Journal of Organometallic Chemistry, 452 (1993) 277–286

JOM 23334

Nature of the hydrogen bridge in transition metal complexes

VI *. A comparison of the electronic structure of Cu–H–B and Cu–H–Cu bridges

Barbara Nissen-Sobocińska and Bogusława Jeżowska-Trzebiatowska †

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 937, PL-50 950 Wrocław (Poland)

(Received October 13, 1992)

Abstract

The electronic structure of a series of homoleptic H-bridged copper–boron complexes ($Cu–H_n–BH_{4-n}$, $n = 1$, 2, and 3) and their phosphine substituted analogues ($(PH_3)_{4-n}Cu–H_n–BH_{4-n}$, $n = 1$, 2, and 3) has been investigated with the Fenske-Hall method. For the sake of comparison parallel calculations have been carried out for H-bridged copper binuclear complexes ($[(PH_3)_{4-n}Cu–H_n–Cu(PH_3)_{4-n}]^k$, $n = 1, 2, 3$, and $k = +1$ for $n = 1$, $k = 0$ for $n = 2$, and $k = -1$ for $n = 3$). The results of the Fenske-Hall method are verified by similar calculations with the aid of the non-iterative Extended Hückel theory (EHT).

The main conclusions of the present study follow from the analysis of the electronic charge distribution in those molecules. This analysis reveals that the H-bridges in copper–boron compounds differ considerably from those in copper binuclear complexes. The former are due to non-covalent electrostatic interactions between the copper atom (coordinated copper atom) and the negative-charged BH_4 group. The covalency of the Cu–H bond turns out to be negligibly small while in copper binuclear complexes the Cu–H bond resembles the usual, strongly polarized covalent bonds. The new interpretation of the electronic structure of the copper–boron H-bridge is different from that usually accepted for those systems and facilitates the understanding of the flexibility of the H-bridged copper–boron complexes with respect to intramolecular isomerization processes.

1. Introduction

The bonding of the hydrogen atom in polynuclear transition metal compounds has received a great deal of attention in both experimental and theoretical studies [1,2]. In addition to the relatively commonly observed terminal position of the hydrogen atom [3] a variety of the so-called hydride bridge (the hydrogen atom(s) located between transition metal atoms) has been established [4]. The bridge bonds $M_1–H–M_2$, which involve two metal atoms (M_1,M_2), have been interpreted as two-electron, three-centre bonds [5]. In several ways they resemble the B–H–B bonds in boron hydrides [6].

The electronic structure of hydrogen bridges in homonuclear (M_1=M_2) transition metal complexes has been extensively studied in our earlier papers [7]. The dominant covalent character that these bridges exhibit in the majority of investigated systems has been established; the covalent character has been interpreted in terms of the presence of molecular orbitals localized primarily in the M–H–M region. Moreover, the Mulliken population analysis shows that each of the two M–H bonds has a rather large (0.1–0.2) two-centre overlap population [7a]. The ionic contribution to M–H regions of the bridge has been found to depend considerably on the metal atom while being almost independent of the terminal ligands [7b–d]. Another characteristic feature of the M–H–M bond is a high negative charge carried by the bridging hydrogen atom [7]. This causes the hydride bridges in transition metal complexes to differ from their homonuclear boron counterparts and supports the term "the hydride bridge".

The above similarities and differences between M–H–M and B–H–B bridges suggest that a study of heteronuclear systems with M–H–B bonds should be

---

Correspondence to: Dr. Nissen-Sobocińska.

* For Part V, see ref. 7e.

† Deceased December 18, 1991.

0022-328X/93/$6.00

of interest. In this paper we report on our calculations for hydride bridged systems with Cu–H–B bonds. The geometry and electronic structure of such bonds has been given considerable attention in earlier papers [8]. Both homoleptic [8b,9] and copper-coordinated [10] systems with $Cu–H_n–BH_{4-n}$, $n = 1, 2, 3$, are known experimentally. A covalent character is commonly assumed for these bridges [4,8,10–12] in the interpretation of the electronic structure of the metal–boron hydrides. However, the differences between transition metal and boron atoms suggest that the M–H–B bonds may possess a significant degree of ionic character. The investigation of this problem is the major objective of the present study.

In order to explore the electronic structure of Cu–H–B bridges we have carried out a series of approximate MO calculations on different $Cu–H_n–BH_{4-n}$ and $(PH_3)_{4-n}Cu–H_n–BH_{4-n}$ systems whose geometry is schematically shown in Fig. 1. The calculated wave functions are analyzed and discussed in terms of the covalent *vs.* ionic character of the bridge by using the Mulliken population analysis. For the sake of comparison we have also carried out analogous calculations for homonuclear $[(PH_3)_{4-n}Cu–H_n–Cu(PH_3)_{4-n}]^k$ bridged complexes (see Fig. 1), with the complex charge k (0, ± 1) which is chosen in such a way that the Cu atoms have the formal oxidation of +1 for each value of $n = 1, 2, 3$. The relevant computational details and the wave function analysis together with a discussion of certain aspects of the isomerization processes, which change the number of bridging hydrogens are presented in the next two sections.

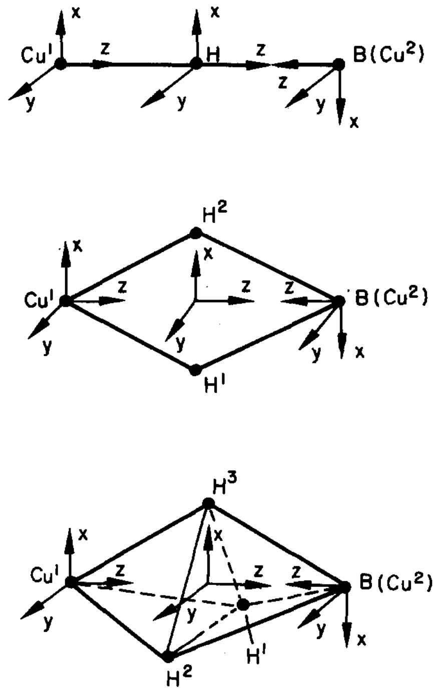


Fig. 1. Schematic representation of the hydrogen and hydride bridges and the orientation of local coordinate systems associated with the bridge atoms.

The commonly accepted interpretation [4,8,10–12] of the character of M–H–B bonds being predominantly covalent is not confirmed by our calculations on copper–boron compounds. The bonding contributions to the $Cu–H_b$ region of the $Cu–H_n–B$ bridge by some molecular orbitals are nearly cancelled by the antibonding contributions of other orbitals. The net effect can be viewed as the BH_4^- group interacting electrostatically with the positively charged Cu atom ($Cu(PH_3)_{4-n}$ group). In contrast to previously studied hydride bridges [7] the Cu–H–B bonds have only a slight degree of three-centre covalent character.

2. Computational details

The major part of the calculations has been performed with the approximate SCF method of Fenske and Hall [13]. Its main advantage over a variety of semiempirical approaches [14] amounts to the non-empirical evaluation of the required matrix elements of the one-electron operator. The valence atomic basis sets for H, B, P, and Cu comprise (1s), (2s 2p), (3s 3p 3d), and (3d 4s 4p) orbitals, respectively. All atomic basis sets are the same as those employed in our earlier calculations [7]. Obviously, the reliability of the Fenske-Hall method in single molecule calculations is uncertain if not questionable. However, the results obtained for a series of similar molecules are expected to reveal the major common features of the electronic structure and its variation within that series being thus much less method-dependent.

The relative simplicity of Fenske-Hall calculations makes this method a convenient and useful tool for investigations of qualitative chemical aspects of the electronic structure of transition metal complexes. This method has been successfully used in our earlier studies of hydride bridges [7].

In order to make our conclusions method-independent as far as possible we have carried out parallel calculations by using the non-iterative Extended Huckel method (EHT) [15]. As shown in the next section the EHT results, though quantitatively different from those of the Fenske-Hall method, lead to the same global picture of the electronic structure of molecules investigated in this study.

Fenske-Hall and EHT calculations are usually carried out on experimentally deduced molecular geometry. For none of the molecules studied in this paper are the corresponding geometric data directly available

TABLE 1. Geometric data assumed in calculations for copper–boron binuclear complexes

Molecule	Symmetry	P–Cu–P angle (deg.)	Bond distances (Å)
$Cu–H_b–B(H_t)_3$ [a]	C_{3v}		$Cu–B = 2.867$ $Cu–H_b = 1.697$ $B–H_b = 1.17$ $B–H_t = 1.07$
$(PH_3)_3Cu–H_b–B(H_t)_3$ [a,b]		115	$Cu–B = 2.867$ $Cu–H_b = 1.697$ $B–H_b = 1.17$ $B–H_t = 1.07$ $Cu–P = 2.287$
$[(PH_3)_3Cu–H_b–Cu(PH_3)_3]^{+1}$		115	$Cu–Cu = 3.394$ $Cu–H_b = 1.697$ $Cu–P = 2.286$
$Cu–(H_b)_2–B(H_t)_2$ [c]	C_{2v}		$Cu–B = 2.185$ Å $Cu–H_b = 1.82$ $B–H_b = 1.07$ $B–H_t = 1.07$
$(PH_3)_2$ $Cu–(H_b)_2–B(H_t)_2$ [b,c]		122	$Cu–B = 2.185$ $Cu–H_b = 1.82$ $B–H_b = 1.07$ $B–H_t = 1.07$ $Cu–P = 2.286$
$(PH_3)_2Cu–(H_b)_2–Cu(PH_3)_2$ [b,c]		122	$Cu–Cu = 3.168$ $Cu–H_b = 1.82$ $Cu–P = 2.286$
$Cu–(H_b)_3–BH_t$	C_{3v}		$Cu–B = 2.185$ $Cu–H_b = 1.91$ $B–H_b = 1.22$ $B–H_t = 1.07$
$(PH_3)Cu–(H_b)_3–BH_t$ [b]			$Cu–B = 2.185$ $Cu–H_b = 1.91$ $B–H_b = 1.22$ $B–H_t = 1.07$
$[(PH_3)Cu–(H_b)_3–Cu(PH_3)]^{-1}$			$Cu–Cu = 3.168$ $Cu–H_b = 1.91$ $Cu–P = 2.286$

[a] All angles in the $B(H_t)_{4-n}$ (n is the number of hydrogen atoms involved in the bridge) are assumed to be 109° 27′; [b] the phosphine group has the same geometry in all molecules: $P–H = 1.42$ Å, $HPH = 93°$; [c] the planes of H_bBH_b and PCuP are mutually perpendicular.

and they have been deduced from the experimental values [10] for similar molecules which differ from the present ones mostly by bulky substituents at phosphorus. It should be mentioned that according to these experimental data [10] the assumed set of geometric parameters in the bridge region depends on the number of bridging hydrogen atoms.

The structure of the investigated H-bridges and the choice of the local coordinate systems are given in Fig. 1. The geometric data employed in present calculations are summarized in Table 1. Some uncertainties with respect to assumed geometries are not expected to be highly important for qualitative investigations for a series of related molecules. Moreover, the results of Fenske-Hall, EHT, and similar approximate methods do not significantly depend on the choice of the geometric data.

Our calculations have been performed for homoleptic $Cu–H_n–BH_{4-n}$ and copper-coordinated $(PH_3)_{4-n}$-$Cu–H_n–BH_{4-n}$ molecules with different number of the bridging hydrogens. A fixed molecular geometry has usually been assumed (Table 1). However, in order to gain some insight into the isomerization processes:

$$Cu–H_n–BH_{4-n} \longleftrightarrow Cu–H_{n+1}–BH_{3-n}$$

and

$$(PH_3)_{4-n}Cu–H_n–BH_{4-n} \longleftrightarrow (PH_3)_{3-n}Cu–H_{n+1}–BH_{3-n},$$

a limited variation of the hydrogen bridge geometry has been studied.

Most of the results are analysed in terms of the Mulliken population analysis by comparing the calculated atomic (atomic group) charges and two-centre overlap populations. In Fenske-Hall calculations the MO energy data may depend markedly on the choice of basis functions [13]. Thus, their absolute values are not given particular attention. The same applies to the results of EHT calculations. In both cases it is the sequence and bonding-antibonding character of MOs which is used to interpret the electronic structure of molecules.

3. Results

In the framework of approximate calculations of the electronic structure of molecules most significance is usually attached to the wave function analysis. This can be accomplished in terms of global considerations, *e.g.*, by using different schemes for the partition of the total density distribution. Among such techniques the

TABLE 2. Mulliken Population Analysis data for compounds CuH_nBH_{4-n} and $(PH_3)_{4-n}CuH_nBH_{4-n}$ ($n = 1, 2, 3$). Results of calculations with the Fenske-Hall method

	CuH_nBH_{4-n}			$(PH_3)_{4-n}CuH_nBH_{4-n}$		
n [a]	1	2	3	1	2	3
Atomic group charges						
[b] CuL_{4-n}	0.837	0.932	0.963	0.945	0.968	0.965
BH_{4-n}	−0.837	−0.932	−0.963	−0.945	−0.968	−0.965
[c] H_b	−0.037	0.027	−0.078	−0.014	0.015	−0.077
[d] H_t	0.055	0.099	0.058	0.063	0.084	0.043
Two-centre overlap populations						
Cu–H_b	0.065	0.002	−0.004	0.010	−0.009	−0.004
B–H_b	0.367	0.432	0.409	0.420	0.449	0.411
B–H_t	0.438	0.430	0.429	0.439	0.434	0.431
Cu–L	–	–	–	0.322	0.165	0.314
Cu–B	0.022	−0.007	−0.004	0.010	−0.009	−0.004

[a] n is the number of hydrogen atoms involved in the bridge; [b] L denotes a ligand group of the copper atom. No ligand at Cu is present in homoleptic complexes; [c] H_b is the hydrogen atom of the bridge bond; [d] H_t is the terminal hydrogen of the BH_4 group.

Mulliken population analysis is frequently used and will be employed here to investigate the electronic structure of hydride bridges. Another possibility is given by a direct analysis of the form of particular molecular orbitals. This reveals additional features associated with a pair of atomic orbitals contributing to the given MO. In this way one can identify the bonding, non-bonding, and antibonding character of the MO in a specified region.

The present analysis of the calculated MO levels is virtually limited to the two above aspects. Only marginal attention is paid to the orbital energies, for they are known [14] to depend strongly on the details of the approximate method which is used for their calculation. The orbital energies will be used mostly to obtain compatible sequences of MO energy levels. This feature is further exploited below to discuss the possibility of internal conversion which changes the number of bridging hydrogens. The total energy obtained from methods used in this paper does not seem to provide accurate enough measures of such processes. Therefore, only a qualitative interpretation of the mutual transformation between nH– and $(n+1)$H– bridges has been attempted and the corresponding data are analyzed mainly in terms of the energy and form of the pertinent molecular orbitals.

3.1. Population analysis

The electronic charge distribution in homoleptic systems and their phosphine substituted analogues is analyzed in terms of the net charge attributed to the $Cu(Cu(PH_3)_{4-n})$ atom(group), the hydrogen atom in the bridge, and the BH_4 group. The corresponding data are presented in Table 2. They reveal a strongly ionic character for all systems studied in this paper.

In all systems the BH_4 group (including the H atoms of the bridge) carries the total negative net charge of about minus one. The Cu atom or the $Cu(PH_3)_{4-n}$ group carry an equivalent positive charge. One of the remarkable features is that in all M–H_n–B bridges the bridging hydrogen atoms are almost neutral. This is to be compared with the similar data for Cu–H_n–Cu bridges collected in Table 3.

For all systems presented in Table 3 the bridging hydrogen atoms carry relatively large net negative charges. This is the first indication that the Cu–H_n–B bridges may have a different electronic structure as compared to that of the hydride bridges in binuclear transition metal complexes. Further support to such a conclusion is given by the two-centre overlap population data of Tables 2 and 3.

The Cu–H_b overlap population in Cu–H_n–B bridges is close to zero, indicating the lack of a covalent bond between copper and hydrogen atoms of the bridge. On

TABLE 3. Mulliken Population Analysis data for compounds $[(PH_3)_{4-n}\text{-}CuH_nCu(PH_3)_{4-n}]^k$ ($n = 1, 2, 3$ and $k = +1, 0, -1$ respectively). Results of calculations with the Fenske-Hall method

n [a]	1	2	3
Atomic group charges			
[b] CuL_{4-n}	0.659	0.393	0.178
[c] H_b	−0.326	−0.394	−0.445
Two-centre overlap populations			
Cu–H_b	0.162	0.115	0.095
Cu–L	0.307	0.176	0.330
Cu–Cu	−0.002	−0.008	−0.002

[a] n is the number of hydrogen atoms involved in the bridge; [b] L denotes a ligand group of the copper atom; [c] H_b is the hydrogen atom of the bridge bond.

the other hand, the overlap population data for H_b–B are typical for the covalent bonds usually encountered.

The two-centre Cu–H_b populations of Table 2 are to be contrasted with those for homonuclear complexes of Table 3. In the latter case the Cu–H_b pairs exhibit a marked degree of covalent character in spite of relatively high negative net charges on hydrogens of the bridge. In is a rather remarkable feature of hydride bridges in transition metal compounds that the multicentre bonds of the bridge have a considerable covalent character while simultaneously exhibiting a marked internal polarization.

For all the compounds listed in Table 2 the Fenske-Hall method predicts that almost all of the negative charge of the BH_4 group is carried by the boron atom. Both the terminal and bridge hydrogen atoms are principally neutral. The total negative charge of the BH_4 group results also from parallel non-iterative EHT calculations. However, the charge distribution within the BH_4 group as predicted by the non-iterative EHT method favours a small negative charge on all hydrogens. This is a rather typical result of non-iterative EHT calculations. The Fenske-Hall method, though of approximate character, has a closer resemblance to non-empirical SCF approaches and its results seem to give more reliable charge distributions. A similar overestimated charge shift towards hydrogens also follows from our EHT calculations on binuclear complexes in Table 3. In this particular case both the Fenske-Hall and EHT methods uniformly predict a large negative charge on hydrogen atoms of the bridge, the EHT results being definitely larger than those in Table 3. This again points to the overestimation of the polar character of bonds in the non-iterative EHT method.

The two-centre overlap populations for Cu–H_b pairs are consistently independent of the method employed in approximate calculations. The Cu–H_b overlap population in copper–boron compounds of Table 2 is negligible while that in molecules of Table 3 is within the range of the values characteristic for typical covalent bonds (*cf.* Cu–P and B–H overlap populations, Tables 2 and 3).

Let us also remark that according to the Fenske-Hall data of Table 2 there is no direct covalent bonding between copper and boron while the Cu–P bonds in phosphine substituted molecules turn out to be uniformly covalent. Principally, the same conclusions follow from the corresponding EHT calculations.

The population analysis results discussed in this section permit some general conclusions concerning the electronic structure of the Cu–H–B systems and its comparison with formally similar Cu–H–Cu linkages. In copper–boron compounds neither of the two methods used in our calculations predict that there is any

TABLE 4. Occupied H-bridge molecular orbitals for CuH_nBH_{4-n} as calculated by the Fenske-Hall method

Molecular orbital [a]		Energy (eV)	Coefficients of atomic orbitals of the bridge atoms [b]	Type of contribution to the Cu–H bond
$CuHBH_3$ HOMO	9	−13.82	$\frac{-0.53d_{z^2}Cu}{0.22sCu} + 0.42sH_b + 0.43p_zB$	antibonding bonding [c]
	2	−17.17	$0.83d_{z^2}Cu + 0.26sH_b + 0.20p_zB$	bonding
CuH_2BH_2 HOMO	9	−14.02	$\frac{-0.60d_{z^2}Cu}{0.20sCu} + 0.22(sH_b^1 + sH_b^2) + 0.39p_zB$	antibonding bonding [d]
	8	−14.10	$0.70d_{xz}Cu + 0.30(sH_b^1 - sH_b^2) + 0.46p_xB$	antibonding
	3	−16.63	$0.73d_{z^2}Cu + 0.12(sH_b^1 + sH_b^2) + 0.34p_zB$	bonding
	2	−17.16	$0.71d_{xz}Cu - 0.28(sH_b^1 - sH_b^2) - 0.33p_xB$	bonding
CuH_3BH HOMO	8, 9	−13.02	$0.42\frac{d_{xz}}{d_{yz}}Cu + 0.20\frac{(sH_b^1 + sH_b^2 - 2sH_b^3)}{2(-sH_b^1 + sH_b^2)} + 0.42\frac{p_x}{-p_y}B$	antibonding
	7	−14.45	$\frac{-0.67d_{z^2}Cu}{0.18sCu} + 0.16(sH_b^1 + sH_b^2 + sH_b^3) + 0.33p_zB$	antibonding bonding [e]
	4	−16.44	$0.69d_{z^2}Cu + 0.06(sH_b{}^1 + sH_b{}^2 + sH_b{}^3) + 0.34p_zB$	bonding
	2, 3	−16.55	$0.83\frac{d_{xz}}{d_{yz}}Cu - 0.12\frac{(sH_b^1 + sH_b^2 - 2sH_b^3)}{2(sH_b^1 - sH_b^2)} - 0.20\frac{p_x}{-p_y}B$	bonding

[a] MOs are numbered according to increasing order of orbital energies; [b] For the definition of local coordinate systems see Fig. 1; [c] Bonding contribution involves the 4s AO of Cu while the antibonding effect follows from the $3d_{z^2}$ AO of Cu. The net antibonding effect cancels the bonding contribution from 2 MO; [d] See note c. The net antibonding effect cancels the bonding contribution from 3 MO; [e] See note c. The net antibonding effect cancels the bonding contributions from 4 MO.

covalent Cu–H_b bond. Hence, the copper–boron compounds cannot be classified as featuring the three centre H-bridges. The Cu (or $Cu(PH_3)_{4-n}$) and H_nBH_{4-n} groups are held together principally by electrostatic interactions. In this sense the bonding in copper–boron compounds resembles the usual hydrogen bonds which are of predominantly electrostatic nature [16]. In this context the Cu–H–Cu bridges of compounds presented in Table 3 are distinctively different from the Cu–H–B links. Above all the Cu–H_b overlap populations indicate their definite covalent character. A large negative charge on the bridge hydrogen atoms combined with the overlap population values permits us to classify the Cu–H–Cu bridges as typical three(multi)-centre hydride bonds which have been studied in a variety of transition metal complexes [2,7].

Our conclusion concerning the electronic structure of the Cu–H–B bridge is different from the characterization of this bridge put forward by other authors [4,8,10]. There is no support found in our calculations for the claims [4,8,10] that the Cu–H–B bridge represents a polar covalent bond.

3.2. Hydrogen bridges in terms of MO shapes and energies

In our search for additional support for our interpretation of diversities in the electronic structure of hydrogen/hydride bridges we have analyzed the shape of the calculated molecular orbitals in both Cu–H–B and Cu–H–Cu systems. The form of molecular orbitals as calculated by the Fenske-Hall method for $Cu{-}H_n{-}BH_{4-n}$, $(PH_3)_{4-n}Cu{-}H_n{-}BH_{4-n}$, and $[(PH_3)_{4-n}Cu{-}H_n - Cu(PH_3)_{4-n}]^k$ is shown explicitly in Tables 4, 5, 6, respectively. The MO coefficients given there are restricted to orbitals directly involved in the hydrogen bridge. Those data are accompanied by the MO energy values.

Let us first analyze the data for $Cu{-}H_n{-}BH_{4-n}$ species. It can be seen that the bonding and antibonding H-bridge orbitals occur throughout the energy spectrum and differ by the amount and type of participating valence orbitals of Cu and B. Of particular importance are relatively large contributions from the 4s and 4p orbitals of Cu. The d-type orbitals of Cu do not seem to make an important contribution to the bonding in the H-bridge region. Actually, the H-bridge orbitals with the considerable participation of d_{Cu} orbitals could have been classified as almost nonbonding in the region of interest.

The data of Table 4 reveal the background of our interpretation of the electronic structure of H-bridges in Cu–H–B systems pursued earlier on a basis of the population analysis data (previous section). On inspecting those data one finds that the bonding effect of some MOs is always nearly cancelled by the antibond-

TABLE 5. Occupied H-bridge molecular orbitals for $(PH_3)_{4-n}CuH_nBH_{4-n}$ as calculated by the Fenske-Hall method

Molecular orbital [a]		Energy (eV)	Coefficients of atomic orbitals of the bridge atoms [b]	Type of contributions to the Cu–H bond
$(PH_3)_3CuHBH_3$				
HOMO	21	−11.58	$0.34d_{z^2}Cu - 0.53sH_b - 0.53p_zB$	antibonding
	16	−17.26	$0.68d_{z^2}Cu + 0.10sH_b + 0.22p_zB$	bonding
$(PH_3)_2CuH_2BH_2$				
HOMO	17	−11.75	$0.43d_{z^2}Cu + 0.29d_{x^2-y^2}Cu - 0.20(sH_b^1 + sH_b^2) - 0.33p_zB$	antibonding [c]
	15	−13.90	$0.45d_{xz}Cu + 0.37(sH_b^1 - sH_b^2) + 0.53p_xB$	antibonding
	13	−14.73	$0.21d_{x^2-y^2}Cu + 0.26sCu + 0.18(sH_b^1 + sH_b^2) + 0.38p_zB$	bonding
	9	−18.07	$0.82d_{xz}Cu - 0.17(sH_b^1 - sH_b^2) - 0.17p_xB$	bonding
	5	−20.92	$0.32d_{z^2}Cu + 0.13d_{x^2-y^2}Cu + 0.20(sH_b^1 + sH_b^2)$	bonding
$(PH_3)CuH_3BH$				
HOMO	13, 14	−12.37	$0.34\dfrac{d_{xz}}{d_{yz}}Cu + 0.25\dfrac{(sH_b^1 + sH_b^2 - 2sH_b^3)}{2(-sH_b{}^1 + sH_b{}^2)} + 0.50\dfrac{p_x}{-p_y}B$	antibonding
	11	−14.11	$\dfrac{0.48d_{z^2}Cu}{-0.21sCu} - 0.17(sH_b^1 + sH_b^2 + sH_b^3) - 0.39p_zB$	antibonding bonding [d]
	6, 7	−17.12	$0.89\dfrac{d_{xz}}{d_{yz}} - 0.10\dfrac{(sH_b^1 + sH_b^2 - 2sH_b^3)}{2(-sH_b^1 + sH_b^2)}$	bonding
	5	−18.39	$0.35d_{z^2}Cu + 0.12sCu - 0.15(sH_b^1 + sH_b^2 + sH_b^3) - 0.38sB$	antibonding
	4	−19.93	$0.49d_{z^2}Cu + 0.16(sH_b^1 + sH_b^2 + sH_b^3) + 0.36sB$	bonding

[a] MOs are numbered according to increasing order of orbital energies; [b] For the definition of local coordinate systems see Fig. 1; [c] The antibonding effect follows from the $3d_{z^2}$ AO and cancels the bonding contributions from MOs 13 and 5; [d] The antibonding contribution from the $3d_{z^2}$ AO of Cu cancels the bonding contribution from the 4s AO of Cu.

ing contribution to the Cu–H_b region by another occupied MO. This leads effectively to the nonbonding interaction between Cu and H_b. Simultaneously, the MOs are strongly polarized either towards copper or boron. This makes the whole system strongly ionic.

The same pattern of the shapes of molecular orbitals as discussed for the systems of Table 4 is also found for phosphine substituted systems of Table 5. Both these tables confirm our conclusions concerning the negligible covalency of the H-bridge in Cu–H–B species. The effect of ligands attached to the Cu atom does not seem to change the basic features of the electronic structure of those systems.

Quite different are the conclusions which can be reached from similar data for copper binuclear hydrogen-bridged systems (Table 6). In all those molecules it is only the d_{Cu} orbitals whose bonding contribution to the three-centre Cu–H–Cu region is virtually cancelled by their antibonding counterparts. The bonding effect due to overlap between 4s and 4p orbitals of Cu and the 1s orbital of H_b is not cancelled and determines the electronic structure of the three-centre hydride bridges. Simultaneously, the relatively large amplitudes of 1s of H_b make the system internally ionic. On comparing the data of Table 6 with those of Tables 4 and 5 one concludes that the Cu–H–Cu bridges are

TABLE 6. Occupied H-bridge molecular orbitals for $[(PH_3)_{4-n}CuH_nCu(PH_3)_{4-n}]^k$ as calculated by the Fenske-Hall method

Molecular orbital [a]		Energy (eV)	Coefficients of atomic orbitals of the bridge atoms [b]	Type of contributions to the Cu–H bond
$[(PH_3)_3CuHCu(PH_3)_3]^{+1}$				
HOMO	35	−11.66	$\frac{0.28(d_{z^2}Cu^1 + d_{z^2}Cu^2)}{-0.22(p_zCu^1 + p_zCu^2)} - 0.61sH_b$	antibonding bonding [c]
	25	−20.22	$\frac{0.35(d_{z^2}Cu^1 + d_{z^2}Cu^2)}{0.19(sCu^1 + sCu^2)} + 0.31$	bonding
	19	−21.61	$0.49(d_{z^2}Cu^1 + d_{z^2}Cu^2) + 0.21sH_b$	bonding
$(PH_3)_2CuH_2Cu(PH_3)_2$				
HOMO	28	−6.56	$\frac{0.18(d_{xz}Cu^1 + d_zCu^2)}{0.17(-p_xCu^1 + p_xCu^2)} + 0.50(sH_b{}^1 - sH_b{}^2)$	antibonding bonding [d]
	27	−8.24	$0.17(d_{z^2}Cu^1 + d_{z^2}Cu^2)$ $0.18(d_{x^2-y^2}Cu^1 + d_{x^2-y^2}Cu^2) - 0.38(sH_b{}^1 + sH_b{}^2)$ $-0.14(p_zCu^1 + p_zCu^2)$	antibonding antibonding bonding [e]
	23	−12.73	$0.23(sCu^1 + sCu^2) + 0.27(sH_b{}^1 + sH_b{}^2)$	bonding
	15	−16.20	$0.61(d_{xz}Cu^1 - d_{xz}Cu^2) - 0.21(sH_b{}^1 - sH_b{}^2)$	bonding
	13	−16.86	$\frac{0.44(d_{z^2}Cu^1 + d_{z^2}Cu^2)}{0.38(d_{x^2-y^2}Cu^1 + d_{x^2-y^2}Cu^2)} + 0.16(sH_b{}^1 + sH_b{}^2)$	bonding
$[(PH_3)CuH_3Cu(PH_3)]^{-1}$				
HOMO	20, 21	0.36	$0.14\left(\frac{d_{xz}}{d_{yz}}Cu^1 + \frac{-d_{xz}}{d_{yz}}Cu^2\right) + 0.30\frac{(sH_b{}^1 + sH_b{}^2 - 2sH_b{}^3)}{-2(sH_b{}^1 - sH_b{}^2)}$ $-0.15\left(\frac{p_x}{p_y}Cu^1 + \frac{-p_x}{p_y}Cu^2\right)$	antibonding bonding [f]
	19	−3.53	$\frac{0.14(d_{z^2}Cu^1 + d_{z^2}Cu^2)}{-0.20(sCu^1 + sCu^2)} - 0.38(sH_b{}^1 + sH_b{}^2 + sH_b{}^3)$	antibonding bonding [g]
	17	−6.94	$\frac{0.53(d_{z^2}Cu^1 + d_{z^2}Cu^2)}{-0.18(sCu^1 + sCu^2)} + 0.10(sH_b{}^1 + sH_b{}^2 + sH_b{}^3)$	antibonding bonding [h]
	9, 10	−8.74	$0.64\left(\frac{d_{xz}}{d_{yz}}Cu^1 + \frac{-d_{xz}}{d_{yz}}Cu^2\right) - 0.10\frac{(sH_b{}^1 + sH_b{}^2 - 2sH_b{}^3)}{-2(sH_b{}^1 - sH_b{}^2)}$	bonding

[a] MOs are numbered according to increasing order or orbital energies; [b] For the definition of local coordinate systems see Fig. 1; [c] Bonding contribution involves the $4p_z$ AOs of Cu while antibonding effect follows from $3d_{z^2}$ AOs of Cu; [d] Bonding contribution involves the $4p_x$ AOs of Cu while antibonding effect follows from $3d_{xz}$ AOs of Cu; [e] Bonding contribution involves the 4s and $4p_z$ AOs of Cu while antibonding effect follows from $3d_{x^2-y^2}$ and $3d_{z^2}$ AOs of Cu; [f] See note d; [g] See note c; [h] Bonding effect follows from $3d_z8d^2$ AOs of Cu and is cancelled by antibonding effect from 19 MO while antibonding contribution following from 4s AOs of Cu cancels bonding contribution from 19 MO.

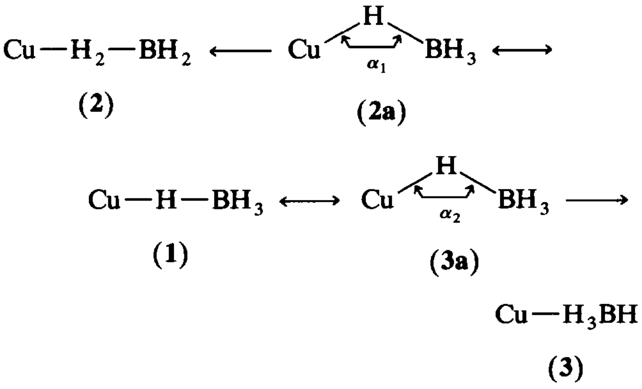
determined by covalent character of the bonding. Only a negligible covalent character of Cu–H–B bridges is found and this arises from the mechanism which is responsible for the covalency of binuclear hydrides. Let us also mention that the pattern of molecular orbitals which follows from Fenske-Hall calculations is qualitatively reproduced by the EHT method. However, the energy sequence and the shapes of particular MOs have frequently been found to be considerably different from each other. Nevertheless, the same mutual cancellation mechanism is found to be operative for EHT molecular orbitals.

3.3. *The hydrogen bridge isomerization in terms of the MO correlation diagrams*

The methods employed in our calculations do not permit sophisticated evaluation of molecular geometries *via* total energy minimization. However, certain information concerning the intramolecular isomerization processes can be acquired by analyzing the accompanying changes in the form and energy of molecular orbitals.

It has been claimed [8b,10] that the Cu–H_n–B systems may undergo internal isomerization processes which change the number of hydrogen atoms involved in the bridge. The relative ease of such processes follows to some extent from the conclusions presented in the two previous sections. If the systems were of ion-pair structure then the rotation of the nearly spherical charge distribution of a BH_4^- group would involve only small gains or losses of energy.

To investigate this problem further we have considered the bending of the Cu–H–B bridge which leads to either C–H_2–B or Cu–H_3–B bridges, *i.e.*,



$$\underset{(2)}{\mathrm{Cu{-}H_2{-}BH_2}} \longleftarrow \underset{(2a)}{\mathrm{Cu}\overset{\mathrm{H}}{\underset{\alpha_1}{\frown}}\mathrm{BH_3}} \longleftrightarrow$$

$$\underset{(1)}{\mathrm{Cu{-}H{-}BH_3}} \longleftrightarrow \underset{(3a)}{\mathrm{Cu}\overset{\mathrm{H}}{\underset{\alpha_2}{\frown}}\mathrm{BH_3}} \longrightarrow \underset{(3)}{\mathrm{Cu{-}H_3BH}}$$

The bending mode indicated in this scheme is presumably the most important one for the isomerization processes. However, the final products 2 or 3 require a full relaxation of the molecular geometry along the isomerization reaction path. Our data which follow from the variation of a single geometry parameter (α_1 for the isomerization 1 → 2 via **2a**, α_2 for the isomerization 1 → 3 via **3a**) provide only a very approximate picture of the whole process.

It has been observed that the energy of the bonding and antibonding Cu–H–B orbitals of Cu–H–BH_3 remains almost the same for a wide range of the α_1 and α_2 angles. One can consider this as an indication of relatively small energy changes in the systems upon the variation of the Cu–H–B angle. However, if the complete geometry relaxation, which leads to the final products, is taken into account the energies of MOs representing the Cu–H–B region undergo more pronounced changes. This is illustrated on the MO energy diagram in Fig. 2.

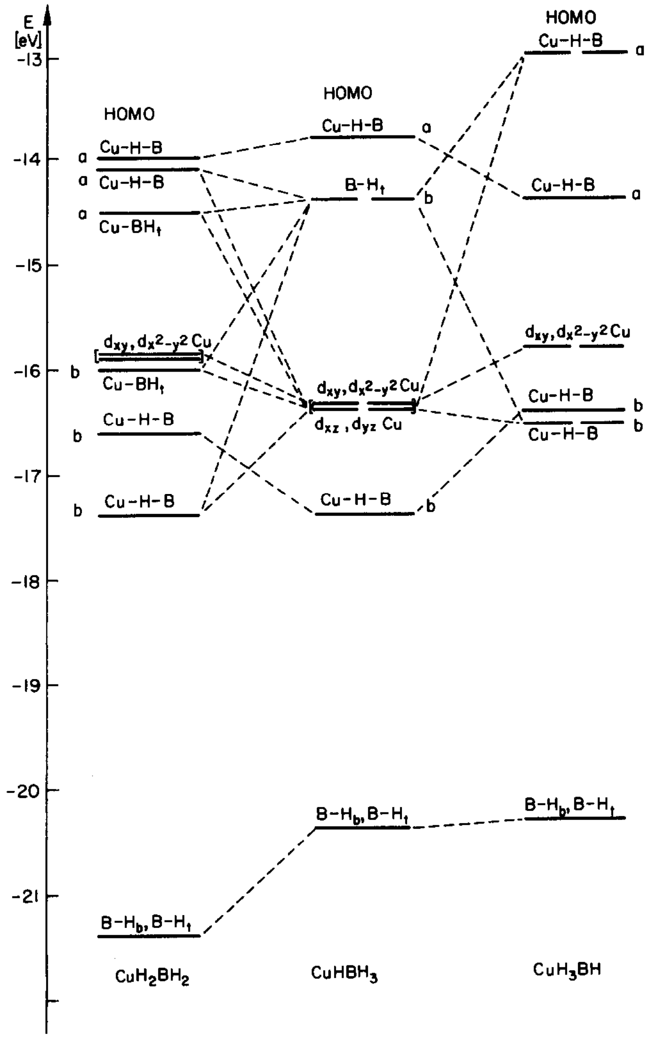


Fig. 2. The MO energy levels for three different H-bridged forms of $CuBH_4$ as calculated by the Fenske-Hall method. The orbitals which are bonding in the Cu ··· H_b region are denoted by 'b' while those which are antibonding in this region have a label 'a'.

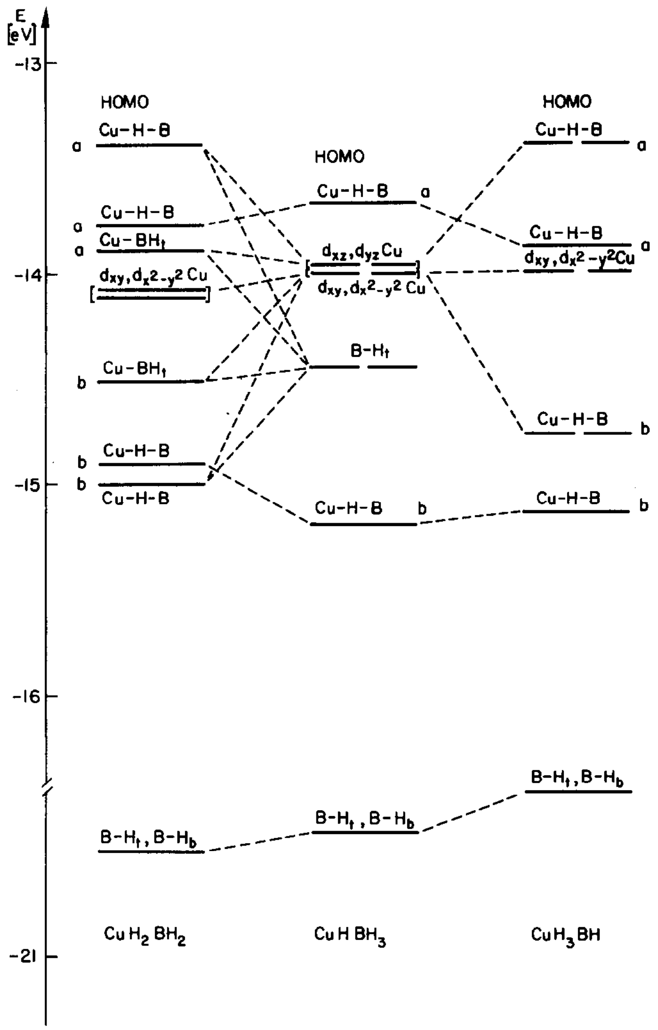


Fig. 3. The MO energy levels for three different H-bridged forms of $CuBH_4$ as calculated by the non-iterative EHT method. The orbitals which are bonding in the $Cu \cdots H_b$ region are denoted by 'b' while those which are antibonding in this region have a label 'a'.

It follows from Fig. 2 that the interaction of the terminal B–H molecular orbital in **1** with the non-bonding d_{Cu} orbitals of this system leads to the formation of new bonding and antibonding pairs of the occupied bridge MOs, thus securing the mutual cancellation effect (see previous section). In spite of the highly qualitative character of those considerations they are likely to indicate a considerable flexibility of the H-bridged copper–boron compounds.

The orbital energy diagram of Fig. 2 has been obtained from Fenske-Hall MO calculations. To verify that our conclusions based on Fig. 2 are independent of the approximations inherent in the calculations an analogous diagram based on the non-iterative EHT data is presented in Fig. 3. The relative position of different MO levels can be seen to depend significantly on the method. However, the general pattern of MOs and in particular the cancellation of the bonding and antibonding effects in the Cu–H_b region remain essentially the same.

The H-bridge isomerization processes in phosphine-substituted complexes turn out to be more complicated than those in homoleptic systems. The change of the number of hydrogens in the bridge must be accompanied by either formation or cleavage of the Cu–PH_3 bond. Thus, the overall relaxation of the molecular geometry will involve significant energy changes.

A series of exploratory calculations on phosphine substituted copper–boron complexes shows that a simple bending of the Cu–H–B bridge involves a considerable steric hindrance from the bulky PH_3 groups. Nonetheless, the MO diagram for the initial and final systems possesses the same features as those discussed for homoleptic systems.

4. Conclusions

In this paper we have investigated the electronic structure of homoleptic and phosphine substituted copper–boron complexes with hydrogen bridges of the form Cu–H_n–B, $n = 1$, 2, and 3. The major part of our investigations has been carried out in the framework of the approximate Fenske-Hall method. The main results of these calculations have been verified by using the non-iterative EHT approach.

From the analysis of the electronic charge distribution, two-centre overlap populations, and by explicit consideration of the shape of the calculated molecular orbitals we conclude that the electronic structure of Cu–H_n–B bridges is significantly different from the structure of the so-called hydride bonds in binuclear transition metal complexes studied in our earlier papers [7]. The electronic structure data obtained from present calculations show that the H-bridged copper–boron complexes can be regarded as an ion pair, *i.e.*, the positively charged Cu atom (or $Cu(PH_3)_{4-n}$ group) and the negative-charged BH_4 group. While the B–H_b bonds retain their usual covalent character, there is only a negligible covalency involved in the $Cu \cdots H_b$ interaction.

The two moieties of the complex are held together mostly by the electrostatic interaction between the charged groups. This permits a certain freedom of internal rotation to the BH_4 group and facilitates the intramolecular isomerization processes which have also been considered in this paper.

The electronic structure of the H-bridge in copper–boron complexes has been compared with that of the hydride bridge in copper binuclear complexes. It has been found that the hydride bridges involve a considerable amount of covalency and differ significantly from the H-bridges in copper–boron complexes. The inspection of the form of molecular orbitals in the two series of molecules has revealed the mechanism conferring either ionic or covalent character on the corresponding bonds. It follows that the ionic character of the H-bridge in copper–boron complexes results from near-cancellation of the bonding and antibonding contributions from different occupied orbitals. This cancellation turns out to be incomplete in the case of hydride bridges in copper binuclear complexes and the three(many)-centre $Cu–H_n–Cu$ bond, *i.e.*, the hydride bond, follows mostly from the bonding interaction which involves 4s and 4p atomic orbitals of Cu and the 1s orbital(s) of the hydrogen atom(s).

The results of calculations presented in this paper contradict a rather commonly proposed interpretation of the electronic structure of Cu–H–B bridges in terms of covalent bonding [8b,10]. Our interpretation which follows from Fenske-Hall and EHT data stresses the strongly ionic character of the $Cu–H_nBH_{4-n}$ bond and the electrostatic nature of the interactions between Cu (or the corresponding coordinated Cu atom) and the BH_4 group. Such a picture of the bonding in H-bridged copper–boron complexes facilitates the understanding of the flexibility of these molecules with respect to intramolecular isomerization processes.

By comparing the electronic structure of H-bridges in copper–boron and copper binuclear complexes one concludes that the purely electrostatic interaction in $Cu–H_n–B$ bridges makes them similar to ordinary hydrogen bonds. In the latter case the electrostatic interaction is the major contributor to the total H-bond energy. There is, however, a certain difference which arises from a substantial charge transfer between the copper (coordinated copper) and BH_4 moieties of the copper–boron H-bridged complexes. On the other hand, the uniqueness of hydride bonds in copper binuclear complexes follows from the considerable contribution of covalent effects to the binding of negatively charged H_b atom by two copper atoms.

References

1 (a) R. Bau (ed.), *Transition Metal Hydrides*, Washington, DC, Am. Chem. Soc. Adv. Chem. Ser., Washington, DC, Vol. 167, 1978; (b) E. L. Muetterties (ed.), *Transition Metal Hydrides*, M. Dekker, New York, 1971.

2 (a) A. Dedieu, T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc., 101* (1979) 3141; (b) A. Bino, B. E. Burnsten, F. A. Cotton and A. Fang, *Inorg. Chem., 21* (1982) 3755; (c) D. E. Sherwood, jr. and M. B. Hall, *Inorg. Chem., 21* (1982) 3458; (d) P. T. Chesky, M. B. Hall, *Inorg. Chem., 22* (1983) 3327.

3 R. B. Saillant and H. D. Kaesz, *Chem. Rev., 72* (1972) 231.

4 R. Bau, P. Gutlich and R. G. Teller, *Struct. Bonding, 44* (1981) 3.

5 (a) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. A. Andrews, D. L. Tipton and R. Bau, *J. Amer. Chem. Soc., 96* (1974) 6621; (b) R. Bau, R. G. Teller, S. W. Kirtley, *Acc. Chem. Res., 12* (1979) 176; (c) R. Bau, T. F. Koetzle, *Pure Appl. Chem., 50* (1978) 55.

6 N. M. Greenwood, A. Earn, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1989, p. 179.

7 (a) B. Jeżowska-Trzebiatowska and B. Nissen-Sobocińska, *J. Organomet. Chem., 322* (1987) 331; (b) B. Jeżowska-Trzebiatowska and B. Nissen-Sobocińska, *J. Organomet. Chem., 342* (1988) 215; (c) B. Jeżowska-Trzebiatowska and B. Nissen-Sobocińska, *J. Organomet. Chem., 342* (1988) 353; (d) B. Jeżowska-Trzebiatowska and B. Nissen-Sobocińska, *J. Organomet. Chem., 369* (1989) 69; (e) B. Jeżowska-Trzebiatowska and B. Nissen-Sobocińska, *J. Organomet. Chem., 376* (1989) 67.

8 (a) B. D. James and M. G. H. Wallbridge, *Prog. Inorg. Chem., 11* (1970) 99; (b) T. J. Marks and J. R. Kolb, *Chem. Rev., 77* (1977) 263.

9 (a) E. Wiberg, *Angew. Chem., 65* (1953) 16; (b) E. Wiberg, W. Henle, *Z. Naturforsch., Teil B, 7* (1952) 582.

10 (a) Ch. Kutal, P. Grutsch, J. L. Atwood and R. D. Rogers, *Inorg. Chem., 17* (1978) 3558; (b) J. T. Gill and S. J. Lippard, *Inorg. Chem., 14* (1975) 751.

11 C. E. Housecroft, *Adv. Organomet. Chem., 33* (1991) 1.

12 (a) H. Nöth and M. Seitz, *J. Chem. Soc., Chem. Commun.*, (1976) 1004; (b) M. M. Lynam, D. M. Chipman, R. D. Barreto and T. P. Fehlner, *Organometallics, 6* (1987) 2405.

13 M. B. Hall and R. F. Fenske, Inorg. Chem., 11 (1972) 768.

14 (a) J. P. Dahl and C.J. Ballhausen, *Adv. Quantum Chem., 4* (1968) 170; (b) R. F. Fenske, *Pure & Appl. Chem., 60* (1988) 1153.

15 R. Hoffmann, *J. Chem. Phys., 39* (1963) 1397.

16 P. Schuster, in P. G. Zundel and R. C. Sandorfy (eds.), *The Hydrogen Bond, Vol. I. Theory*, North Holland, Amsterdam, 1976.