}$  is 0.0242 au. According to the topological criteria for DHB given by Popelier [8], in the BCP the  $\rho_{cp}$  and  $\nabla^2\rho_{cp}$  should be within the ranges 0.0020–0.0350 au, and 0.0240–0.1390 au respectively. Both Si–H3...H–C interactions are in these ranges. However, the  $\nabla^2\rho_{cp}$  for C<sub>Me</sub>–H4...H1–C<sub>c</sub> at B3LYP/6-311(d,p) level is near to the minimum limit according to  $\nabla^2\rho_{cp}$  criterion. The bond paths ellipticities ( $\varepsilon$ ) reflect the structural instability for each interaction [14]. In Table 5 it can be seen that at B3LYP/6-311(d,p) level, the C<sub>Me</sub>–H4...H1–C<sub>c</sub> ellipticity is larger than both Si–H3...H–C<sub>c</sub> interactions confirming that the former bond is weaker. The  $\varepsilon$  decreases in all levels from Si–H3...H1–C<sub>c</sub> to Si–H3...H2–C<sub>c</sub>, the last being the strongest according to the  $\varepsilon$  criterion in DHB [8]. In line with these topological parameters from QTAIM, the observed geometry and the atomic charge populations above, the Si–H3...H1–C<sub>c</sub> and Si–H3...H2–C<sub>c</sub> form an asymmetric bifurcated DHB whereas the C<sub>Me</sub>–H4...H1–C<sub>c</sub> would be classified as a weak H–H interaction (only found at B3LYP/6-311(d,p) level). Fig. 3 represents the contour lines for  $\rho$  in the plane of the bifurcated DHB dihydrogen bond formed by H1, H2 and H3 at BP86/TZ2P(+) level.

### 4. Bonding energies in the intramolecular interactions

Dihydrogen bonding has been classified as a medium-strong interaction with binding energies that generally lie between 0.5 and 7 kcal/mol [2b,6b,6q]. High-level ab initio calculations have already been performed on dihydrogen-bonded simple molecules with SiH<sub>4</sub> as a proton-acceptor and HF as a proton-donating molecule shows that H-bond energies for such systems are in the range 0.65–0.89 kcal/mol [6m]. Also, experimental values around 2 kcal/mol for Si–H3...H–O interactions have been found for mixtures of phenol-diethylmethylsilane [15]. In the scheme of the QTAIM theory, the strength of a DHB, as a subgroup of hydrogen bond, can be classified using the criteria of energy density at the BCP ( $H_{cp}$ ) and  $\nabla^2\rho_{cp}$  [6q,16]. The weak-medium strength dihydrogen bond

**Table 5**  
Topological parameters (au) of this H-bonded system at two different levels of theory.

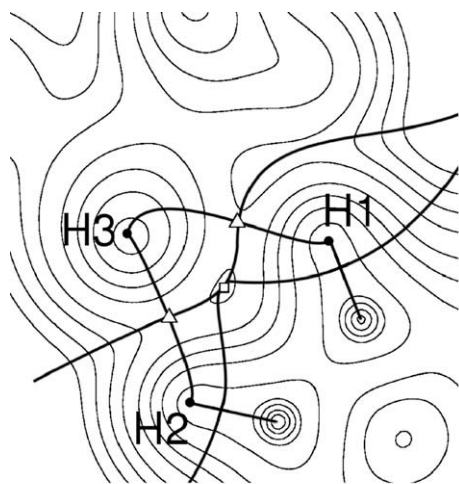
	Short contact	$\Delta_{\text{H}\cdots\text{H}} - \text{VdW}^{\text{a}}$	$\rho_{\text{cp}}^{\text{b}}$	$\nabla^2\rho_{\text{cp}}^{\text{c}}$	$\epsilon^{\text{d}}$
B3LYP/6-311G(d,p)	H3···H1	0.040	0.0088	0.0269	0.534
	H3···H2	-0.233	0.0101	0.0293	0.178
	H4···H1	-0.176	0.0077	0.0242	1.322
BP86/TZ2P(+)	H3···H1	0.013	0.0098	0.0302	0.528
	H3···H2	-0.246	0.0106	0.0316	0.189
	H4···H1	-0.243	-	-	-

<sup>a</sup> Length<sub>H···H</sub>-VdW radii, distance H···H minus sum of Van der Waalls radii (2.4 Å).

<sup>b</sup> Electronic density at BCP.

<sup>c</sup> Laplacian of electronic density at BCP.

<sup>d</sup> Ellipticity.



**Fig. 3.** Superposition of the contour lines (thin) of the electron density, bond paths connecting nuclei (bold) and interatomic zero flux surfaces (bold) for the H1–H2–H3 plane at BP86/TZ2P(+) level of theory. The two BCPs (Δ) and the RCP (□) corresponding to the bifurcated DHB are depicted as projections on the plane.

(closed shell interactions) has bonding energies of  $0.5 < |E_{\text{HB}}| < 7$  kcal/mol, H···H distances in the range 1.70–2.60 Å and both parameters  $H_{\text{cp}}$  and  $\nabla^2\rho_{\text{cp}}$  with positive values. Strong interaction, partially covalent has bonding energy of  $7 < |E_{\text{HB}}| < 20$  kcal/mol, H···H distances in 1.20–1.70 Å, negative  $H_{\text{cp}}$  and positive  $\nabla^2\rho_{\text{cp}}$ , and finally, very strong interaction is a covalent hydrogen bond with  $20 < |E_{\text{HB}}| < 30$  kcal/mol, H···H distances in 1.06–1.20 Å, and both  $H_{\text{cp}}$  and  $\nabla^2\rho_{\text{cp}}$  are negative.

$H_{\text{cp}}$  is defined as the sum of potential energy at BCP ( $V_{\text{cp}}$ ) and kinetic energy at BCP ( $G_{\text{cp}}$ ) [17].  $G_{\text{cp}}$  can be evaluated theoretically with the wavefunction [13], and  $V_{\text{cp}}$  can be obtained with the virial

theorem [7]. In Table 6, the values for  $G_{\text{cp}}$ ,  $V_{\text{cp}}$ , and  $H_{\text{cp}}$  for the BCPs have been calculated at two different levels of theory.  $H_{\text{cp}}$  and  $\nabla^2\rho_{\text{cp}}$  are positive values and the H···H distances are within the range 1.7–2.6 Å that indicate that the H···H interactions reported here can be classified as of weak-medium strength closed shell interactions. The H-bond energy ( $E_{\text{HB}}$ ) has been estimated from the energy parameters of QTAIM according to the empirical relationship of Espinosa et al. [18] Values for  $E_{\text{HB}}$  in the range 1.24 kcal/mol for  $\text{C}_{\text{Me}}-\text{H4}\cdots\text{H1}-\text{C}_{\text{c}}$  at B3LYP/6-311(d,p) level and 1.70 kcal/mol for  $\text{Si}-\text{H3}\cdots\text{H2}-\text{C}_{\text{c}}$  at BP86/TZ2P(+) level have been calculated.

A second procedure to obtain an estimation of the bonding energy of these interactions is by optimizing the anion  $[1-\text{SiMe}_2\text{H}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})(1',2'-\text{C}_2\text{B}_9\text{H}_{11})]^-$  in such a way that the moiety  $-\text{SiMe}_2\text{H}$  is rotated so that it cannot generate the hydrogen interactions in the molecule. However, other effects as the steric hindrance could be present that may distort the energy difference between the two conformations [6b]. Energy difference values of 27.5 at B3LYP/6-311G(d,p) and 30.2 kcal/mol at BP86/TZ2P(+) have been found. This fact indicates a clear overestimation of the H···H interaction energy. They are exceedingly large compared to the sum of the computed H···H bonding energies both at B3LYP/6-311(d,p) level and BP86/TZ2P(+) level (Table 6), that compute 4.35 and 3.30 kcal/mol, respectively.

As there is a large discrepancy between the two previous methods, we have applied a new approach to estimate the bonding energy for each H···H interaction. For this purpose we applied the simple Coulomb's Law (Eq. (1)). The charge on each participating hydrogen atom is known either by NPA or VDD; the distance between the interacting hydrogen atoms is also known, therefore a simple application of Eq. (1) led to the Coulombic energy  $U$  (see Table 6)

$$U = k \frac{q_1 \cdot q_2}{r} \quad (1)$$

**Table 6**  
Topological parameters (au) of this H-bonded system at two different levels of theory.

	Short contact	$G_{\text{cp}}^{\text{a}}$	$V_{\text{cp}}^{\text{b}}$	$H_{\text{cp}}^{\text{c}}$	$E_{\text{HB}}^{\text{d}}$	$U^{\text{e}}$
B3LYP/6-311G(d,p)	H3···H1	0.00572	-0.00471	0.00101	-1.48	-7.08
	H3···H2	0.00625	-0.00518	0.00107	-1.63	-8.42
	H4···H1	0.00498	-0.00392	0.00106	-1.24 <sup>f</sup>	8.92
BP86/TZ2P(+)	H3···H1	0.00631	-0.00506	0.00125	-1.60	-1.52
	H3···H2	0.00665	-0.00540	0.00125	-1.70	-1.60
	H4···H1	-	-	-	-	0.50

<sup>a</sup> Kinetic electron energy density at BCP.

<sup>b</sup> Potential electron energy density at BCP.

<sup>c</sup> Total electron energy density at BCP.

<sup>d</sup> Bonding energy (kcal/mol) according to Espinosa empirical relationship.

<sup>e</sup> Bonding energy (kcal/mol) according to Eq. (1).

<sup>f</sup> The Espinosa equation is not strictly applicable in this case because according to atomic charges the two atoms are not forming a hydrogen bond (DHB).

An inspection of the results indicates that NPA charges do not produce a good matching between  $E_{\text{HB}}$  and  $U$ . However, this is reasonable when  $U$  is evaluated using VDD charges. This procedure to estimate bonding energies in this kind of intramolecular DHB, taken it with caution, could be useful as a fast estimation of the interacting energy due to the inherent difficulty to calculate bonding energies in intramolecular DHB [6b,n].

## 5. Conclusion

$[1,1'-\mu\text{-SiMe}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  was generated in very mild conditions from  $[1\text{-SiMe}_2\text{H-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$  without the aid of any additional reagent. The reaction implies a loss of dihydrogen, that presumes the existence of a DHB in  $[1\text{-SiMe}_2\text{H-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ . These two compounds represent the only examples, at least structurally characterized, of a  $\text{Si-H}\cdots\text{H-C}_c$  to  $\text{Si-C}_c$  conversion. To get more insight into this process the crystal structure of  $[\text{NMe}_4][1\text{-SiMe}_2\text{H-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$  was carefully studied. Three  $\text{H}\cdots\text{H}$  short contacts were observed, two  $\text{Si-H}\cdots\text{H-C}_c$  and one  $\text{SiCH}_2\text{-H}\cdots\text{H-C}_c$  contact. The shortest one corresponds to  $\text{SiCH}_2\text{-H}\cdots\text{H-C}_c$  with the  $\text{H}\cdots\text{H}$  distance equal to 2.059 Å, whereas the two longest correspond to  $\text{Si-H}\cdots\text{H-C}_c$  with 2.212 and 2.409 Å, according to X-ray. From this data it could be deduced that the  $\text{C-H}\cdots\text{H-C}_c$  and one of the  $\text{Si-H}\cdots\text{H-C}_c$  were clear  $\text{H}\cdots\text{H}$  interactions, while the second  $\text{Si-H}\cdots\text{H-C}_c$  would not exist or would be very weak. However, by using QTAIM and Charge Analyses Population on the hydrogen atoms, it has been concluded that the  $\text{C-H}\cdots\text{H-C}_c$  is not a DHB or it is a weak  $\text{H-H}$  interaction. On the contrary, the  $\text{Si-H}\cdots\text{H-C}_c$  with a 2.409 Å distance is a real DHB, as it is the second  $\text{Si-H}\cdots\text{H-C}_c$ . Therefore the two  $\text{Si-H}\cdots\text{H-C}_c$  short contacts can be considered part of an asymmetric bifurcated DHB. The preorganization of  $[1\text{-SiMe}_2\text{H-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$  generated by the  $\text{Si-H}\cdots\text{H-C}_c$  DHB and the geometrical characteristics of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  may be the reason for the singular transformation from  $\text{Si-H}\cdots\text{H-C}_c$  to  $\text{Si-C}_c$  bond.

## 6. Experimental

### 6.1. Computational details

Optimized geometries were performed using Density Functional Methods [19] of the GAUSSIAN 03 [20] sets of codes using the hybrid functional B3LYP [21] with the 6-311G(d,p) basis set for all atoms. Atomic charges and population analysis were computed within the Natural Population Analysis (NPA) [22]. Also, density functional geometries optimizations were carried out using the Amsterdam Density Functional Package [23]. The generalized gradient approximation (GGA nonlocal) method was used, by means of Vosko, Wilk and Nusair's local exchange correlation [24] with nonlocal exchange corrections by Becke [25] and nonlocal correlation corrections by Perdew [26]. The basis set employed in the calculations for C, B and H atoms are all-electron double-zeta Slater type orbital in the core and triple-zeta in the valence shell with two polarization functions (TZ2P according to ADF nomenclature) and TZ2P+ basis set for the cobalt atom. This TZ2P+ basis set are nearly identical to TZ2P except for a better description introducing 4 d-functions instead of 3. We label in this paper the choice of basis set for each atom as TZ2P(+). Atomic charges were computed within Voronoi Deformation Density method (VDD) as implemented in ADF [12]. Topological Bader analyses [7] were performed using Xaim software [27] and AIM2000 [28]. QTAIM calculations were also carried out for the full ionic systems (cation + anion) and no significant difference was encountered analyzing the electronic density.

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