Table V. Comparison of Axial Ligand Labilities of Iron[a] and Ruthenium Phthalocyanine Adducts[b]

trans group	leaving group	k_1(Fe)/k_1(Ru)
$P(OBu)_3$	$P(OBu)_3$	20 000
$P(OBu)_3$	MeIm	890
$P(OBu)_3$	py	260
PBu_3	$P(OBu)_3$	100 000

[a] Data for iron complexes from ref 4. [b] k_1(Fe) at 21 °C in acetone; k_1(Ru) at 25 °C in toluene.

than when the leaving group is MeIm or py. This probably is due to the well-known[13] superior π-back-bonding ability of Ru(II), leading to increased Ru–$P(OBu)_3$ bond strength. This π-back-bonding ability of Ru(II) probably also accounts for the following leaving-group effect differences with $P(OBu)_3$ as the trans group. Fe: py > MeIm < $P(OBu)_3$ (14:1:11). Ru: py > MeIm > $P(OBu)_3$ (50:1:0.5).

The trans effect for both $FePcL_2$ and $RuPcL_2$ follows the order $P(OBu)_3$ > PBu_3 > py, MeIm. This ability of MeIm to inactivate trans ligands is probably also present in iron porphyrin systems[14] and obviously plays an important biological role. Interestingly, in other iron macrocyclic complexes MeIm seems to be a trans activator.[15] Unfortunately the present results with $RuPcL_2$ complexes cannot be compared with those of analogous ruthenium(II) porphyrin complexes except to state that the latter also seem[16] to substitute axial ligands via a dissociative mechanism. We are currently investigating the dynamics of some ruthenium porphyrin complexes.

In summary, the phthalocyanine complexes of iron and ruthenium differ greatly in axial lability and the importance of M→L π bonding but possess the same reaction mechanism, reaction-intermediate discrimination ratios, and trans-effect series. Although the dynamics of axial ligand substitution in phthalocyanine complexes differ from that found with metalloporphyrins in very fundamental ways, it is just such differences that can illuminate the mechanistic details of metalloporphyrin chemistry.

Acknowledgment. It is a pleasure to acknowledge Dr. S. D. Ittel for helpful discussions and E. I. du Pont de Nemours and Co. for permitting the use of the FD-MS facility at the Experimental Station, Wilmington, DE.

Registry No. $RuPc[P(OBu)_3]_2$, 76986-82-8; $RuPc(PBu_3)_2$, 76986-81-7; $RuPc(Cl)(py)_2$, 76986-80-6; $RuPc(Cl)(MeIm)_2$, 76986-79-3; $RuPc(Cl)[P(OBu)_3]_2$, 76986-78-2; $RuPc(Cl)(PBu_3)_2$, 76986-77-1; $FePc[P(OBu)_3]_2$, 61005-31-0; $FePc(PBu_3)_2$, 61005-30-9; $RuPc[P(OBu)_3](MeIm)$, 76986-76-0; $RuPc[P(OBu)_3](py)$, 76986-75-9; $RuPc(PBu_3)[P(OBu)_3]$, 76986-74-8; MeIm, 616-47-7; py, 110-86-1; PBu_3, 998-40-3; $P(OBu)_3$, 102-85-2; $Ru_3(CO)_{12}$, 15243-33-1; RuPc, 27636-56-2.

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Transition-Metal Tetrahydroborate Complexes as Catalysts. 1. Nonempirical Determination of Static, Dynamic, and Chemical Properties of the Model Compounds $NaBH_4$ and AlH_2BH_4

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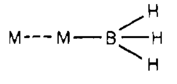
Ab initio computations have been performed on the compounds $NaBH_4$ and AlH_2BH_4 in order to achieve a better understanding of the peculiar characteristics of the M–BH_4 bond. Our results suggest a tridentate coordination for the sodium ion and a bidentate coordination for the aluminum compound. The dynamics of the hydrogen-interchange process has also been analyzed, and a Berry pseudorotation step has been excluded because of its high activation energy. Since BH_4^- is isoelectronic with CH_4, the present results can also give better insight into the structure of intermediate complexes in the saturated hydrocarbon activation process.

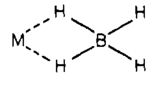
Introduction

The tetrahydroborate ion, BH_4^-, is one of the most useful and extensively used reagents, both in organic synthesis[2] and in inorganic or organometallic chemistry.

Among its chemical properties, the BH_4^- ion shows the tendency to reduce metal carbonyls to clusters with bridging hydride ligands[3] and, more generally, to form unusual covalent complexes with several transition metals.[4] The coordination always occurs through bridging hydrogen atoms, as exemplified by[4] the following (m = monodentate, b = bidentate, t = tridentate):



m



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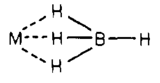

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Interconversion between the various coordination modes is possible,[4,5] and a variety of metal complexes incorporating BH_4^- as a ligand exhibits an interesting fluxional behavior.[4,6]

Recently, inorganic and organometallic chemists have been much interested in the chemical and physical nature of BH_4^- complexes not only within the general context of activation by metals of small, electron-rich molecules but also considering the relevance of the peculiar coordination mode in catalytic processes. However, this last facet of the chemistry of transition-metal tetrahydroborates has not yet received, in our opinion, due attention. This is far more surprising on account of considerable experimental evidence about the effectiveness of tetrahydroborates as catalysts for polymerization, oligomerization, and hydrogenation of olefins.[7-11]

In homogeneous catalysis the BH_4^- anion could exhibit a many-sided behavior. It may reduce the central metal to a lower oxidation state, thus enhancing its tendency to undergo oxidative addition reactions (the first step in homogeneous hydrogenation catalysis). BH_4^- may also provide a source of hydrogen in the form of a metal hydride. Even if the coordination of BH_4^- to metals always occurs through bridging hydrogens, it is necessary to inquire further to known how the chemical and structural properties of the hydride bridging system are affected by variations in metal, metal oxidation state, and accompanying ligands. The discovery of these relationships would be a valuable step forward in the investigation of the metal-to-substrate and reductant-to-metal hydride transfer processes.

The BH_4^- ligand is also able to provide a variable coordination sphere for the metal atom by means of a series of fluctuations of the bonding mode, effective in determining the coordinative saturation of the metal. This property is far more noteworthy, since the presence of a vacant coordination site is of primary importance in homogeneous catalysis.[12]

Last but not least, BH_4^- may simply act as an activation ligand toward other ligands bound to the same metal.

From an examination of the BH_4^- behavior, in any of its roles, we could see why covalent metal tetrahydroborates can be successfully employed as effective catalysts in many homogeneous processes.[7-11] In this respect, a better understanding of the peculiar characteristics of the $M-BH_4$ bond and then possible forecastings about the coordination mode of tetrahydroborate with different metals and in the presence of different ligands may be of use in building up "tailor made" metal catalysts effective in important predetermined processes. Furthermore, since BH_4^- is isoelectronic with CH_4, metal tetrahydroborate complexes can be considered as model structures for intermediate complexes in the saturated hydrocarbon activation process.

As we are much interested in the investigation of homogeneous hydrogenation catalysis and in the determination of catalysts build-up patterns, the purpose of the present paper is to report the results of some calculations on the possible bonding mode in simple metal tetrahydrobroate systems, as a starting point for a systematic study of the homogeneous catalysis facet of the metal tetrahydroborate complexes. The compounds examined in the present context are $NaBH_4$ and AlH_2BH_4. This choice has been made considering that the former ($NaBH_4$) provides a good example of the bonding situation for ionic species containing the BH_4^- ligand and the latter (AlH_2BH_4) for covalent ones. Further, these two compounds are simple enough to allow a comprehensive analysis of the dynamics of the hydrogen interchange process.

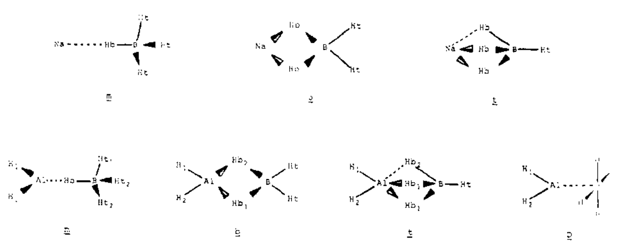

Figure 1. Different possible coordinations of the BH_4^- anion.

Table I. Optimized M-B Distances and Energetical Values for $NaBH_4$ and AlH_2BH_4 in Different Configurations on the Assumption of Tetrahedral Geometry for the BH_4^- Moiety[a]

	$NaBH_4$				H_2AlBH_4	
confign	r_{Na-B}, Å	ΔE, kcal/mol	r_{Na-B}, Å	ΔE, kcal/mol	r_{Al-B}, Å	ΔE, kcal/mol
monodentate	2.990	20.77	3.07[b]	15.8[b]	2.791	28.72
bidentate	2.350	1.37	2.52[b]	2.5[b]	2.180	0.0
tridentate	2.210	0.0	2.35[b]		2.020	13.16
Berry					2.066	166.25

[a] ΔE values refer to the differences from the best configuration taken as zero. [b] Reference 18.

Experimental Section

All the computations have been performed by the nonempirical Hartree–Fock–Roothan method since it has been shown that semiempirical methods often lead to unrealistic potential surfaces for nonrigid molecules.[13]

The minimal STO-3G basis set of the GAUSSIAN 70 package[14] has been used because of the great number of calculations to be performed to obtain potential surfaces detailed enough to discuss dynamic behaviors. This choice has been made also to permit the extension of this kind of studies to large transition-metal complexes.

The STO-3G basis set, according to published studies on several boron compounds,[15,16] gives quite reliable results, even if in some cases a sensible underestimation of the BH bond lengths is reported to occur. Consequently, we have used in all our computations a fixed distance $R(B-H) = 1.256$ Å, i.e., the BH distance found in crystalline sodium and potassium borohydrides.[17,18] Free-molecule calculations could show a possible influence of the formal positive ion on this bond length. Actually, previous good quality ab initio calculations on $LiBH_4$ led to a BH bond length of 1.26 Å[13,19] (on the assumption of a tetrahedral geometry for the BH_4^- moiety) in excellent agreement with the experimental solid-state value. The distance M-B (M = Na or Al) has been optimized for the monodentate (m), bidentate (b), and tridentate (t) complexes. In the case of the most stable coordination modes b and t (see Results and Discussion) also the angles HBH have been optimized.

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Table II. Optimized Geometries and Energies for the Bidentate and Tridentate Configurations of $NaBH_4$ and AlH_2BH_4 Molecules[a]

$NaBH_4$

confign	total energy, au	r_{Na-B}, Å	H_tBH_t, deg	H_bBH_b, deg	ΔE, kcal/mol
bidentate	−186.549 92	2.351	114	110	1.71
tridentate	−186.552 65	2.198		107	0.0

H_2AlBH_4

confign	total energy, au	r_{Al-B}, Å	H_tBH_t, deg	H_bBH_b, deg	$H_cAl\text{-}H_c$, deg	ΔE, kcal/mol
bidentate	−266.842 25	2.169	119.3	104.4	129.9	0.0
tridentate	−266.813 49	2.058		111.8	123.3	18.05

[a] ΔE values refer to the differences from the best configuration taken as zero.

A problem could arise concerning the ability of the STO-3G basis set to give physically significant results for the stability differences of the various coordination modes. These differences may be in some cases about 1 kcal mol^{-1}. However, our results on $NaBH_4$ (with an undistorted tetrahedral geometry for the BH_4^- anion) are in good agreement, at least for trends and orders of magnitude, with previous accurate theoretical studies,[13,19] allowing us to consider quite reliable and physically significant the reported results.

Results and Discussion

(a) Geometric and Electronic Structure. Despite the perturbing effect of Na^+ or AlH_2^+, which lowers the tetrahedral symmetry of the isolated BH_4^- anion, a first analysis of the most interesting configurations of $NaBH_4$ and AlH_2BH_4 (Figure 1) has been performed on the assumption of a rigid tetrahedric geometry for the BH_4^- moiety.

From the results collected in Table I, it appears that the t configuration is the most stable for the sodium complex, the b configuration being only slightly less stable. Just the contrary occurs in the case of the aluminum complex, for which the b configuration is far more stable than the t one. In this connection it might seem surprising at first sight that in the $NaBH_4$ complex a very small energy difference corresponds to a quite large increase (0.153 Å) of the NaB distance going from tri- to bidentate complexes. However, the Na–H_b distances decrease at the same time (from 2.16 to 1.92 Å) due to different H_b–B–Na angles (70° vs. 54.75°). Therefore, the small energy change results from a compensation between (at least) these structural changes. On the other hand, for the AlH_2BH_4 complex the bidentate ligation pattern allows a very effective tetrahedral coordination around Al (sp^3 hybridization). This explains the much greater energy differences between b and t modes of coordination. For both $NaBH_4$ and AlH_2BH_4 complexes the m configurations are by far the least stable. This result is not unexpected since bi- and tridentate complexes of BH_4^- have been known for a long time,[4] while the first definitive structural characterization of a monodentate bonding mode has been reported only recently for the $Cu(PPh_2Me)BH_4$ complex.[20]

From Table I it can be observed that the minimal basis set used in the present context, comparatively to larger ones, slightly underestimates both stability differences for different coordination modes and M–B bond lengths.[19] However, the orders of magnitude of physically significant results are well reproduced also for very small energy differences.[19,21] Furthermore it has been shown, in agreement with our findings, that the complexes AlR_2BH_4[22] and, in particular, AlH_2BH_4[23] are bidentate. These considerations let us be rather confident with the general scheme outlined by our computations.

For analysis of the relevance of geometrical distortions of the BH_4^- ligand, the geometries of b and t complexes have been completely optimized for both $NaBH_4$ and LaH_2BH_4 with the exception of the BH bond lengths, for which the experimental value has been assumed (see Experimental Section). These results are reported in Table II. It can be seen that, even if the distortions in the angles are quite relevant, the NaB and AlB equilibrium distances are not greatly affected and the energy differences remain of the same order of magnitude for all the complexes.

We cannot confidently give the values of the formation energies of the studied molecules (e.g., $NaBH_4$ from NaH and BH_3 and AlH_2BH_4 from AlH_3 and BH_3) because it is well-known that the adopted method (not including correlation) and the employed basis set do not suffice to provide reliable predictions. However, a comparision of our computed energies with those of the fragment[24] shows unquestionably that all our complexes are stable, in agreement with previous computations.[13,19] The further result that the $NaBH_4$ complex is more stable than AlH_2BH_4 when compared to their respective fragments (Table II and ref 24) seems convincing on the basis of the chemistry of the two compounds; while $NaBH_4$ is a well-known molecule, AlH_2BH_4 has been only recently synthesized and appears to be very unstable.

In Table III the results of the Mulliken population analysis of the considered compounds are reported. The greater ionicity of the $NaBH_4$ complex with respect to AlH_2BH_4 (see Introduction) is confirmed by the decrease in the Na–B and Na–H_b overlap populations compared with Al–B and Al–H_b ones and also by the positive net charge on Na^+ (0.860) greater than on the whole AlH_2 group (0.516 and 0.575, respectively, for b and t complexes). The negative charge on the BH_4^- group in the $NaBH_4$ molecule is comparatively greater than in AlH_2BH_4, the additional electron density being redistributed on the whole BH_4^- moiety.

The trends of alteration in net charges and overlap populations going from bi- to tridentate complexes are the same for both the compounds: while the net charge on boron increases, the net charges on H_b and H_t decrease.

On the whole, the present results show that BH_4^-, in both bi- and tridentate situations, is capable of donating electron density to the metal ion. This donation is quite large also for the $NaBH_4$ complex, which, hence, can be hardly considered as purely ionic.

In agreement with experimental results,[4] the tridentate configuration allows a shorter metal–boron contact, which results in a larger metal–boron overlap population.

(b) Fluxional Behavior. The thermodynamic and kinetic details of the hydrogen-interchange process in metal tetrahydroborates are well-known; however the detailed mechanism of the process remains open to speculation. Several possible pathways have been suggested (none has been identified) for bridge–terminal hydrogen permutation in bi- and tridentate tetrahydroborate complexes. A first mechanism, schematized in Figure 2a, involved a monodentate transition state (or intermediate).[25] Subsequently, bi- and tridentate intermediates were suggested[26,27] (Figure 2b,c). Some recent results seem to suggest an interconversion mechanism involving a twist

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Table III. Net Atomic Charges (q) and Overlap Population (Q) According to Mulliken

NaBH$_4$

confign	q(Na)	q(B)	q(H$_b$)	q(H$_t$)	Q(Na–H$_b$)	Q(Na–B)	Q(B–H$_b$)	Q(B–H$_t$)	dipole moment
bidentate	0.860	−0.086	−0.222	−0.156	0.061	0.058	0.656	0.748	9.55
tridentate	0.860	−0.104	−0.207	−0.136	0.030	0.058	0.690	0.752	8.92
monodentate^a	0.860	−0.046	−0.286	−0.179	0.121	0.024	0.582	0.739	
BH$_4^-$		−0.0786	−0.230	−0.230			0.721	0.721	

AlH$_2$BH$_4$

confign	q(H$_1$)	q(H$_2$)	q(Al)	q(B)	q(H$_{b_1}$)	q(H$_{b_2}$)	q(H$_t$)	Q-(Al–H$_1$)	Q-(Al–H$_2$)	Q-(Al–H$_{b_1}$)	Q-(Al–H$_{b_2}$)	Q-(Al–B)	Q-(B–H$_{b_1}$)	Q-(B–H$_{b_2}$)	Q-(B–H$_t$)	dipole moment
bidentate	−0.239	−0.239	0.994	−0.041	−0.156	−0.156	−0.081	0.671	0.671	0.192	0.192	0.146	0.548	0.548	0.768	2.824
tridentate	−0.245	−0.248	1.068	−0.163	−0.125	−0.111	−0.051	0.664	0.660	0.095	0.062	0.195	0.636	0.672	0.671	2.554
monodentate	−0.233	−0.233	1.061	0.0136	−0.253		−0.118	0.661	0.661	0.385		0.041	0.352		0.755	4.738
AlH$_2^+$	−0.100	−0.100	1.200					0.666	0.666							

^{a} Without optimization of HBH angles.

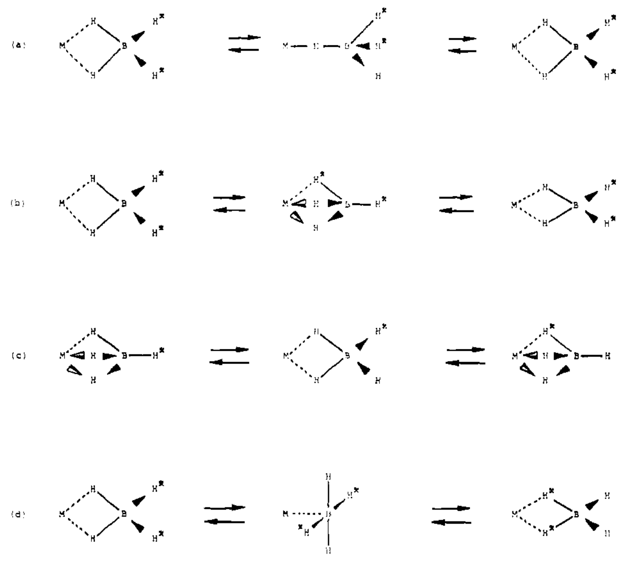

Figure 2. Possible reaction paths for the dynamic hydrogen interchange process.

about a H$_b$–B bond.[4,28] Although this mechanism is in some respect similar to a bidentate ⇄ tridentate equilibration, the metal–H$_b$ distances are no longer equivalent in the transition state. This would involve a complete geometry optimization: due to the poor ability of the adopted basis set to reproduce B–H bond lengths this mechanism shall be discussed in a forthcoming paper by means of a more extended basis set. Anyway, the results corresponding to a bi- or tridentate intermediate can be considered as upper bounds even for such a mechanism. Finally, reaction paths reminiscent of a Berry pseudorotation have also been taken into account[4] (Figure 2d): such mechanisms, even concerted, must involve an intermediate (or transition state) with C_{4v} local symmetry at boron (D configuration of Figure 1).

As reported in Table I for AlH$_2$BH$_4$, our computations show that this intermediate has a very high energy (the activation energy is at least 166 kcal mol^{-1}). On the other hand, the b state is a transition state between the t configuration in which the BH$_4^-$ ligand bonds over one face of the tetrahedron and an equivalent state t′ in which BH$_4^-$ bonds over the adjacent face. Conversely, the t configuration is a transition state between a b configuration in which BH$_4^-$ bonds over one edge and an equivalent configuration b′ in which BH$_4^-$ bonds over the adjacent edge. Since the energy difference between b and t configurations is at least 1 order of magnitude lower than the difference between b (or t) and D configurations, we may conclude that the hydrogen interchange occurs without complete inversion of BH$_4^-$. This is in agreement with previous experimental results, which ruled out the possibility of a rearrangement of BH$_4^-$ reminescent of a Berry pseudorotation.[28] Furthermore, at least for the studied compounds, the monodentate configuration is always very unstable comparatively to bi- and tridentate configurations; then a mechanism not involving the monodentate intermediate seems to be more sounded.

As shown in the preceding section, different coordination modes of BH$_4^-$ involve different geometrical parameters, and hence the migration of AlH$_2^+$ or Na$^+$ may be visualized as a concerted process. Anyway, as the energy differences are not highly dependent on the BH$_4^-$ distortion and as we look for general trends only, we have calculated the potential energy

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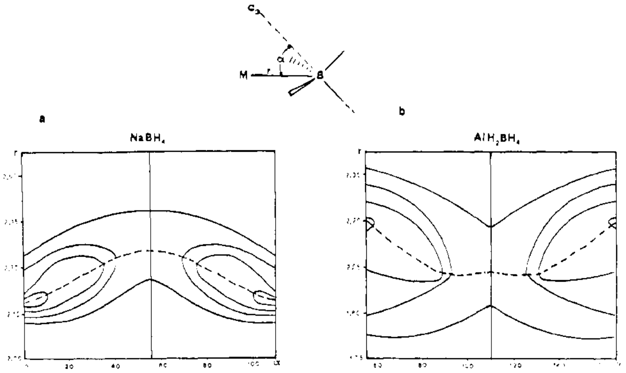

Figure 3. Potential energy surface and minimum energy path (broken line) as a function of α and r (see text): (a) $NaBH_4$ molecule (the isoenergetic curves are spaced of 0.6 kcal/mol until 1.8 kcal/mol); (b) AlH_2BH_4 molecule (the isoenergetic curves are spaced of 6.0 kcal/mol until 18 kcal/mol).

surface for cation migration with the assumption of a rigid tetrahedric structure for the BH_4^- anion. The minimum energy path for the cation migration will obviously lie in a plane containing the B atom and two C_3 axes of the BH_4^- tetrahedron. The angle (α) of one of the C_3 axes with the M–B (M = Na or Al) bond lying in the above plane and the M–B bond length (r) have been chosen as the relevant coordinates in the migration process. Figure 3 shows the resulting potential energy surface for $NaBH_4$ and AlH_2BH_4, respectively. It can be seen that for $NaBH_4$ (for which the t configuration is the most stable) the b configuration is associated with the saddle point and the opposite occurs for AlH_2BH_4. Hence, the values quoted in the preceding section as energy differences between t and b configurations (at the optimized geometries) can be actually considered as activation energies. It is evident that Na^+ undergoes a quasi-free migration, while AlH_2^+ has an activation energy comparable with those reported for some transition metals.[3] Therefore, the AlH_2^+ complex can be regarded as a first simple model of nearly covalent tetrahedral complexes of BH_4^- with metals further coordinated to substituents which are not too bulky.

Another interesting feature of Figure 3 is the coupling between the M–B distance and the angle α. In fact the minimum energy path involves nonnegligible variations of the M–B distance, this effect being more marked for AlH_2^+ than for Na^+.

Conclusions

From the reported results (Table III) it appears clear that BH_4^- is able to act as an electron donor even when bonded to very electropositive elements. Therefore it should be a very interesting ligand in complexes containing metals in low oxidation states.

The preferred coordination mode of BH_4^- appears to be strongly affected not only by the metal nature and its oxidation state but also by its environment in the first coordination sphere. This behavior is well-known in organometallic chemistry where the metal complex properties are strongly dependent on the coordinated ligands. In the tetrahydroborate chemistry this behavior is examplified by the $Cu(P)_3BH_4$ complexes, when P = PPh_2Me or PPh_3. As said before, in the complex with P = PPh_2Me the tetrahydroborate group is attached through a single hydrogen bridge[20] (m bonding mode). On the contrary, the complex with P = PPh_3 has a b bonding mode.[29]

As for the hydrogen-interchange process, we can exclude that it occurs via a mechanism reminiscent of a Berry pseudorotation because of the high activation energy (see Table I). Also mechanisms involving a monodentate intermediate can be excluded on the same ground. Our results suggest, instead, a permutation of bridge and terminal hydrogens going via a bidentate transition state for t complexes (e.g., $NaBH_4$) or via a tridentate transition state for b complexes (e.g., AlH_2BH_4). Further work is in order to analyze possible concerted mechanisms involving a twist about a H_b–B bond.[28]

As for the reliability of our results, they agree with previous empirical observations in suggesting that, at least for early transition metals, bidentate and tridentate ligation patterns do not show marked energy differences.[30] For instance, the experimental interconversion barrier for the b complex $BH_4Mo(CO)_4$ is of about 10 kcal mol^{-1} [31] vs. a computed barrier for AlH_2BH_4 of 14 kcal mol.

The results reported in the present paper appear, hence, physically significant at least for trends and orders of magnitude and reliable enough to encourage further studies on transition-metal complexes and their catalytic behavior.

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Registry No. $NaBH_4$, 16940-66-2; AlH_2BH_4, 45632-34-6.

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