Molecular and Electronic Structures of $TiXH_6^+$ (X = B, Al, Ga) Compounds

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The molecular and electronic structures of $TiXH_6^+$ compounds have been studied. All stable structures found have strong two-electron three-center Ti−H−X bonds, which determine their geometrical characteristics. One important structural feature, found for all the isomers studied, is the absence of Ti−X bonding interactions, so that the molecular structure is held together by their Ti−H−X electron deficient bonds. Accurate relative energies of the various isomers are also calculated and discussed.

1. Introduction

The propensity of titanium to form two-electron three-center Ti−H−X hydrogen bridge bonds has been discussed recently.[1,2] Indeed, it has been found that the bridged structures are the global minima[1] on the potential energy surfaces of $TiSiH_6$ and $TiPH_5$, when dynamic electron correlation is included in the calculation *via* Møller−Plesset perturbation theory.[3] Similarly, on the basis of a high-level calculation of the Ti_2H_6 potential energy surface we have concluded[2] that the global minimum is a structure with three Ti−H−Ti two-electron three-center bonds, where the three bridge hydrogens are disposed in an eclipsed conformation with respect to the three terminal hydrogens. The corresponding staggered isomer is found to be only 1.9 kcal/mol more unstable.[2]

The structural features of these compounds have been found to be determined by the remarkable stability of the Ti−H−X three-center bonds. For instance, one salient characteristic is the absence of Ti−X bonding interactions, even though their separation is smaller than the sum of their corresponding covalent radii. Consequently, these molecular structures should be held together by the hydrogen bridges. Boron-containing compounds are well-known for their propensity toward molecular hydrogen bridges.[4] Indeed, transition metal hydroborate compounds also exhibit similar behavior.[5] In particular, there are several examples in the literature of titanium compounds containing the BH_4 unit, characterized by multiple hydrogen bridges between Ti and B within each BH_4 moiety.[6−8] Therefore, we believe it is worthwhile investigating the $TiBH_6$ potential energy surface in order to find out whether the stable structures have open or bridged structures. It is noteworthy that the first row elements C and N only form open structures,[1] namely, molecular structures with a Ti−X bonding interaction and all the hydrogens bonded either to Ti or to X, pointing away from the Ti−X binding region.

In this paper we discuss the molecular geometries and bonding features of various isomers of the $TiXH_6^+$ (X = B, Al, Ga) in order to learn about the structures of this interesting kind of compounds, where the Ti and the X atoms are held together by electron deficient hydrogen bridge three-center bonds.

2. Methods

Geometries for the species studied in this work were optimized at the B3LYP level of theory.[9] Frequencies were also calculated at this level of theory and used to assess that all species were true minima, as well as to estimate the zero-point vibrational energy (ZPVE) corrections.

The basis set used in the present paper for titanium is the triple-ζ valence polarization of Schäfer, Huber, and Ahlrichs[10], supplemented by the two 4p polarization functions optimized by Wachters[11] for excited states and augmented with a diffuse s function (with exponent 0.36 times that of the most diffuse s function on the original set). For all of the other atoms the standard 6-31++G(d,p) basis set[12] has been used. This basis set will be referred to hereafter as A. Notice that the Cartesian coordinates of all the B3LYP/A optimum structures and their IR frequencies and intensities are given in Tables 1 and 2, respectively, of the Supporting Information.

The additivities of the basis set and electron correlation effects[13] were used to improve the energies. Thus, the corrections due to the deficiencies in the basis set were estimated by calculating the B3LYP energies with a larger basis set. Namely, basis set A was augmented for Ti with a diffuse d function (optimized by Hay[14]) and the effects of f functions were accounted for adding three uncontracted f functions, including both the tight and diffuse exponents, as recommended.[15] For all the other atoms instead of the standard 6-31++G(d,p) basis set, the larger on the 6-311++G(df,pd)[16] was used. This basis set is named as B. Next, we calculate the contributions of successive improvements in the method to the MP4/A//B3LYP/A base level energy, to obtain the CCSD(T)/B energies, by the following additivity scheme

$$E^{[\mathrm{CCSD(T)/B}]} = E^{[\mathrm{MP4/A}]} + \Delta E^{[\mathrm{CCSD(T)/A}]} + \Delta^{\mathrm{B3LYP}} + \mathrm{HLC} + \mathrm{ZPVE}$$

with

$$\Delta E^{[\mathrm{CCSD(T)/A}]} = E^{[\mathrm{CCSD(T)/A}]} - E^{[\mathrm{MP4/A}]}$$

$$\Delta^{\mathrm{B3LYP}} = E^{[\mathrm{B3LYP/B}]} - E^{[\mathrm{B3LYP/A}]}$$

where HLC is the empirical high level correlation correction of Curtiss et al.[17]

These calculations were performed using the Gaussian94/DFT[18] suite of programs. In addition, we have explored the bonding characteristics by means of both the natural bond orbital (NBO) analysis[19] and the Bader's topological analysis of the electron charge density.[20] The former was carried out with the NBO code,[21] as implemented with the Gaussian94/DFT, and the latter with the AIMPAC series of programs.[22]

3. Results and Discussion

The geometries of the local minima structures found on the B3LYP/A potential energy surfaces of the $[TiXH_6]^{+1}$ (X = B,

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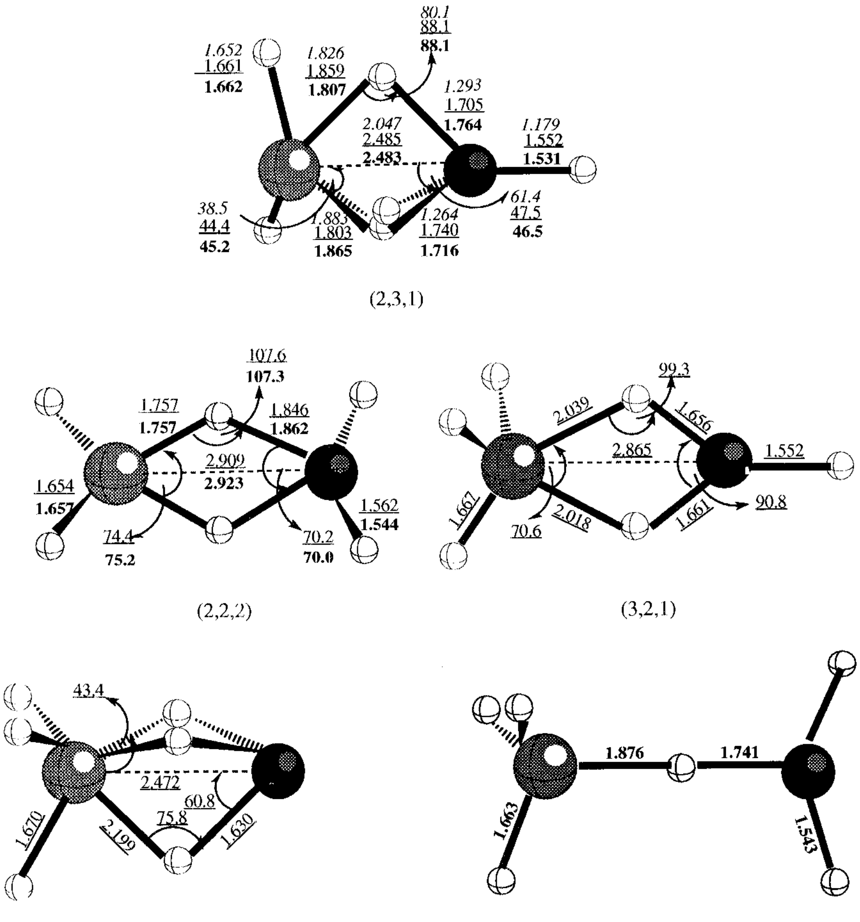

(2,3,1)

(2,2,2)

(3,2,1)

(3,3,0)

(3,1,2)

Figure 1. B3LYP/A structures of the isomers of the $TiXH_6^+$ system. Ti is on the left; X is on the right. In each case, the geometrical data corresponding to X = B are shown in italic, underlined for X = Al, and bold face for X = Ga. Bonds lengths are given in angstroms and bond angles in degrees.

Al, Ga) systems are shown in Figure 1. Each structure can be characterized by a set of three figures (*a*, *b*, *c*) with *a* corresponding to the number of terminal hydrogens (H_t) bound to Ti, *b* to the number of bridge hydrogens (H_b) in between Ti and X, and *c* to the number of terminal hydrogens bound to X. It is worth noting that we have not been able to locate any stable open structure with a Ti−X bond and all the hydrogens pointing away from the Ti−X bond region. However, when we looked for structures containing hydrogen bridges with $a = 2, 3$, $b = 1, 2, 3$, and $c = 0, 1, 2$, those shown in Figure 1 were found. Indeed, every stable structure found has a least one and at most three hydrogens turned inside forming two-electron three-center (2e,3c) covalent bonds, as will be shown below. This structural trend has also recently been found for the H_3TiH_2P[1] and H_3TiH_3Ti[2] systems. For the latter, two nearly energy-degenerated structures, eclipsed and staggered respectively, with the three hydrogens of one titanium turned inside, have been characterized separated by a calculated internal rotational barrier of 5.3 kcal/mol. For the H_3TiH_3Si system, both an open staggered structure and a structure in which the three Si hydrogens turn inside have been described,[1] the latter being 7.3 kcal/mol more stable than the former, at the MP4/TZVP level of theory.

$TiBH_6^+$. We have found only one stable structure on the B3LYP/A potential energy surface, namely, the (2,3,1) isomer, whose salient geometrical features are shown in Figure 1. Its inspection reveals that the three bridge hydrogens lie far more distant from Ti than from B. Two of them are 1.883 Å from Ti (1.264 Å from B), and the third is 1.826 Å from Ti (1.293 Å from B). However, the natural bond orbital analysis clearly indicates that all the three bridge hydrogens are involved in (2e,3c) bonds. Thus, we have been able to find three covalent doubly occupied (two with an occupation of 1.95 and one with 1.98 electrons) Ti−H−B two-electron three-center bonds, which are summarized in Table 1. These bonds are formed by a linear combination of a sd hybrid orbital on Ti, a sp^3 on B, and the 1*s* on H atomic orbitals. Naturally, we have not found any natural bond orbital between Ti and B.

Comparison with the recently resolved structure[6] of $Ti(BH_4)_3$, which has three tridentate BH_4 units, suggests that the bonding interactions between H_b and both Ti and B are more covalent in $TiBH_6^+$. Thus, the H_b−Ti, 2.06 Å, H_b−B, 1.23 Å, and Ti−B 2.218 Å, bond lengths in $Ti(BH_4)_3$ are respectively 0.23 Å, 0.06 Å, and 0.17 Å longer, shorter, and shorter respectively than in $TiBH_6^+$, which is indicative of the larger covalent character of the Ti−H−B two-electron three-center bonds of the latter molecule. This supports the earlier suggestion[2] that these hydrogen bridges constitute covalent skeletal bonds. In fact it is found that they lie 86.4 kcal/mol below the HOMO, which corresponds to the Ti−H_t bond, and even below the B−H_t bonding orbital by 40.4 kcal/mol.

This picture comes along with the Bader's topological analysis of the charge density.[20] Remarkably, a bond path linking Ti and B has been found, as shown in Table 2. However, attending to the small value of the electron density at the bond critical point and to its large ellipticity (4.5 au) we should conclude that the electron density on that bond path spreads over the TiH_bB plane. Hence, the occurrence of the Ti−B bond critical point should be attributed to the geometrical

TABLE 1: Atomic NBO Coefficients of the Two-Electron Three-Center Ti−H−X Molecular Orbitals and, in Parentheses, Their Corresponding Hybridization Pattern, from the B3LYP/A Molecular Wave Function

			coefficient		
no. of bonds	bond	occupancy	Ti	X	H
		Isomer (2,3,1)			
2	Ti−H−B	1.949	0.42 (s, 17.35)	0.61 (s, 23.14)	0.67 (s, 99.89)
			(p, 0.84)	(p, 79.86)	(p, 0.11)
			(d, 81.81)		
1	Ti−H−B	1.985	0.38 (s, 12.01)	0.61 (s, 20.76)	0.69 (s, 99.91)
			(p, 1.69)	(p, 78.88)	(p, 0.09)
			(d, 86.30)	(d, 0.35)	
1	Ti−H−Al	1.950	0.42 (s, 14.09)	0.40 (s,14.55)	0.81 (s, 99.92)
			(p, 1.89)	(p, 82.72)	(p, 0.08)
			(d, 84.03)	(d, 2.74)	
2	Ti−H−Al	1.906	0.47 (s, 18.28)	0.41 (s, 14.87)	0.79 (s, 99.90)
			(p, 1.26)	(p, 82.29)	(p, 0.10)
			(d, 80.46)	(d, 2.85)	
2	Ti−H−Ga	1.890	0.47 (s, 18.37)	0.42 (s,13.78)	0.77 (s, 99.93)
			(p, 1.47)	(p, 85.52)	(p, 0.07)
			(d, 80.16)	(d,0.69)	
1	Ti−H−Ga	1.941	0.43 (s, 14.69)	0.41 (s, 13.14)	0.80 (s, 99.94)
			(p, 1.942)	(p, 86.27)	(p, 0.06)
			(d, 83.37)	(d, 0.59)	
		Isomer (2,2,2)			
2	Ti−H−Al	1.959	0.48 (s, 20.53)	0.31 (s, 7.51)	0.81 (s, 99.93)
			(p, 1.56)	(p, 90.26)	(p, 0.07)
			(d, 77.87)	(d, 2.24)	
2	Ti−H−Ga	1.957	0.49 (s, 21.24)	0.32 (s, 5.56)	0.81 (s, 99.94)
			(p, 1.56)	(p, 94.02)	(p, 0.06)
			(d, 77.21)	(d, 0.42)	
		Isomer (3,2,1)			
1	Ti−H−Al	1.932	0.31 (s, 12.01)	0.46 (s,22.21)	0.83 (s, 99.90)
			(p, 1.47)	(p, 74.45)	(p, 0.10)
			(d, 86.52)	(d, 2.34)	
1	Ti−H−Al	1.951	0.32 (s, 20.94)	0.44 (s, 20.18)	0.84 (s, 99.92)
			(p, 1.51)	(p, 77.30)	(p, 0.08)
			(d, 77.55)	(d, 2.52)	
		Isomer (3,3,0)			
3	Ti−H−Al	1.944	0.30 (s, 10.83)	0.52 (s, 31.58)	0.80 (s, 99.90)
			(p, 1.53)	(p, 66.21)	(p, 0.10)
			(d, 87.64)	(d, 2.22)	
		Isomer (3,1,2)			
1	Ti−H−Ga	1.967	0.35 (s, 26.27)	0.34 (s, 8.95)	0.87 (s, 100.00)
			(p, 0.18)	(p, 90.82)	
			(d, 73.55)	(d, 0.22)	

constrains, imposed by the three angular (2e,3c) Ti−H_b−B bonds, that could result in a marginal overlap on the tails of the electron densities of Ti and B. Compare the sum of Ti and B covalent radii,[23] 2.14 Å, with our predicted separation of 2.05 Å, namely, 0.09 Å shorter.

$TiAlH_6^+$. Four minima have been found on the ground state potential energy surface of this compound (Figure 1), none of which has an open structure. Indeed, two of them have three bridge hydrogens (isomers (2,3,1) and (3,3,0)) and two have two bridge hydrogens (isomers (2,2,2) and (3,2,1)). Every bridge hydrogen atom builds a (2e,3c) Ti−H−Al skeletal bond with a population of two electrons, which has been conveniently characterized using the natural bond analysis of Weinhold *et al.*[19] The coefficients of these (2e,3c) molecular natural bonding orbitals, collected in Table 1, suggest that they consist of a combination of an sd hybrid on the titanium atom, a sp hybrid on the aluminum atom, with a non-negligible participation of the d-type polarization functions, and the 1s orbital of the hydrogen atom. As found for the $TiBH_6^+$ (see previous section) and Ti_2H_6[2], these (2e,3c) bonds lie well down in energy with respect to the HOMO, i.e.: 62.3, 38.1, 73.5, and 64.8 kcal/mol lower, for the (2,3,1), (2,2,2), (3,2,1), and (3,3,0) isomers respectively. Also, it should be mentioned that the proposed molecular structures are fully confirmed by the topological analysis of the charge density.[20] Thus, for the (2,3,1) and (3,3,0) isomers both a cage critical point and the corresponding three ring critical points have been characterized properly, and for the (2,2,2) and (3,2,1) isomers we have found one ring critical point in between the Ti and Al atoms. None of the isomers studied exhibits either a Ti−Al bond critical point or a Ti−Al bonding natural bond.

The Ti−Al distance is larger for isomers with two bridge hydrogens than for isomers with three bridge hydrogen atoms, by *ca.* 0.4 Å. As a consequence, the Ti−H_b−Al bond angle is wider in this case (see Figure 1). This can be attributed to the smaller d coefficient of the sd hybrid of Ti in the (2e,3c) Ti−H_b−Al skeletal bonds, which ultimately govern the intermetal separation. It is also worth mentioning that among the studied isomers, the bond lengths between the terminal hydrogens and both Ti and Al vary very little with respect to their average values of 1.66 and 1.55 Å, respectively.

Energies shown in Table 3 indicate that the (2,3,1) isomer is the lowest energy minimum of all structures investigated. Transferring one of the bridge hydrogens over either the aluminum or the titanium atom destabilizes the system. For the former case, the resulting (2,2,2) isomer lies 18.11 kcal/mol higher in energy, and for the latter, the resulting (3,2,1) isomer is predicted to be 22.75 kcal/mol more unstable than

TABLE 2: Bonding Properties, in au, of the Bond Critical Points of TiXH6+, (X = B, Al, Ga) at the B3LYP/A Level of Theory

bond	ρ(rc)	∇^2r(rc)	*H*(rc)	ϵ
Isomer (2,3,1)				
Ti−B	0.0849	0.2039	−0.0251	4.497
Ti−H$_t$	0.1220	−0.0310	−0.0544	0.046
B−H$_b$	0.1403	−0.1528	−0.1440	0.206
B−H$_b$	0.1442	−0.0946	−0.1405	0.168
B−H$_t$	0.1910	−0.4146	−0.2087	0.003
Ti−H$_t$	0.1180	−0.0073	−0.0509	0.043
Al−H$_t$	0.0870	0.2760	−0.0293	0.002
Ti−H$_b$	0.0640	0.1584	−0.0113	0.229
Al−H$_b$	0.0601	0.1921	−0.0155	0.078
Al−H$_b$	0.0590	0.1626	−0.0169	0.129
c.c.p.	0.0440	0.0940	−0.0107	
ring crt.	0.0480	0.0457	0.0245	
ring crt.	0.0440	0.0960	0.0337	
Ti−H$_t$	0.1167	−0.0018	−0.0500	0.056
Ga−H$_t$	0.1223	0.1221	−0.0628	0.000
Ti−H$_b$	0.0631	0.1535	−0.0113	0.225
Ga−H$_b$	0.0759	0.0858	−0.0313	0.189
ring crt.	0.0512	0.0936	−0.0121	
Isomer (2,2,2)				
Ti−H$_t$	0.1182	−0.0300	−0.0545	0.013
Al−H$_t$	0.0848	0.2721	−0.0281	0.009
Ti−H$_b$	0.0857	0.0896	−0.0259	0.052
Al−H$_b$	0.0402	0.1114	−0.0081	0.236
r.c.p.	0.0354	0.0335	−0.0097	
r.c.p.	0.0363	0.0591	−0.0035	
Ti−H$_t$	0.1223	−0.0274	−0.0541	0.0132
Ga−H$_t$	0.1188	0.1284	−0.0602	0.0207
Ti−H$_b$	0.0863	0.0804	−0.0266	0.0522
Ga−H$_b$	0.0536	0.0928	−0.0172	0.0407
ring crt.	0.0354	0.0596	−0.0035	
Isomer (3,2,1)				
Ti−H$_t$	0.1182	−0.0201	−0.0511	0.024
Al−H$_t$	0.0876	0.2721	−0.0303	0.019
Ti−H$_b$	0.0375	0.1297	−0.0002	0.291
	0.0412	0.1118	−0.0024	0.644
Al−H$_b$	0.0712	0.2055	−0.0224	0.121
	0.0681	0.2072	−0.0199	0.147
r.c.p.	0.0304	0.0694	−0.0024	
Isomer (3,3,0)				
Ti−H$_t$	0.1165	−0.0150	−0.0500	0.011
Ti−H$_b$	0.0308	0.1062	0.0002	0.008
Al−H$_b$	0.0759	0.2178	−0.0256	0.004
c.c.p.	0.0273	−0.0910	−0.0039	
r.c.p.	0.0278	−0.0036	−0.0036	
Isomer (3,1,2)				
Ti−H$_t$	0.1204	−0.0275	−0.0528	0.001
Ga−H$_t$	0.1196	0.1222	−0.0610	0.026
Ti−H$_b$	0.0554	0.1042	−0.0097	0.006
Ga−H$_b$	0.0676	0.1063	−0.0260	0.110

the (2,3,1) lowest energy isomer. Recall that the (3,3,0) isomer is predicted to lie high in energy, *ca.* 54.89 kcal/mol, with respect to the (2,3,1) isomer.

The additive corrections used to deal with the deficiencies in the basis set and the electron correlation treatment decrease the relative energies between all the four studied isomers.

TiGaH$_6^+$. Three minina, none of them having an open structure, have been characterized on the ground state PES of this compound. Their salient geometrical parameters are found in Figure 1. Notice that, as for the case of TiAlH$_6^+$, the (2,3,1) and (2,2,2) isomers have been found, but apparently neither the (3,2,1) nor (3,3,0) isomers, which exist for the TiAlH$_6^+$, exist on the TiGaH$_6^+$ PES. In addition an isomer with signature (3,1,2), not found for the TiAlH$_6^+$, has been found for the TiGaH$_6^+$ system. Our calculations suggest that there is no Ti-Ga bonding interaction for any of the isomers found; hence the bridge hydrogens held the molecular structures together. As it is observed in Table 1, each isomer is held by the (2e,3c) Ti−H$_b$−Ga bonds formed by the bridge hydrogens, which consist of linear combinations of sd hybrids on Ti, sp on Ga, and the 1s atomic orbital of the bridge hydrogen. That the (2e,3c) bonds are skeletal bonds is confirmed further by the fact that they are considerably stabilized with respect to their corresponding HOMOs, namely by 61.7, 38.5, and 58.1 kcal/mol for the (2,3,1), (2,2,2), and (3,1,2) isomers, respectively. This picture agrees with the Bader's topological analysis of the electron density. Thus, we have not found any bond path connecting the titanium and the gallium atoms. Accordingly, a cage critical point has been found for the (2,3,1) isomer in between the Ti and Ga and a ring critical point for the (2,2,2) isomer. For the (3,1,2) isomer the corresponding bond critical points between Ti and H$_b$ and Ga and H$_b$ have been also found, as shown in Table 2.

The Ti−Ga distance of the (2,3,1) isomer, 2.483 Å, is substantially shorter than the sum of their atomic covalent radii,[23] *i.e.*, 2.58 Å. However, as pointed out in the preceding paragraph, we have not been able to find any bonding interaction between Ti and Ga. This puts into perspective the very stringent geometrical constrains imposed by the three skeletal two-electron three-center bonds formed by the bridge hydrogens. Removing one of these bonds results in a remarkable lengthening of the Ti−Ga distance, namely, the Ti−Ga distance of the (2,2,2) isomer is 2.923 Å, 0.44 Å larger than in the (2,3,1) isomer. Finally, notice that the bond lengths of the terminal hydrogen either with Ti or Ga vary very little from one isomer to another, with respect to their average values of 1.54 and 1.66 Å, respectively.

The calculated energies of the three isomers studied, shown in Table 3, demonstrate that the (2,3,1) isomer is the most stable and that the (2,2,2) and (3,1,2) isomers lie very close in energy (3.53 kcal/mol) with respect to each other, but *ca.* 16 kcal/mol higher than the (2,3,1) isomer.

TABLE 3: MP4/A Base Level and CCSD(T)/B Energies in hartrees, Energies Corrections, in mhartrees, to the Base Level Energy, and Relative Energies, in kcal/mol, at the CCSD(T)/B Level of Theory, for the TiXH$_6^+$ (X = B, Al, Ga) Stable Structures

TiXH$_6^{+1}$	MP4/A	$\Delta E^{\mathrm{CCSD(T)/A}}$	Δ^{B3LYP}	ZPVE	$E^{\mathrm{CCSD(T)/B}}$	rel energies
X = B						
(2,3,1)	−876.475 96	−13.70	−14.54	51.46	−876.511 45	
X = Al						
(2,3,1)	−1093.682 93	−12.47	−31.29	42.80	−1093.742 60	0.00
(2,2,2)	−1093.644 00	−19.53	−31.54	40.04	−1093.713 74	18.11
(3,2,1)	−1093.635 93	−18.28	−31.61	38.19	−1093.706 34	22.75
(3,3,0)	−1093.589 28	−12.90	−30.76	36.53	−1093.655 12	54.89
X = Ga						
(2,3,1)	−2772.888 95	−13.52	−2075	41.95	−2774.995 11	0.00
(2,2,2)	−2772.864 20	−13.10	−2073	40.24	−2774.969 65	15.98
(3,1,2)	−2772.856 69	−12.26	−2073	36.96	−2774.964 03	19.50

4. Conclusions

A careful analysis of the ground electronic state potential energy surfaces of the $TiXH_6^{+1}$ (X = B, Al, Ga) species has been carried out. All stable structures characterized have strong (2e,3c) hydrogen bridge electron deficient bonds, which constitute one salient characteristic structural feature, for all the isomers studied. Another important structural feature is the predicted absence of any Ti−X bonding interaction indicating that the structure is held together by the bridging hydrogen atoms. This reinforces earlier evidence on the skeletal character of this sort of bonds.[1,2]

We have found only one stable structure on the potential energy surface of $TiXH_6^+$, with X = B, which can be characterized as a (2,3,1) isomer. The three bridge hydrogens form a very stable (2e,3c) electric deficient bond each, and on the basis of our calculations there is no evidence of any Ti−B bonding interactions, though their separation is smaller than the sum of the corresponding covalent radii. Therefore, it is concluded that the structural features of this molecule are dictated by its three (2e,3c) bonds.

For X = Al, we have been able to characterize four isomers of the $TiXH_6^+$ system. However, it is remarkable that none of them have an openlike structure. Two of the isomers have two (2e,3c) Ti−H−Al, the other two isomers have three, and neither of the four isomer have an intermetallic bond, although the Ti−Al separation in all of the isomers is shorter than the sum of their corresponding covalent radii. Hence, on the basis of our calculations one should conclude that the structural features of these compounds stem from the stringent geometrical constraints imposed by their angular (2e,3c) Ti−H−Al bonds. The (2,3,1) isomer is the lowest energy structure of the system, followed by the (2,2,2) isomer at 18.11 kcal/mol above, the (3,2,1) isomer, 22.75 kcal/mol above the (2,3,1) isomer, and the (3,3,0) isomer, 54.89 kcal/mol higher in energy than the (2,3,1) lowest energy isomer.

For the $TiGaH_6^+$ system we have found three stable isomers, with signatures (2,3,1), (2,2,2), and (3,1,2), respectively. The lowest energy isomer corresponds to the (2,3,1) structure, which is 15.98 and 19.50 kcal/mol more stable than the (2,2,2) and (3,1,2) isomers respectively. The three isomers of $TiGaH_6^+$ have three, two and one hydrogen bridge (2e,3c) electron deficient bonds, respectively, and no Ti−Ga bonding interaction.

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Supporting Information Available: Tables giving the Cartesian coordinates of B3LYP/A optimum structures and their IR frequencies and intensities (6 pages). Ordering information is given on any current masthead page.

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