Ab Initio Study of the Coordination Modes of the Tetrahydroborato Ligand: Structure of the $[Cu(BH_4)(PH_3)_n]$ ($n = 1, 2, 3$) Complexes

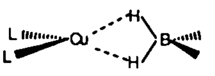
A. Jarid, A. Lledos,* Y. Jean* and F. Volatron*

Abstract: All-electron ab initio calculations (MP4/MP2 level) have been performed on $[Cu(BH_4)(PH_3)_n]$ ($n = 1, 2, 3$) complexes. Full-geometry optimizations were carried out in each case, and the stationary points were characterized by the diagonalization of the analytically calculated Hessian matrix. The η^2 coordination mode, with a tetrahedral arrangement around the copper atom, is the most stable structure for $n = 2$, while for $n = 3$ a strongly nonlinear η^1 coordination mode is preferred. These results are in agreement with the experimental data available on related complexes. For $n = 1$, for which there is no experimental data, the η^3 structure turns out to be the most stable. The energy differences associated with some changes in the coordination mode ($\eta^1 \rightarrow \eta^2$ for $n = 3$ and $\eta^3 \rightarrow \eta^2$ for $n = 1$) are small. Finally, a mechanism for the exchange between terminal and bridging hydrogen atoms is proposed for each complex under study.

Keywords
ab initio calculations · copper compounds · organometallic compounds · tetrahydroborato ligand · theoretical chemistry

Introduction

The tetrahydroborato ligand BH_4^- can bind a transition metal with one (η^1), two (η^2) or three (η^3) bridging hydrogen atoms (H_b).[1–5] In this work, we have been interested in the structure of d^{10} copper(I) complexes $[CuL_n(BH_4)]$, where $n = 1$, 2 and 3. To our knowledge, no experimental data are available for $n = 1$. In the $[CuL_2(BH_4)]$ complexes ($n = 2$), X-ray crystallographic analysis and/or infrared spectral studies on $[Cu(PPh_3)_2(BH_4)]$ (**1a**),[6] $[Cu(dmdp)(BH_4)]$[7] (**1b**, dmdp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), $[Cu(dmp)(BH_4)]$[7,8] (**1c**, dmp = 2,9-dimethyl-1,10-phenanthroline), and $[Cu(PPh_2Me)_2(BH_4)]$ (IR only)[9] show the presence of two bridging hydrogen atoms between the copper and boron atoms and pseudo-tetrahedral coordination around the copper atom (**1**). For $n = 3$ ($[CuL_3(BH_4)]$ complexes),[7, 9–12] two crystal structure analyses of $[Cu(PPh_2Me)_3(BH_4)]$ (**2a**) have been reported, both showing the presence of a single bridging hydrogen atom. However, while the Cu-H1-B arrangement is found to be almost linear in one structure ($\theta = 170°$),[9] it is strongly bent in the other ($\theta = 126(6)°$),[11] a result confirmed by a neutron diffraction study ($\theta = 121.7(4)°$).[11] Although the η^1 coordination deviates strongly from linearity, the distance between Cu and H2 in **2a** is definitely not within the bonding range of the copper atom: Cu···H2 = 272.2(7) pm, whereas Cu···H1 = 169.7(5) pm (neutron diffraction).[11] In addition, the Cu···B distance (251.8(3) pm, neutron diffraction)[11] is much longer than in the η^2 complexes **1** (between 208 and 218 pm); this trend is consistent with a change in the coordination mode of the tetrahydroborato ligand ($\eta^2 \rightarrow \eta^1$) on going from the $[CuL_2(BH_4)]$ to the $[CuL_3(BH_4)]$ complexes. In the crystal structure of $[Cu(triphos)(BH_4)]$[12] (**2b**, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) a strongly nonlinear η^1 binding is observed with Cu···B = 244(2) pm, Cu-H1-B = 121(3)°, Cu···H1 = 160(4) pm and Cu···H2 = 268(6) pm. However, X-ray and neutron diffraction studies on $[Cu(phen)(PPh_3)(BH_4)]$[7] (**2c**, phen = 1,10-phenanthroline) led to rather puzzling results. The Cu···B distance is only 229(2) pm (neutron), a value intermediate between those for η^2 coordinated complexes **1** and those for η^1 coordinations in **2a** and **2b**. Furthermore, while the H1 atom is still strongly bound to copper (Cu···H1 = 163(7) pm), the H2 hydrogen atom is now rather close to the metal (Cu···H2 = 203(9) pm vs. 272.2(7) and 268(6) pm in **2a** and **2b**, respectively). It is thus not very clear if there are one or two bridging hydrogen atoms in **2c** and, in many respects, the structure of this complex, obtained by neutron diffraction studies, may be viewed as a distorted η^2 rather than as an η^1 structure.



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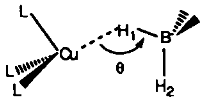
(a): L = PPh_3 (ref. [6])
(b): L_2 = dmdp (ref. [7])
(c): L_2 = dmp (ref. [8])



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(a): L = PPh_2Me (ref. [9, 11])
(b): L_3 = triphos (ref. [12])
(c): L_3 = (phen)(PPh_3) (ref. [7])

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In this paper we report the first high-level (MP4/MP2) ab initio calculations on the complexes $[Cu(PH_3)_2(BH_4)]$ and $[Cu(PH_3)_3(BH_4)]$, used as models for the experimental complexes **1** and **2**, respectively, and on the hypothetical $[Cu(PH_3)(BH_4)]$ complex. Mechanisms for the exchange between bridging (H_b) and nonbridging (H_t) hydrogen atoms are also proposed for the various complexes.

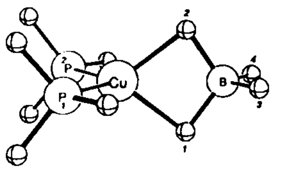
Method of Calculation

Ab initio calculations were performed with the GAUSSIAN 92 system of programs [13]. For the Cu atom, d functions with an exponent of 0.1682 were added to a valence double-dzeta basis set [14] in order to obtain a triple-dzeta description of the d orbitals. The valence shell was considered to include 3d, 4s and 4p orbitals, that is, the basis set for the metal is 33321/3321/211. For all the atoms of the BH_4^- group, the 6-31 G** basis set [15] was used. In the phosphine ligands, the 6-31 G* basis set [16] was chosen for the phosphorus atom and the 3-21 G basis set [17] for the hydrogen atoms.

For each type of $[Cu(PH_3)_n(BH_4)]$ complexes, all the geometrical parameters were optimized at the SCF level. The nature of the extrema reached is characterized by the diagonalization of the analytically calculated Hessian matrix. Finally, these extrema were fully reoptimized at the MP2 level (MP2/MP2 calculations), and their energies further corrected by using the MP4 (SDTQ) algorithm (MP4/MP2 calculations). The reliability of the perturbative treatment of correlation energy (MP2 or MP4) has been tested by CISD computation in the case of $[Cu(PH_3)_2(BH_4)]$ complex.

Results and Discussion

$[Cu(PH_3)_2(BH_4)]$ complex: Full geometry optimizations (C_1 group) led to one minimum and one transition state. In agreement with the experimental data, the minimum **3** is the η^2 structure with a tetrahedral geometry around the copper atom. The transition-state structure **4** may be described either as a distorted η^3 complex, with one bridging hydrogen atom closer to the metal than the other two (Cu–H 1 = 184.8 pm, Cu–H 2 = Cu–H 3 = 222.7 pm), or as a strongly nonlinear η^1 complex with H 1 as the bridging hydrogen atom (Cu-H 1-B = 86.1°). The relative energies of these two extrema at the MP2/MP2 and MP4/MP2 levels are given in Table 1. The energy difference E_{rel} increases as the level of calculation is improved, from 3.3 (SCF) to 11.7 kcal mol^{-1} (MP4/MP2). Although the right order of energies for the structures **3** (η^2) and **4** (pseudo-η^1 or pseudo-η^3) is given by the simple SCF optimization, it appears that the correlation energy strongly affects the energy gap between these two structures.



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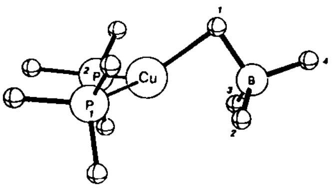

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Table 1. Energy of the η^2 minimum **3** of $[Cu(PH_3)_2(BH_4)]$ (E(3)/hartree) and of the transition-state structure **4** relative to E(3) (E_{rel}(4)/kcal mol^{-1}).

	SCF	MP2/SCF	MP2/MP2	MP4/MP2
E(3)	−2342.87955	−2343.53209	−2343.54441	−2343.66190
E_{rel}(4)	3.3	6.6	7.4	11.7

The main geometrical parameters associated with structures **3** and **4** are reported in Table 2, for both SCF and MP2 optimizations. The corresponding experimental values from the crystal structure of $[Cu(PPh_3)_2(BH_4)]$ are also given.

Table 2. Main geometrical parameters (distances/pm, angles/°) associated with the η^2 minimum-energy (**3**) and transition-state (**4**) structures (SCF and MP2 optimizations), and the corresponding experimental values from the η^2 crystal structure of $[Cu(PPh_3)_2(BH_4)]$ (ref. [6]).

	η^2 minimum (3)			TS (4)	
	SCF	MP2	Exp.	SCF	MP2
Cu–B	224.4	213.2	218.4(9)	217.7	210.6
Cu–P 1	250.3	227.2	227.6(1)	253.8	229.8
Cu–P 2	250.3	226.6	227.6(1)	253.8	229.8
Cu–H 1	183.4	172.9	182(3) [a]	184.8	172.0
Cu–H 2	183.4	172.9	182(3) [a]	222.7	220.9
Cu–H 3	305.9	294.1		222.7	220.9
Cu–H 4	306.5	295.1		334.9	324.9
B–H 1	128.0	128.3	107(3)	128.2	129.0
B–H 2	128.0	128.3	107(3)	123.9	122.4
B–H 3	120.6	119.8	109(5)	123.9	122.4
B–H 4	120.6	119.8	109(5)	119.9	119.2
P 1-Cu-P 2	123.1	126.1	123.3(1)	120.0	122.5

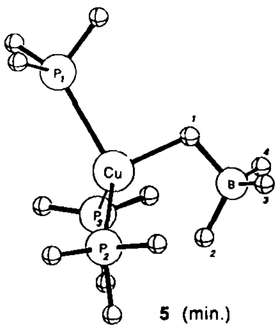
[a] Refined values: see ref. [22].

Let us first consider the minimum-energy structure **3**. The most important difference between SCF and MP2 optimizations concerns the Cu–P bond lengths: they are overestimated by about 25 pm at the SCF level, but are nearly equal to experimental values at the MP2 level (227.2 and 226.6 pm vs. 227.6 pm[6]). In addition, the MP2 optimization shortens the Cu ⋯ B distance from 224.4 (SCF) to 213.2 pm. The latter value is in better agreement with the experimental bond lengths found in substituted phenanthroline complexes (208(2)[8] and 212(1) pm[7]). For the transition state **4** (Table 2), MP2 optimization also shortens the Cu–P bond lengths and, to a lesser extent, the Cu ⋯ B distance (210.6 pm). This value is slightly shorter than that found in the η^2 minimum (213.2 pm). It is thus better to view this transition-state structure as a distorted η^3 rather than a nonlinear η^1 structure, in which the Cu ⋯ B distance would have been significantly longer.

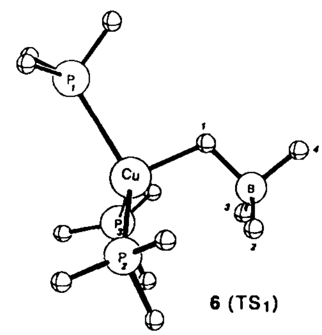
Mechanism for the hydrogen exchange: The transition state **4** located on the potential energy surface allows the exchange of a bridging and a terminal hydrogen atom in the minimum-energy structure **3**. The reaction coordinate associated with this mechanism is essentially the rotation around one of the B–H_b bonds in the minimum (Scheme 1). At our higher level of calculation, the activation energy for this exchange process is 11.7 kcal mol^{-1} (Table 1).

Scheme 1. Mechanism of exchange of a bridging and a terminal hydrogen atom in **3**.

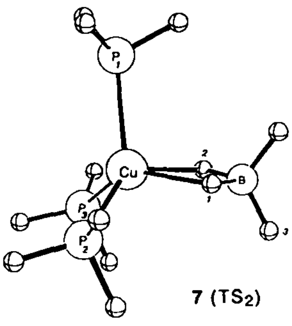
$[Cu(PH_3)_3(BH_4)]$ complex: For this complex, one minimum (**5**) and two transition states (**6** and **7**) were found. The minimum can be described either as a strongly nonlinear η^1 structure, with Cu-H 1-B = 98° and Cu ⋯ B = 237.8 pm, or as a distorted η^2 structure with one bridging hydrogen atom closer to the metal than the other (Cu ⋯ H 1 = 183.7 pm, Cu ⋯ H 2 = 208.1 pm).



5 (min.)



6 (TS1)



7 (TS2)

This structure is in good agreement with the experimental data (neutron diffraction) on the [Cu(phen)(PPh$_3$)(BH$_4$)] complex[7] (Cu···B = 229(2), Cu···H1 = 163(7) and Cu···H2 = 203(9) pm, and Cu-H1-B = 85(2)°). It is, however, at variance with the structure (neutron diffraction) of the [Cu(PMePh$_2$)$_3$-(BH$_4$)] complex,[11] in which the H2 hydrogen atom remains out of the bonding range of the copper atom (Cu···H2 = 272.2(7) pm). Therefore, the approach of the H2 atom towards the metal seems to vary from one complex to the other—the energy difference between a strongly nonlinear η^1 coordination and η^2 coordination is, as we will see later (Table 3), very small.

The transition state **6** (TS1) can be described as a nonlinear η^1 structure with Cu···B = 244.1, Cu–H1 = 176.7 and Cu–H2,3 = 264.4 pm. The main geometrical differences between **5** and **6** are a rotation around the B–H1 bond and a displacement of the H2,3 hydrogen atoms in the latter away from the copper, compared to the position of H2 in the former. The second transition state **7** (TS2) is characterized by a symmetrical η^2 coordination of the tetrahydroborato ligand.

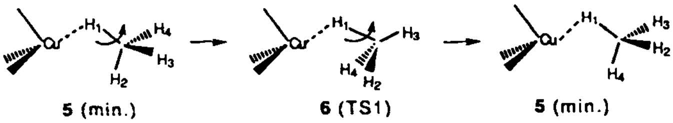
In Table 3 the relative energies of the three stationary structures (**5**–**7**) at the various levels of calculation are given. The energies of structures **5** and **6** become closer and closer, the computed energy gap even vanishing at the MP4/MP2 level.

Table 3. Energy of the minimum **5** of [Cu(PH$_3$)$_3$(BH$_4$)] (E(**5**)/hartree) and of the transition-state structures TS1 (**6**) and TS2 (**7**) relative to E(**5**) (E_{rel}(**6**) and E_{rel}(**7**)/kcal mol^{-1}).

	SCF	MP2/SCF	MP2/MP2	MP4/MP2
E(**5**)	−2685.32383	−2686.08100	−2686.09885	−2686.24459
E_{rel}(**6**)	1.6	1.2	0.8	0.0
E_{rel}(**7**)	0.2	0.7	1.4	3.0

The main geometrical parameters associated with structures **5**–**7** are reported in Table 4 for both SCF and MP2 optimizations. Experimental data for the two complexes, obtained by neutron diffraction studies ([Cu(phen)(PPh$_3$)(BH$_4$)][7] and [Cu(PPh$_2$Me)$_3$(BH$_4$)][11]), are also given. In the minimum-energy structure (**5**), the largest geometrical change between SCF and MP2 optimizations is again the shortening of the Cu–P bond lengths. Compared to the experimental values, they are overestimated by 30–40 pm at the SCF level, while the agreement is excellent at the MP2 level. The Cu···H2 distance (228.6 pm) is found to be intermediate between those found experimentally (272.2[7] and 203(9) pm[11]). Here again there are two ways of describing this structure: either as a strongly nonlinear η^1 complex with H2 out of the bonding range of Cu, or as a η^2 distorted structure with H1 and H2 as the bridging hydrogen atoms. The computed Cu···B distance (238.1 pm) also reflects this ambiguity, since it is intermediate between the experimental values (251.8(3) pm for the η^1 complex;[11] 229(2) pm for the pseudo-η^2 complex[7]). Finally, the surprisingly long (133.0(6) pm) and as yet unexplained B–H4 bond length in the [Cu(PMePh$_2$)$_3$(BH$_4$)] complex[11] is not reproduced by our calculations.

The transition-state structure **6** can be described as a nonlinear η^1 complex, with a single bridging hydrogen atom (Cu–H1 = 165.1 pm vs. 276.2 pm for Cu–H2,3). The energy difference with the minimum **5** is very small and even vanishes at the MP4/MP2 level (Table 3). This transition-state structure allows an exchange between nearly bridging H2 and unbridged H4 through the mechanism depicted in Scheme 2. The reaction coordinate associated with this process is mainly the rotation



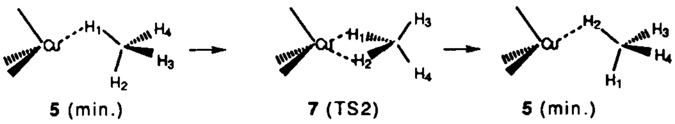
Scheme 2. Mechanism of exchange between nearly bridging H2 and unbridged H4 in **5**.

Table 4. Main geometrical parameters (distances/pm, angles/°) associated with the minimum-energy (**5**) and transition-state structures (**6** and **7**) of [Cu(PH$_3$)$_3$(BH$_4$)] at both SCF and MP2 optimization levels, and experimental values for [CuL$_3$(BH$_4$)] (L$_3$ = (phen)(PPh$_3$) [7] and (PPh$_2$Me)$_3$ [11]), obtained by neutron diffraction studies.

	minimum (**5**)				TS1 (**6**)		TS2 (**7**)	
	SCF	MP2	Exp. [11]	Exp. [7]	SCF	MP2	SCF	MP2
Cu–B	237.8	238.1	251.8(3)	229(2)	244.1	244.7	236.6	230.8
Cu–P1	268.1	232.5	228.2(2)	226(2)	262.5	229.8	256.9	229.3
Cu–P2,3	259.2	231.0	226.0(2)	–	258.0	230.6	266.0	235.8
B–H1	127.5	128.3	117.0(5)	117(3)	128.9	129.2	126.4	124.9
B–H2	125.3	122.6	118.5(5)	124(3)	122.6	121.2	126.4	124.9
B–H3	121.1	120.5	118.2(6)	118(4)	122.6	121.2	121.1	120.5
B–H4	121.1	120.5	133.0(6)	121(4)	120.8	120.5	120.9	120.3
Cu–H1	183.7	168.2	169.7(5)	163(7)	176.7	165.1	194.8	190.6
Cu–H2	208.1	228.6	272.2(7)	203(9)	264.4	276.2	194.8	190.6
Cu–H3	319.2	316.3	–	–	264.4	276.2	316.7	310.5
Cu–H4	319.2	316.3	–	–	351.8	341.4	319.9	313.0
Cu-H1-B	98.0	106.1	121.7(4)	85(2)	104.9	111.9	92.4	91.6

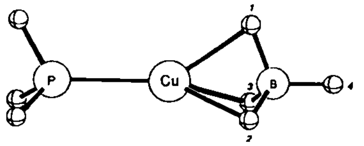
around the B–H1 bond. The almost zero activation energy associated with this process simply means that there is free rotation of the tetrahydroborato ligand around the B–H1 bond in the $[Cu(PH_3)_3(BH_4)]$ complex.

Mechanism for the hydrogen exchange: The transition-state structure **7** is a symmetrical η^2 complex with Cu–H1,2 = 190.6 pm. It allows the exchange between the strongly and the weakly bridged hydrogen atoms (H1 and H2, respectively) in the minimum-energy structure **5**. Here, the reaction coordinate can be mainly described as the rotation around the Cu ··· B axis (Scheme 3). As in the preceeding process, a very low energy barrier is predicted for this mechanism (3.0 kcal mol^{-1} at the MP4/MP2 level, Table 3).



Scheme 3. Mechanism of exchange between the strongly and the weakly bridged hydrogen atoms (H1 and H2, respectively) in **5**.

$[Cu(PH_3)(BH_4)]$ complex: Since this complex is rather small, optimization and *characterization* were performed at both SCF and MP2 levels. In each case, two minima are found on the MP2 potential energy surface (η^3 (**8**) and η^2 (**9**)).



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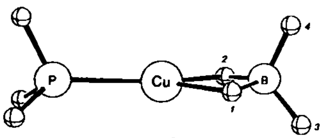

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It is noteworthy that the η^3 structure becomes the most stable at the higher level of calculation (Table 5), although the energy gap with η^2 remains small. The main geometrical parameters of these two structures are reported in Table 6 (MP2 optimization level).

Table 5. Energy of the η^2 structure **9** of $[Cu(PH_3)(BH_4)]$ (E(**9**)/hartree) and of the η^3 structure **8** relative to E(**9**) (E_{rel}(**8**)/kcal mol^{-1}).

	SCF	MP2/SCF	MP2/MP2	MP4/MP2
E(**9**)	−2000.42473	−2000.96731	−2000.97365	−2001.05486
E_{rel}(**8**)	0.2	0.4	−1.2	−2.5

Table 6. Main geometrical parameters (distances/pm, angles/°) associated with the η^2 (**9**) and η^3 (**8**) structures of $[Cu(PH_3)(BH_4)]$ at both SCF and MP2 levels of optimization.

	η^2 (**9**)		η^3 (**8**)	
	SCF	MP2	SCF	MP2
Cu–B	216.4	206.0	203.8	192.4
Cu–P	237.4	219.3	236.1	217.4
Cu–H1	177.4	169.4	197.1	185.5
Cu–H2	177.4	169.4	197.1	184.8
Cu–H3	297.7	293.4	197.1	184.8
Cu–H4	297.7	279.8	323.0	310.5
B–H1	128.6	128.3	125.7	125.5
B–H2	128.6	128.3	125.7	125.6
B–H3	120.2	119.3	125.7	125.6
B–H4	120.2	119.6	119.1	118.1
B-Cu-P	180	177.4	180	179.9

Mechanism for the hydrogen exchange: Two minima (η^2 (**9**) and η^3 (**8**)) have been characterized on the MP2 potential energy surface, but, surprisingly, no transition state connecting these structures was found. In order to clarify this point, a reaction path between structures **9** and **8** was computed in the following way: for each value of θ (Scheme 4), which varies from 116° in **9** to 68.9° in **8**, all the other geometrical parameters were optimized at the MP2 level. The computed energy curve is given in Figure 1.

Scheme 4.

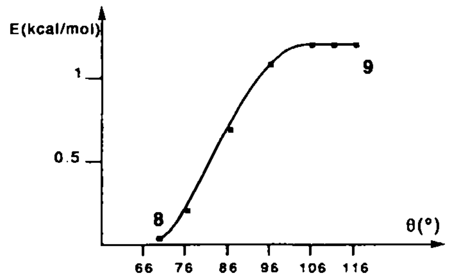
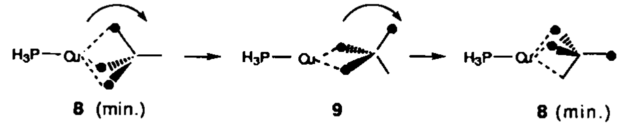


Fig. 1. Energy profile (MP2 level) associated with the change from η^3 to η^2 coordination mode in the $[Cu(PH_3)(BH_4)]$ complex according to the mechanism depicted in Scheme 5.

For a rather large variation of θ (from 116 to 106°), there is no change in the energy up to the fifth decimal place (hartree). Therefore, while the η^2 structure has been numerically identified as a minimum, the potential energy surface is actually flat around it, and the only true minimum seems to be the η^3 structure. This result is to be related to the value of almost zero found for the lowest frequency in the η^2 structure (13 cm^{-1}). Now we can propose a mechanism for the exchange of bridging and nonbridging hydrogen atoms in the η^3 structure **8** via the η^2 structure **9** (Scheme 5). The activation energy for this exchange mechanism is very low, 2.5 kcal mol^{-1} at the highest level of calculation (MP4/MP2, Table 5).



Scheme 5. Mechanism of exchange of bridging and nonbridging hydrogen atoms in the η^3 structure **8**.

Conclusion

Our calculations on $[(PH_3)_nCu(BH_4)]$ complexes (n = 1, 2 and 3) show that the coordination mode of the tetrahydroborato ligand depends upon the number of phosphine ligands bound to the metal atom. It changes from η^1 (strongly nonlinear) to η^2 and η^3 for n = 3, 2 and 1, respectively. However, the energy differences associated with some changes in the coordination mode ($\eta^1 \rightarrow \eta^2$ for n = 3 and $\eta^3 \rightarrow \eta^2$ for n = 1) are small.[18] A last point concerns the method of calculation: MP2 geometry optimizations give more reliable results and are therefore required for such complexes.

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[18] In a first version of this article, the three coordination modes of the BH_4^- ligand were studied in each copper complex and discussed with respect to the 18-electron rule. In particular, the reasons why very small energy differences were sometimes found between structures with formally 18 and 16 or 20 electrons were analyzed through qualitative FMO analysis. Following the strong recommendation of a referee, we have had to restrict ourselves to the presentation and the discussion of the energy minima and the mechanisms of hydrogen exchange. All the interpretative part of this work will be published elsewhere.