J. Phys. Chem. A 1998, 102, 2055−2064

Molecular and Electronic Structures of $(TiXH_6)^{0/-}$, X = B, Al, Ga, Compounds

América García,[†] Jose M. Mercero, Joseph E. Fowler, and Jesus M. Ugalde*

Kimika Fakultatea, Euskal Herriko Unibertsitatea, P.K. 1072, 20080 Donostia, Euskadi, Spain

Received: October 16, 1997

The molecular and electronic structures of the isomers of both neutral and negative $(TiXH_6)^{0/-}$, X = B, Al, Ga, systems have been studied. For each of the neutral systems, a C_s isomer of signature (2, 3, 1) (where (a, b, c) signifies *a* is the number of terminal Ti−H bonds, *b* is the number of hydrogen bridging bonds, and *c* is the number of terminal X−H bonds) was characterized as a stable minimum. The X = Al, Ga neutral systems also had two additional minima of signature (2, 2, 2) (C_{2v}) and (3, 3, 0) (C_{3v}). In the anionic cases, each system has a stable C_s structure of signature (3, 2, 1). The X = Al, Ga systems, again showing more complexity, have minima on their anionic singlet potential energy surfaces of signatures (2, 2, 2), (3, 3, 0), and (3, 0, 3). The bonding characteristics of these various minima have been analyzed in detail through examination of molecular orbitals, natural bond orbitals, and Bader topological analysis. One important structural feature of the stable isomers is that strong hydrogen bridging electron-deficient bonds are responsible for holding the molecular structure together. For the neutrals, the (2, 3, 1) and (2, 2, 2) isomers have almost the same energy and the (3, 3, 0) isomer lies more than 30 kcal/mol higher. However, for the anions, the three structures with hydrogen bridging bonds are the most stable and lie very close in energy, within 0.31 kcal/mol for X = Al and within 5.96 kcal/mol for X = Ga. Ionization energies and electron affinities have also been calculated and discussed.

1. Introduction

The remarkable stability of Ti−H−B two-electron three-center hydrogen bridging bonds has been well-demonstrated. For example, the UV photoelectronic spectrum of gaseous titanium tris(tetrahydroborate)[1] reveals that these bonds lie 86 kcal/mol lower than the 3d orbitals of the titanium of this molecule. This suggests that the capacity of titanium to form these bonds is very high indeed.

The propensity of titanium to form two-electron three-center Ti−H−X hydrogen bridge bonds has been discussed recently.[2,3] Indeed, it has been found that the bridged structures are the global minima 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.[2] Similarly, on the basis of a high-level calculation of the Ti_2H_6 potential energy surface, we earlier concluded[3] that the global minimum is a structure with three Ti−H−Ti two-electron three-center bonds, where the three bridging 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 higher in energy.[3]

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 feature 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 are held together by the hydrogen bridges.

Boron-containing compounds are well-known for their tendency toward molecular hydrogen bridges.[5] Indeed, transition metal−hydroborate compounds also exhibit a similar behavior.[6] 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.[1,7,8] However, the next first row elements, C and N, only form open structures,[2] namely, molecular structures with a Ti−X bonding interaction and all the hydrogens bonded either to Ti or to X, directed away from the Ti−X binding region.

Particularly relevant to this paper is our previous research[9] on the $(TiXH_6)^+$, X = B, Al, Ga, cations. A careful analysis of their ground-state potential energy surfaces revealed that all stable structures characterized have strong skeletal two-electron three-center hydrogen bridging bonds, which constitute the salient structural feature for all the isomers.

In this paper we extend this research to both the neutral and anionic $(TiXH_6)^{0/-}$ systems and carry out a detailed theoretical study of the isomers of these systems, in order to learn more about this interesting kind of compound, where Ti and X are held together by electron-deficient hydrogen bridging three-center bonds.

2. Methods

Geometries for the species studied in this work were optimized at the B3LYP level of theory;[10] in the neutral species the method UB3LYP was used. Frequencies were also calculated at this level of theory and used to assess that all species were true minima, as well as to compute 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 Ahlrich,[11] supplemented by the two 4p polarization functions optimized by Wachters[12] for excited states and augmented with a diffuse s function (with exponent 0.36 times that of the most diffuse s

---

[†] On leave from: Dpto. de Química, Fac. de Ciencias Nat. y Mat., Universidad de Oriente, Avenida Patricio Lumumba S/N, 90500 Santiago de Cuba, Cuba.

S1089-5639(97)03365-3 CCC: $15.00

function in the original set). For all of the other atoms the standard 6-31++G(d,p) basis set[13] has been used. This basis set will be referred to hereafter as A. Note that the Cartesian coordinates of all the B3LYP/A optimum structures and their IR frequencies and intensities are given in the Supporting Information.

The additivities of the basis set and electron-correlation effects[14] 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[15]), and the effects of f functions were accounted for adding three uncontracted f functions, including both the tight and diffuse exponents, as recommended by Raghavachari and Trucks.[16] For all the other atoms instead of the standard 6-31++G(d,p) basis set, the larger 6-311++G(df,pd)[17] set was used. This basis set is named as B. Additionally, more complete descriptions of electronic correlation were calculated using the MP4/A[18] and CCSD(T)/A[19] levels of theory applied at the B3LYP/A equilibrium geometries.

Next, the following additivity scheme was used to give our "Best Result" (estimated CCSD(T)/B)

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

with

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

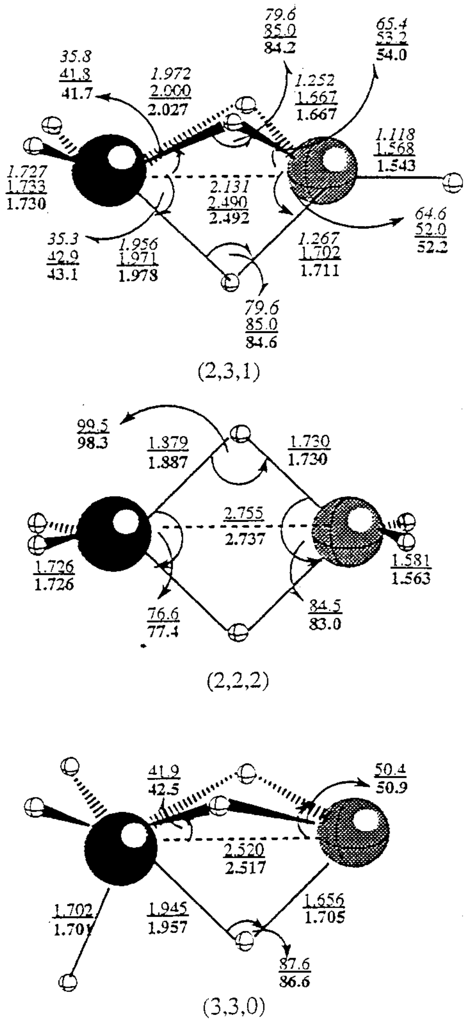
$$\Delta \text{B/A}^{\text{B3LYP}} = E^{[\text{B3LYP/B}]} - E^{[\text{B3LYP/A}]}$$

where HLC is the empirical high-level correlation correction of Curtiss et al.[20]

These calculations were performed using the Gaussian94/DFT[21] suite of programs. In addition, we have explored the bonding characteristics by means of both the natural bond orbital (NBO) analysis[22] and Bader's topological analysis of the electron charge density.[23,24] The former was carried out with the NBO code,[25] as implemented in Gaussian 94/DFT, which gives the so-called "chemist's basis set", a set of orbitals that would correspond closely to the picture of localized bonds, lone pairs, and their interactions as basic units of the molecular structure. The latter, based on a nonarbitrary partition of the molecular electron density into atomic basins, provides a complementary picture in terms of the properties of the bond critical point (r_c), such as its density, $\rho(r_c)$, its Laplacian, $\nabla^2\rho(r_c)$, and the value of the energy density, $H(r_c)$; the latter has been found to be a very sensitive indicator of the covalency of the bond ($H(r_c)$; < 0 for covalent bonds, $H(r_c)$ > 0 for ionic bonds[23]).

3. Results and Discussion

The geometry of the stable structures found on the B3LYP/A potential energy surfaces of neutral and anionic $(\text{TiXH}_6)^{0/-}$, X = B, Al, Ga, systems are shown in Figures 1 and 2, respectively. As suggested in our earlier paper,[9] we characterized each of the structures by a set of three numbers (a, b, c), which correspond to the number of terminal hydrogens bound to Ti, the number of bridging hydrogens, and the number of terminal hydrogens bound to X, respectively.



(2,3,1)

(2,2,2)

(3,3,0)

Figure 1. B3LYP/A structures of the isomers of the neutral $(\text{TiXH}_6)^0$ 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 boldface for X = Ga. Bonds lengths are given in angstroms and bond angles in degrees.

$(\text{TiBH}_6)^0$. As found earlier for its cation, the (2, 3, 1) isomer with C_s symmetry is the only stable structure characterized on the B3LYP/A potential energy surface of the neutral doublet $(\text{TiBH}_6)^0$ system. Compared with its cation,[9] the Ti$-$H$_b$ bond lengths of the neutral species are appreciably longer, while the B$-$H$_b$ ones remain almost unaltered. This is reflected in the atomic coefficients of the natural bonds, given in Table 1. While the Ti coefficient for the (2e, 3c) bonds was 0.42 for the cation,[9] it is only 0.3 for the neutral. Therefore, we conclude that the hydrogen bridging bonds of the neutral are more polarized toward the tetrahydroborate moiety than the cation. The reason for these bond length differences can be appreciated by considering the molecular orbital of the additional electron. The singly occupied orbital (see Figure 3) is basically a d_{z^2} nonbonding orbital on Ti. This additional electron density at the titanium end pushes the bridging hydrogens toward the boron.

As was the case for the cation, no natural bond orbital between Ti and B exists. Thus, these hydrogen bridging bonds ought to be regarded as skeletal bonds. In fact, it is found that they lie 142.31 kcal/mol below the singly occupied molecular orbital (SOMO), and even below the Ti$-$H$_t$ bond orbitals by 93.06 kcal/mol according to the NBO analysis. This supports earlier assignments of UV photoelectron spectra of closely related gaseous titanium tetrahydroborates.[1]

Bader's analysis of the electron charge density[23] agrees with this picture. Nevertheless, it should be mentioned that a bond

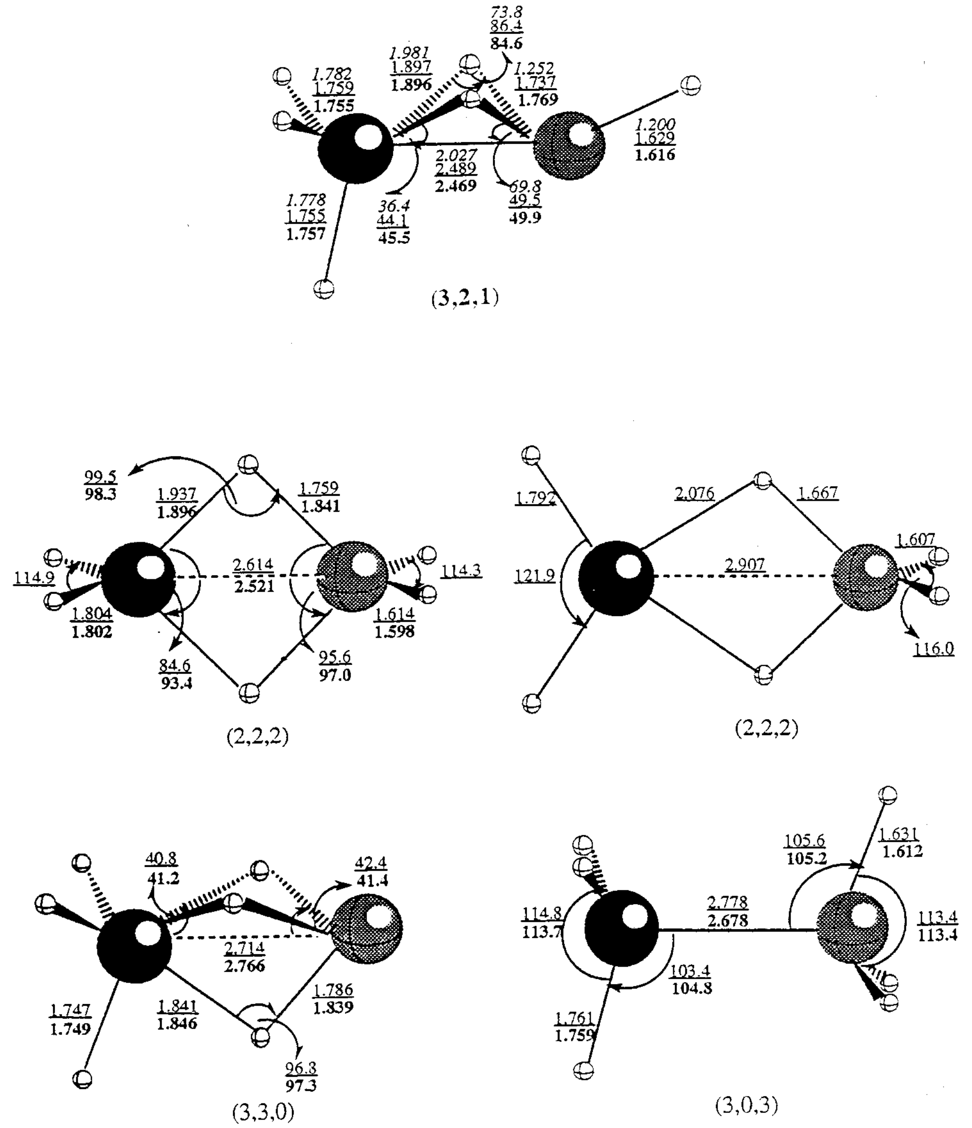


Figure 2. B3LYP/A structures of the isomers of the negative $(TiXH_6)^-$ system. Ti is on the left; X is on the right. In each case, the geometrical data corresponding to X = B are shown in italic, underlined for X = Al, and boldface for X = Ga. Bonds lengths are given in angstroms and bond angles in degrees.

path linking Ti and B has been found, as shown in the Supporting Information. However, the small value of electron density at the bond critical point, $\rho(r_c) = 0.067$ e/Å^3, is indicative of a very weak bonding interaction between the Ti and B atomic basins. This residual value might simply be due to the geometrical constraints imposed by the three angular (2e, 3c) bonds, which yield a Ti−B distance of 2.131 Å, slightly shorter than the sum of their covalent radii,[26] 2.14 Å.

We have also located the $Ti(H_t)_2$ rotation transition state. This structure, has one imaginary frequency of a″ symmetry at 276.1i cm^{-1}. Its energy at the B3LYP/A level of theory, including the ZPVE energy corrections, is only 0.75 kcal/mol higher than the ground-state conformation. This is suggestive of an easy rotation around the Ti−B axis.

Our best calculated energy for the $^2A'$ ground state of $(TiBH_6)^0$ is −876.783 78 au (see Table 3), which, when compared with its positive analog[9] at the same level of theory, yields a value for its adiabatic ionization energy of 7.41 eV. Notice that the outermost electron of the neutral species corresponds to a 3d orbital on Ti.

$(TiBH_6)^-$. The B3LYP/A optimum geometry of the only stable isomer characterized for the anionic $(TiBH_6)^-$ can be found in Figure 2. Notice that its signature is (3, 2, 1) instead of (2, 3, 1) as it was for both the neutral and cation $(TiBH_6)^{0/+}$ systems.

This structure has C_s symmetry with two of the H_t atoms eclipsed with the two H_b atoms. Note also that the BH_3 moiety is substantially pyramidalized. Indeed, this geometrical disposition favors the interaction between the $2p_z$ orbital of B and the $3d_{xz}$ orbital of Ti, giving rise to a molecular bonding orbital between the two metals (see Figure 6). Shown in Table 4 are its occupancy of 1.91 e and its composition as a linear combination of $3d_{xz}$(Ti) and $2p_z$(B) atomic orbitals with some admixture of the 4s and 2s orbitals of Ti and B, respectively. This picture is fully consistent with the Bader's analysis of the charge density, which predicts a charge density of $\rho(r_c) = 0.103$ e/Å^3 at the Ti−B bond critical point (see the Table in the Supporting Information). Our best prediction for the Ti−B bond length is 2.027 Å, slightly shorter than those of the cation (2.047 Å) and the neutral (2.131 Å).

In considering the differences between the stable (2, 3, 1) isomers of the cation and the neutral and the (3, 2, 1) minimum of the anion, it is again important to consider the placement of the additional electron. Starting with the neutral (2, 3, 1) isomer,

TABLE 1: Atomic NBO Coefficients of the Two-Electron Three-Center Ti−H−X Molecular Orbitals on $(TiXH_6)^0$, X = B, Al, Ga, and, in Parentheses, Their Corresponding Hybridization Pattern, from the B3LYP/A Molecular Wave Function[a]

			coefficient		
bond no.	bond	occupancy	Ti	X	H
			Isomer (2, 3, 1)		
1−α	Ti−H−B	0.983	0.30 (s,11.69) (p,1.78) (d, 86.53)	0.65 (s, 21.28) (p, 78.47) (d, 0.25)	0.70 (s,99.92) (p, 0.08)
1−β	Ti−H−B	0.903		0.68 (s, 22.14) (p, 77.16) (d, 0.25)	0.73 (s, 99.92) (p, 0.08)
Σ		1.886			
2−α	Ti−H−B	0.983	0.30 (s, 11.76) (p, 1.76) (d, 86.47)	0.65 (s, 21.25) (p, 78.50) (d, 0.25)	0.70 (s, 99.92) (p, 0.08)
2−β	Ti−H−B	0.903		0.49 (s, 22.11) (p, 77.64) (d, 0.25)	0.81 (s, 99.92) (p, 0.08)
Σ		1.886			
1−α	Ti−H−Al	0.988	0.35 (s, 19.83) (p, 2.06) (d, 78.12)	0.45 (s, 16.36) (p, 81.81) (d, 1.83)	0.82 (s, 99.94) (p, 0.06)
1−β	Ti−H−Al	0.987	0.33 (s, 14.72) (p, 1.4) (d, 83.89)	0.46 (s, 16.31) (p, 81.82) (d, 1.87)	0.82 (s, 99.93) (p, 0.07)
Σ		1.976			
1−α	Ti−H−Al	0.967	0.32 (s, 14.07) (p, 1.80) (d, 84.13)	0.48 (s, 17.84) (p, 80.28) (d, 1.87)	0.81 (s, 99.93) (p, 0.07)
1−β	Ti−H−Al	0.970	0.31 (s, 10.26) (p, 1.66) (d, 88.07)	0.49 (s, 18.16) (p, 79.96) (d, 1.88)	0.82 (s, 99.92) (p, 0.08)
Σ		1.937			
1−α	Ti−H−Al	0.968	0.33 (s, 14.37) (p, 1.75) (d, 83.88)	0.48 (s, 17.79) (p, 80.34) (d, 1.87)	0.81 (s, 99.93) (p, 0.07)
1−β	Ti−H−Al	0.971	0.32 (s, 10.59) (p, 1.61) (d, 87.80)	0.48 (s, 18.09) (p, 80.03) (d, 1.88)	0.82 (s, 99.92) (p, 0.08)
Σ		1.939			
2−α	Ti−H−Ga	0.967	0.32 (s, 13.92) (p,1.82) (d, 84.25)	0.51 (s, 17.06) (p, 82.42) (d, 0.52)	0.80 (s, 99.95) (p, 0.05)
2−β	Ti−H−Ga	0.969	0.31 (s, 10.08) (p, 1.67) (d, 82.24)	0.52 (s, 17.38) (p, 82.10) (d, 0.52)	0.80 (s, 99.95) (p, 0.05)
Σ		1.936			
1−α	Ti−H−Ga	0.987	0.35 (s, 19.68) (p, 2.29) (d, 78.03)	0.47 (s, 14.71) (p, 84.78) (d, 0.51)	0.81 (s, 99.96) (p, 0.04)
1−β	Ti−H−Ga	0.986	0.34 (s, 14.46) (p, 1.58) (d, 83.96)	0.49 (s, 14.74) (p, 84.74) (d, 0.52)	0.81 (s, 99.95) (p, 0.05)
Σ		1.973			
			Isomer (2, 2, 2)		
2−α	Ti−H−Al	0.988	0.38 (s, 21.40) (p, 1.93) (d, 76.90)	0.41 (s, 12.83) (p, 85.34) (d, 1.83)	0.83 (s, 99.93) (p, 0.07)
 2−β	Ti−H−Al	0.987	0.36 (s, 18.66) (p, 1.59) (d, 79.75)	0.42 (s, 13.00) (p, 85.15) (d, 1.85)	0.83 (s, 99.93) (p, 0.07)
		1.9749			
Σ 2−α	Ti−H−Ga	0.986	0.38 (s, 21.19) (p, 2.02) (d, 76.79)	0.44 (s, 11.51) (p, 87.94) (d, 0.55)	0.80 (s, 99.95) (p, 0.05)
 2−β	Ti−H−Ga	0.985	0.36 (s, 18.89) (p, 1.63) (d, 79.47)	0.45 (s, 11.62) (p, 87.83) (d, 0.55)	0.82 (s, 99.95) (p, 0.05)
Σ		1.971			

TABLE 1 (Continued)

			coefficient		
bond no.	bond	occupancy	Ti	X	H
			Isomer (3, 3, 0)		
3−α	Ti−H−Al	0.974	0.39 (s, 11.57) (p, 1.68) (d, 86.75)	0.43 (s, 11.27) (p, 86.71) (d, 2.02)	0.81 (s, 99.91) (p, 0.09)
3−β	Ti−H−Al	0.964	0.37 (s, 9.85) (p, 1.27) (d, 88.87)	0.46 (s, 29.11) (p, 68.47) (d, 2.42)	0.81 (s, 99.91) (p, 0.09)
Σ		1.938			
3−α	Ti−H−Ga	0.973	0.40 (s, 12.07) (p, 1.72) (d, 86.21)	0.45 (s, 9.32) (p, 89.89) (d, 0.72)	0.79 (s, 99.94) (p, 0.06)
3−β	Ti−H−Ga	0.957	0.37(s, 9.76) (p, 1.21) (d, 89.02)	0.48 (s, 29.94) (p, 69.24) (d, 0.82)	0.79 (s, 99.95) (p, 0.05)
Σ		1.930			

[a] Both the α and β electron in the (2e, 3c) bond are separated, their total occupancy is considered by the sum of both electron occupation.

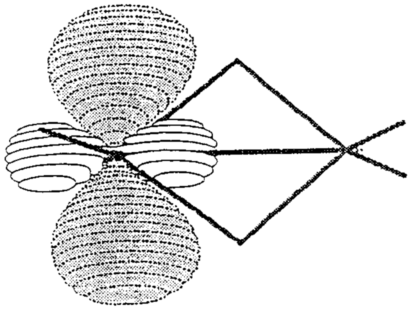


Figure 3. Singly occupied molecular orbital (SOMO) on the $(TiBH_6)^0$ isomer (2, 3, 1) with the contour lines separated by 0.05 au$^{3/2}$. The Ti atom is on the left.

TABLE 2: Bonding Properties, in au, of the Bond Critical Points of the $(TiAlH_6)^0$ (2, 3, 1) Isomer at the B3LYP/A Level of Theory

bond	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	ϵ
$Ti-H_t$	0.097	0.0490	−0.0348	0.047
$Ti-H_b$	0.049	0.1500	−0.0046	0.727
$Ti-H_b$	0.048	0.1248	−0.0054	0.545
$Al-H_b$	0.061	0.1975	−0.0154	0.053
$Al-H_b$	0.067	0.2175	−0.0183	0.031
$Al-H_t$	0.082	0.2742	−0.0249	0.001
rcp	0.040	0.0555	−0.0455	

formation of a singlet anion is accomplished by placing one more electron in the Ti d_{z^2} orbital (Figure 3). However, this orbital is capable of mixing with one of the Ti−H−B bridging orbitals (Figure 4). Two options are available at that point: maintaining three bridging bonds and a lone pair on Ti or H migration to Ti forming a Ti−H σ bond (Figure 5) and a bent bond between Ti and B (Figure 6). Obviously the second option is more energetically favored, and thus the (3, 2, 1) structure is the stable structure for the anion.

The two hydrogen atoms located in the intermetal zone form two very stable Ti−H−B (2e, 3c) bonds, 120 kcal/mol below the Ti−B bonding HOMO. Notice that these (2e, 3c) bonds are more polarized toward the BH_3 moiety than in both neutral and positive (2, 3, 1) isomers of the $(TiBH_6)$ system, as revealed by the atomic coefficients of their NBO's shown in Table 4. Thus, the calculated $B-H_b$ bond length (1.252 Å) is the shortest and the $Ti-H_b$ (1.981 Å) bond length is the longest of all the $(TiBH_6)^{+/0/-}$ isomers.

$(TiAlH_6)^0$. Three isomers, none of which has an open structure, have been characterized on the doublet ground-state potential energy surface of the neutral $(TiAlH_6)$ system. Notice that the (3, 2, 1) isomer is not a minimum for the neutral, although it was found to be a stable structure for the cation.[9]

Both the natural bonding analysis of Weinhold et al.[22] and Bader's topological analysis of the charge density[23] confirm that the molecular structure of the three neutral stable isomers, namely, (2, 3, 1), (2, 2, 2), (3, 3, 0), of $(TiAlH_6)$ are held together by the hydrogen bridge (2e, 3c) bonds and that there exist no Ti−Al bonding interactions, as shown by the lack of Ti−Al direct bonding properties in Tables 1 and 2.

From Bader's topological analysis of the charge density, it can be seen that the charge density at the bond critical points $Ti-H_t$ and $M-H_t$ is greater than the corresponding $Ti-H_b$ and $M-H_b$ (see the $TiAlH_6$ examples given in Tables 2 and 5 and in the Supporting Information for the all isomers calculated). This is logical as the bonds to the terminal hydrogens involve two electrons and two centers whereas the bridging bonds involve two electrons and three centers. Also note that for all of the bond critical points the values of the energy density, $H(r_c)$, are negative indicating that all bonds are of covalent character, the terminal bonds more so than the bridging bonds. Additional points of interest are well-demonstrated in the Bader analysis. The presence of ring critical points (rcp) in each of the closed isomers confirms the skeletal nature of the bridging bonds. The $Ti-H_b$ bonds also demonstrate a rather large ellipticities (ϵ), more so than do the $M-H_b$ bonds. The bent nature of the Ti−Al bond in the anion can be appreciated as well with an ϵ of 1.309 au.

The spin density population analysis for these neutral doublet species suggests that the unpaired electron is essentially located on the Ti atom for the (2, 3, 1) and the (2, 2, 2) isomers (spin densities on Ti, 1.14 and 1.10, respectively). For the (3, 3, 0) isomer the spin density on Ti is 0.14, but 0.83 on Al. Inspection of the SOMO's of the three isomers, depicted in Figure 7, reveals that both the (2, 3, 1) and (2, 2, 2) isomers have the unpaired electron on the $3d_{z^2}$ atomic orbital of Ti, while in the (3, 3, 0) the unpaired electron is located at the opposite side of the molecule in the lone-pair orbital of Al. This should lead to a distinct reactivity for the latter isomer relative to the former.

Comparing with the optimum geometries of their corresponding cations,[9] the $Ti-H_b$ bond lengths of the neutral (2, 3, 1) and the (2, 2, 2) are longer by 0.11 and 0.15 Å, respectively. However for the neutral (3, 3, 0) isomer the $Ti-H_b$ bond length

TABLE 3: MP4/A Base Level and Best Result Energies, in hartrees, Energy Corrections, in mhartrees, to the Base Level Energy Stable Structures, and the Ionization Energy, in eV, for $(TiXH_6)^0$ (X = B, Al, Ga)

$TiXH_6$	MP4/A	$\Delta E^{CCSD(T)/A}$	$\Delta A/B^{B3LYP}$	ZPVE	$E^{Best\ Result}$	ΔE (kcal/mol)	I
X = B							
(2, 3, 1)	−876.770 56	−13.05	−13.14	50.00	−876.783 78		7.41
X = Al							
(2, 3, 1)	−1093.955 45	−12.38	−29.75	39.94	−1093.994 67		6.86
(2, 2, 2)	−1093.953 21	−11.76	−29.98	39.34	−1093.992 64	1.27	7.59
(3, 3, 0)	−1093.899 50	−12.06	−30.02	39.98	−1093.938 64	35.16	7.21
X = Ga							
(2, 3, 1)	−2773.162 42	−13.67	−2072	38.99	−2775.246 54		6.84
(2, 2, 2)	−2773.163 29	−12.94	−2071	39.12	−2775.245 34	0.75	7.50
(3, 3, 0)	−2773.107 84	−13.04	−2073	39.02	−2775.192 96	33.62	

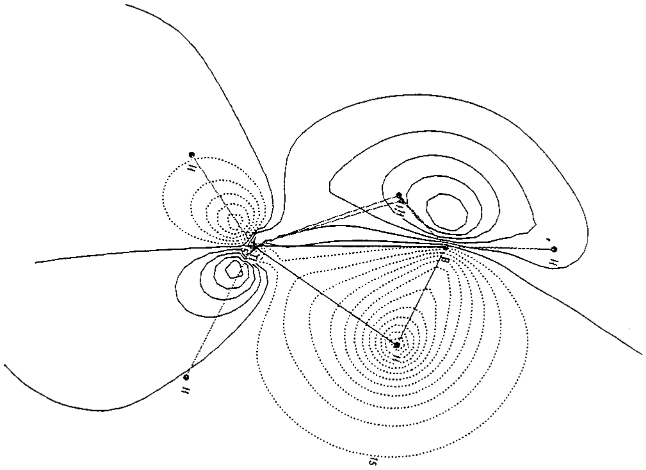


Figure 4. Ti−H−B bridging (2e, 3c) bond on the $(TiBH_6)^0$ (2, 3, 1) isomer with the contour lines separated by 0.05 au$^{3/2}$. The Ti atom is on the left.

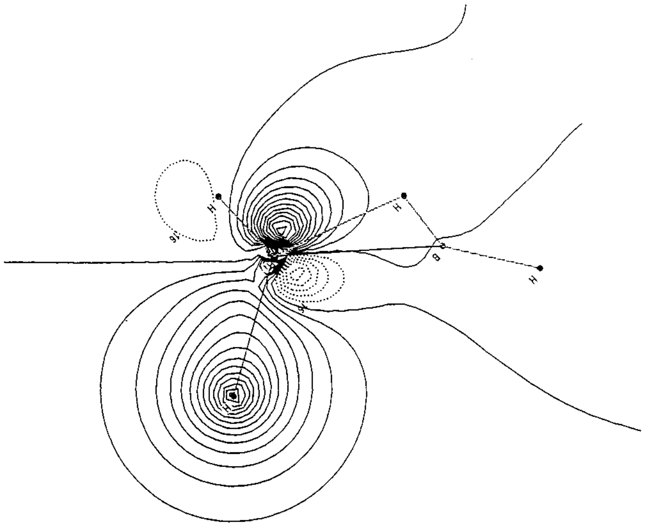


Figure 5. Ti−H_t molecular orbital bond on the $(TiBH_6)^0$ (2, 3, 1) isomer with the contour lines separated by 0.05 au$^{3/2}$. The Ti atom is on the left.

is shorter for the neutral than for the cation by 0.25 Å. The Al−H_b distances, not surprisingly, show the opposite trend, being shorter by 0.073 and 0.116 Å in the (2, 3, 1) and (2, 2, 2) isomers respectively, and larger by 0.026 Å in the (3, 3, 0) isomer when comparing the neutral structures to the cations.[9] By observing Figure 7, we can easily understand these trends in the distances to the bridging hydrogens. In both cases where the unpaired electrons is located on Ti, (2, 3, 1) and (2, 2, 2), the Ti−H_b distances increase and in the one structure when the unpaired electron is located more on Al, the Al−H_b distances increases.

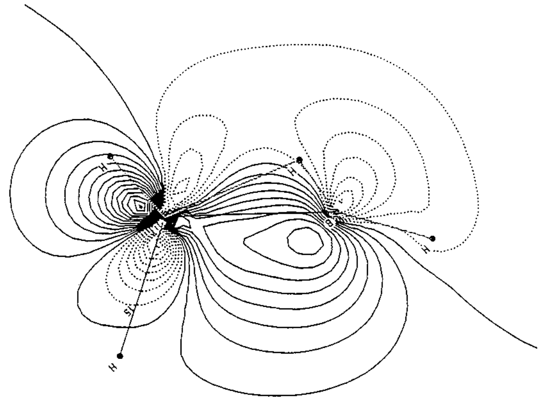


Figure 6. Ti−B bend molecular orbital bond on the $(TiBH_6)^-$ (3, 2, 1) isomer with the contour lines separated by 0.05 au$^{3/2}$. The Ti atom is on the left.

Also it is worth mentioning that the Ti−H_t bond lengths are invariably longer (by 0.072 Å for the (2, 3, 1) and (2, 2, 2) isomers and by 0.032 Å for the (3, 3, 0) isomer) for the neutral than for the cation.

As shown in Table 3, our highest level of theory energy calculations demonstrate that the (2, 3, 1) isomer is the lowest energy minimum of all the investigated structures. Nevertheless, the (2, 2, 2) isomer is almost degenerate in energy, lying only 1.22 kcal/mol above the global minimum. The (3, 3, 0) isomer is much higher in energy, 35.16 kcal/mol above the most stable (2, 3, 1) isomer.

The calculated ionization energies run opposite to the total energy ordering. Thus, the more stable isomer, (2, 3, 1), has the lowest ionization energy (6.86 eV). The $3d_{z^2}$ singly occupied molecular orbital is more stabilized in the (2, 2, 2) isomer, as reflected by its ionization energy of 7.59 eV, 0.77 eV larger than that of Ti. Finally the ionization energy of the (3, 3, 0) isomer is 7.71 eV, which is 1.72 eV larger than that of the Al.[26] Recall that the singly occupied orbital of (3, 3, 0) is on the aluminum atom.

$(TiAlH_6)^-$. Inspection of the stable molecular structures of the anionic $(TiAlH_6)^-$ system shown in Figure 2 reveals that the (2, 3, 1) isomer, stable for both $(TiAlH_6)^{+/0}$ systems, is replaced by the (3, 2, 1) isomer, following the pattern described above for the $(TiBH_6)^-$ system. In addition two isomers with signature (2, 2, 2) and one with signature (3, 3, 0) have also be found.

The bonding structure of the (3, 2, 1) isomer is very similar to the $(TiBH_6)^-$ case. Indeed, there exists a Ti−Al bonding NBO with a population of 1.85 *e*, which correspond to the HOMO (similar to Figure 6), and again we find that the system prefers one Ti−H σ bond and one Ti−X bent bond over maintaining three (2e, 3c) bonds and a lone pair on Ti. The two (2e, 3c) Ti−H−Al bonds are 97.4 kcal/mol more stable than the HOMO and 45.5 kcal/mol more stable than the Ti−H_t bonds.

TABLE 4: 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 of the $(TiXH_6)^-$, X = B, Al, Ga, Isomers

bond no.	bond	occupancy	coefficient Ti	coefficient X	coefficient H
			Isomer (3, 2, 1)		
2	Ti−H−B	1.9743	0.29 (s, 6.06) (p, 1.01) (d, 92.93)	0.63 (s, 23.27) (p, 76.51) (d, 0.22)	0.72 (s, 99.93) (p, 0.07)
1	Ti−B	1.9125	0.71 (s, 9.87) (p, 0.66) (d, 89.47)	0.71 (s, 16.36) (p, 83.55) (d, 0.09)	
2	Ti−H−Al	1.9359	0.38 (s, 9.96) (p, 1.42) (d, 88.62)	0.44 (s,12.69) (p, 85.68) (d, 1.63)	0.81 (s, 99.92) (p, 0.08)
1	Ti−Al	1.8520	0.60 (s, 5.64) (p, 1.14) (d, 93.22)	0.80 (s, 35.37) (p, 64.60) (d, 0.03)	
2	Ti−H−Ga	1.931	0.39 (s, 9.59) (p, 1.37) (d, 89.05)	0.45 (s, 9.80) (p, 89.65) (d, 0.55)	0.80 (s, 99.95) (p, 0.05)
1	Ti−Ga	1.841	0.57 (s, 6.66) (p, 1.09) (d, 92.25)	0.82 (s,39.42) (p, 60.49) (d,0.09)	
			Isomer (2, 2, 2)		
2	Ti−H−Al	1.9772	0.32 (s, 19.27) (p, 1.55) (d, 79.17)	0.47 (s, 17.28) (p, 81.30) (d, 1.42)	0.82 (s, 99.94) (p, 0.06)
2	Ti−H−Ga	1.900	0.38 (s, 21.90) (p, 1.26) (d, 76.84)	0.41 (s, 23.20) (p, 76.75) (d, 0.45)	0.83 (s, 99.97) (p, 0.03)
1	Ti−Ga	1.6440	0.94 (s,1.27) (p,0.78) (d,97.95)	0.34(s, 72.75) (p, 27.60) (d, 0.15)	
			Isomer (3, 3, 0)		
3	Ti−H−Al	1.9280	0.43 (s, 9.19) (p, 1.86) (d, 88.95)	0.37 (s, 6.77) (p, 91.39) (d, 1.84)	0.82 (s, 99.93) (p, 0.07)
3	Ti−H−Ga	1.9233	0.43 (s, 9.30) (p, 1.85) (d, 88.86)	0.38 (s, 4.99) (p, 94.24) (d, 0.77)	0.82 (s, 99.94) (p, 0.06)

The C_{2v} symmetry isomer (2, 2, 2) of $(TiAlH_6)^-$ that is the structural analogue to the neutral is the most stable of the two (2, 2, 2) isomers. Perhaps the most noticeable difference is the shortening of the Ti−Al distance by 0.14 Å with respect to the neutral as a consequence of the widening of both H_b−Ti−H_b and H_b−Al−H_b angles. Notice that despite this short Ti−Al distance, neither the NBO or Bader's analysis predict any Ti−Al bonding interaction for this isomer.

The other C_{2v} symmetry (2, 2, 2) isomer is planar at Ti, has a long Ti−Al distance of 2.907 Å, and is appreciably larger (shorter) Ti−H_b (Al−H_b) bond lengths. Indeed, the NBO analysis describes this isomer as an ionic $TiH_2 \cdot AlH_4^-$ complex, with strong $\sigma_{Al-Hb} \rightarrow 3d_{z^2}$ (Ti) and $\sigma_{Al-Hb} \rightarrow s^*_{Ti-Ht}$ donor−acceptor interactions of 20 kcal/mol.

The (3, 3, 0) isomer of $(TiAlH_6)^-$ has C_{3v} symmetry and its conformation is eclipsed. The corresponding staggered conformer has one imaginary frequency of a_1 symmetry at 135.5 *i* cm^{-1} corresponding to TiH_3 rotation. The energy difference between both conformers at the B3LYP/A + ΔZPVE level of theory is 3.27 kcal/mol, indicative of an easy rotation around the Ti−Al axis. Notice that the Ti−Al length for the (3, 3, 0) anion is 0.19 Å larger than for the neutral. The HOMO of this isomer is the lone-pair orbital of the aluminum. The three (2e, 3c) bonds lie 53.9 kcal/mol lower in energy than the HOMO and 27.51 kcal/mol lower than the Ti−H_t bonding orbitals according to the NBO analysis.

TABLE 5: Bonding Properties, in au, of the Bond Critical Points of the $(TiAlH_6)^{-1}$ (3, 2, 1) Isomer at the B3LYP/A Level of Theory

bond	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	ϵ
Ti−Al	0.042	0.0244	−0.0135	1.309
Ti−H_t	0.089	0.0577	−0.0297	0.052
Ti−H_t	0.091	0.0494	−0.0313	0.019
Ti−H_b	0.057	0.0529	−0.0080	0.264
Al−H_b	0.058	0.1564	−0.0166	0.058
Al−H_t	0.070	0.2222	−0.0197	0.027
rcp	0.042	0.0419	−0.0121	

Finally one more isomer with signature (3, 0, 3) and C_{3v} symmetry has been characterized on the B3LYP/A potential energy surface of $(TiAlH_6)^-$. It has an open staggered conformation, as show in Figure 2. The corresponding eclipsed conformer was found to have one imaginary a_2 frequency at 113.97 *i* cm^{-1}, which corresponds to the rotation around the Ti−Al single bond. The activation energy for this process is only 1.08 kcal/mol at the B3LYP/A + ΔZPVE level of theory. Notice that the Ti−Al bond length of 2.79 Å is very long. Indeed it is 0.29 Å larger than the sum of their covalent radii. In addition, the sum of the natural bond charges of the H_3Ti and the AlH_3 moieties are −0.12 and −0.88 e. Thus we conclude that this Ti−Al bond is largely ionic.

According to our best energy calculations, shown in Table 6, the three most stable isomers of the $(TiAlH_6)^-$ are quaside-

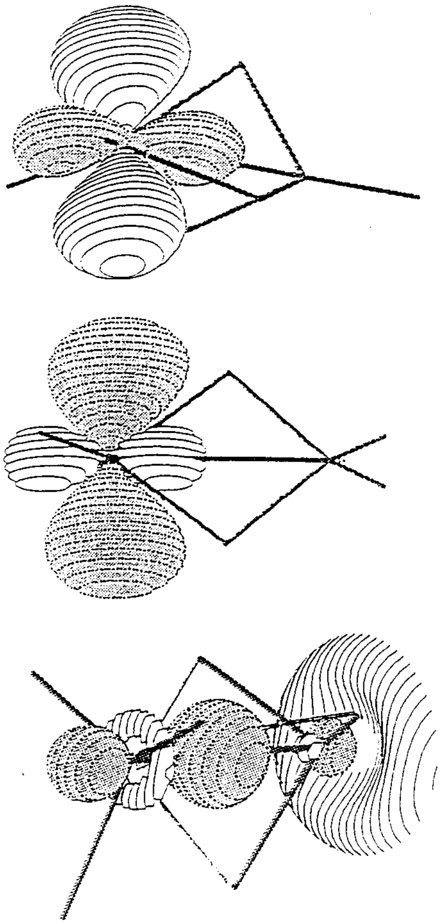


Figure 7. Singly occupied molecular orbital (SOMO) on $(TiAlH_6)^0$ with the contour lines separated by 0.05 au$^{3/2}$. The SOMO of the (2, 3, 1), (2, 2, 2) and (3, 3, 0) neutral isomers are at the top, in the middle, and on the bottom, respectively. The Ti atom is on the left.

generate, all three isomers lying within 0.31 kcal/mol. Finally the (2, 2, 2) isomer with planar Ti is 5.8 kcal/mol above the most stable (2, 2, 2) isomer and the open structure (3, 0, 3) isomer is the least stable, lying 13.21 kcal/mol higher than the global minimum. The additive corrections used to deal with the deficiencies in the basis set and the electron-correlation treatment decrease the relative energy window of the most stable three isomers from 5.0 kcal/mol at the MP4/A to the reported 0.31 kcal/mol as Best Result, both (2, 2, 2) structures and the (3, 0, 3) structure benefiting substantially from the CCSD(T) method.

$(TiGaH_6)^0$. Only two of the three stable isomers characterized earlier[2] on the PES of the $(TiGaH_6)^+$ cation have been located for the neutral $(TiGaH_6)^0$ system, namely, the (3, 1, 2) isomer is stable for cation but not for the neutral. In addition, the (3, 3, 0) isomer not found for the cation has been fully characterized as a local minimum for the neutral. Our calculations suggest that there is no Ti−Ga bonding interaction for any of the stable isomers of the neutral system. All the three isomers are held by their (2e, 3c) $Ti-H_b-Ga$ bonds formed by the bridging hydrogens, which consist of linear combinations of sd hybrids on Ti, sp on Ga, and the 1s atomic orbital of the bridging hydrogen similar to the $TiBH_6$ orbital depicted in Figure 4.

Compared to their corresponding (2, 3, 1) and (2, 2, 2) cations,[9] the $Ti-H_b$ and $Ga-H_b$ bond lengths of the neutral isomers are longer and shorter, respectively. This follows the pattern we have already seen for the other $(TiXH_6)^{+/0}$ systems, the umpaired electron on Ti pushing the bridging hydrogens away from that center. Remarkably, while the Ti−Ga distance (2.992 Å) is only 0.009 Å longer for the neutral (2, 3, 1) isomer, with respect to its cation, in the neutral (2, 2, 2) this distance is 2.737 Å, 0.19 Å shorter than its corresponding cation. However, the $Ti-H_t$ are longer for both neutral species by approximately 0.07 Å, with respect to their cations.

A (3, 3, 0) isomer with C_{3v} symmetry was also characterized as a local minima at the B3LYP/A level of theory. This isomer has an eclipsed conformation. The corresponding staggered structure was found to correspond with the transition state of the intramolecular rotation process. The energy barrier at the B3LYP/A + ΔZPVE level of theory is 3.73 kcal/mol.

Analysis of the atomic spin densities indicates that the unpaired electron of the neutral (2, 3, 1) and (2, 2, 2) isomers is on Ti. However, for the (3, 3, 0) isomer the unpaired electron is on the Ga atom. We see that again the trends established in the X = B and Al systems is followed, the SOMO's of these structures being very similar to those depicted in Figure 7. It is worth pointing out that the (2, 3, 1) and (2, 2, 2) isomers and the (3, 3, 0) isomer have their corresponding unpaired electrons on opposite ends. Consequently their reactivity should be very different.

The two most stable neutral isomers are predicted to be almost isoenergetic; the (2, 2, 2) isomer is calculated to lie only 0.75 kcal/mol above the (2, 3, 1) isomer according to our Best Results. Notice that this energy degeneracy among the neutral isomers is unlike their corresponding positively charged isomers,[9] which, at the same level of theory, have the same ordering but are separated by an energy gap of 15.98 kcal/mol. The neutral (3, 3, 0) isomer is considerably higher in energy than the other neutral minima. Our best estimation places it 33.62 kcal/mol above the lowest energy (2, 3, 1) neutral isomer.

$(TiGaH_6)^-$. The optimized geometries, at the B3LYP/A level of theory, of the four local minima found on the negative $(TiGaH_6)^-$ PES can be seen in Figure 2. Notice that there is no stable (2, 3, 1) isomer on this PES. Instead, an isomer with signature (3, 2, 1), which was not stable for the $(TiGaH_6)^{+/0}$ systems, was characterized as a local minima for the $(TiGaH_6)^-$ system. This (2, 3, 1) → (3, 2, 1) transformation from neutral to anionic species follows the established trend demonstrating the greater stability of a Ti−H σ bond and a Ti−X bent bond over one (2e, 3c) bond and a Ti lone pair. A (3, 0, 3) open structure was also characterized as a local minimum.

Once again, each of the hydrogens located between Ti and Ga are participants in (2e, 3c) bonds. Both the NBO and Bader's analysis are agreement with this picture, as shown in Table 4 and in the Supporting Information. However, we have found sound clues for the existence of a Ti−Ga binding interaction for the (3, 2, 1) and (2, 2, 2) isomers. No such clues are found for the (3, 3, 0) isomer. As shown in Table 4, a Ti−Ga natural bond orbital with an occupation of 1.84 *e* and slightly polarized toward Ga exists in the (3, 2, 1) isomer. This is the reoccurring bent bond, similar to that depicted in Figure 4. The Ti−Ga natural bond orbital of the (2, 2, 2) isomer, however, has the opposite polarization, namely toward Ti, and a population of only 1.64 electrons.

Finally an isomer with signature (3, 0, 3) and C_{3v} symmetry has also been found for $(TiGaH_6)^-$. Its geometrical parameters, which can be found in Figure 2, indicate that it has an staggered conformation. The eclipsed conformer corresponds to the transition state for rotation around the Ti−Ga bond. It has an a_2 imaginary normal mode at 129.4 i cm^{-1}. Inspection of the

TABLE 6: MP4/A Base Level and Best Result Energies, in hartrees, Energies Corrections, in mhartrees, and the Electron Affinity, in eV, to the Base Level Energy for the $(TiXH_6)^{-1}$ (X = B, Al, Ga) Stable Structures

$(TiXH_6)^{-1}$	MP4/A	$\Delta E^{\mathrm{CCSD(T)/A}}$	$\Delta A/B^{\mathrm{B3LYP}}$	ZPVE	$E^{\mathrm{Best\ Resultt}}$	ΔE (kcal/mol)	EA
X = B							
(3, 2, 1)	−876.781 40	−16.47	−13.08	43.70	−876.810 38		
X = Al							
(3, 2, 1)	−1093.979 18	−12.64	−29.09	36.22	−1094.027 81	0.31	
(2, 2, 2)	−1093.973 99	−18.36	−28.83	35.99	−1094.028 31	0.00	0.97
(3, 3, 0)	−1093.981 93	−12.49	−28.86	38.20	−1094.028 21	0.06	2.44
(2, 2, 2)(Ti pl)	−1093.962 88	−20.94	−28.60	36.49	−1094.019 06	5.80	
(3, 0, 3)	−1093.947 64	−22.65	−27.64	33.81	−1094.007 25	13.21	
X = Ga							
(3, 2, 1)	−2773.200 05	−12.81	−2072.6	35.41	−2775.293 14	0.58	
(2, 2, 2)	−2773.186 94	−19.37	−2069.8	34.66	−2775.284 57	5.96	1.07
(3, 3, 0)	−2773.200 53	−13.11	−2074.1	36.77	−2775.294 07	0.00	2.75
(3, 0, 3)	−2773.164 64	−24.87	2068.2	33.45	−2775.267 42	16.73	

TABLE 7: Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) at the B3LYP/A Level of Theory for $(TiXH_6)^0$, X = B, Al, Ga, Isomers

freq.	int.	freq.	int.	freq.	int.	freq.	int.
X = B (2, 3, 1)							
227	18.7	651	13.9	1293	3.3	2113	97.2
334	188.8	709	175.8	1317	118.9	2212	13.5
345	13.5	1105	13.7	1665	469.2	2231	56.1
538	19.9	1128	16.7	1686	224.7	2688	76.0
608	0.6	1291	148.6				
X = Al (2, 3, 1)							
253	25.5	463	12.61	1004	121.9	1659	491.4
295	5.8	641	129.5	1134	1091.9	1673	121.5
325	184.0	839	123.2	1504	153.3	1683	183.1
383	24.6	856	116.5	1586	27.9	2006	145.2
447	9.2	971	104.9				
X = Al (2, 2, 2)							
157	12.7	563	118.8	1211	340.2	1667	531.2
289	252.7	648	98.9	1334	596.0	1694	204.6
292	0.0	711	0.0	1354	18.5	1941	65.2
312	0.0	726	317.6	1468	595.9	1955	220.1
319	7.9	823	194.4				
X = Al (3, 3, 0)							
328	0.0	558	114.5	912	7.3	1623	0.0
386	14.11	650	110.8	1112	811.6	1692	351.6
395	0.1	863	28.6	1533	2.2	1692	351.6
395	0.2	863	28.6	1533	2.2	1736	170.6
558	114.5	912	7.3				
X = Ga (2, 3, 1)							
237	26.1	447	9.2	954	246.9	1658	9.2
293	42.3	642	110.3	1046	804.1	1661	471.1
294	0.7	790	89.2	1472	141.1	1681	284.1
342	150.4	809	87.3	1574	7.4	2080	96.6
409	0.0	916	36.2				
X = Ga (2, 2, 2)							
176	8.3	528	81.2	1207	232.5	1667	519.1
230	0.9	648	53.4	1301	775.4	1694	245.8
285	247.6	700	265.4	1373	60.4	1999	58.1
309	0.0	734	0.0	1430	278.8	2007	174.0
330	9.6	788	139.9				
X = Ga (3, 3, 0)							
303	12.1	559	115.4	846	17.5	1573	15.2
329	0.0	633	93.9	983	621.7	1690	314.2
370	1.5	825	2.0	1492	4.9	1690	314.2
370	1.5	826	0.4	1492	4.9	1735	165.7
559	115.4	846	17.5				

energies of the minimum and transition state indicates that the rotation barrier is very low, i.e., 1.03 kcal/mol, at the B3LYP/A + ΔZPVE level of theory. Its Ti−Ga bond length of 2.678 Å is, however, 0.1 Å longer that the sum the their covalent radii. This, along with sum of the natural bond charges of the H_3Ti and GaH_3 moieties, 0.17 and −1.17 *e*, respectively, are suggestive of an electrostatic Ti−Ga bonding interaction.

Inspection of our Best Results for the energies of the three most stable isomers of $(TiGaH_6)^-$ reveals that the (3, 3, 0) and (3, 2, 1) isomers are almost degenerate (the latter is 0.58 kcal/mol higher) and the (2, 2, 2) isomer lies only 5.96 kcal/mol above the lowest energy isomer (3, 3, 0). Finally the (3, 0, 3) is a good bit higher in energy, i.e., 16.73 kcal/mol higher that the (3, 3, 0) most stable isomer. Again, it is seen that the CCSD(T) method stabilizes the (2, 2, 2) and (3, 0, 3) isomers more than the other two.

Owing to the fact that for this system there are numerous stable isomers lying very close in energy, experimental determination of which isomer is present will best be achieved by infrared spectroscopy. For this reason, we report the infrared harmonic vibrational frequencies of the neutrals in Table 7.

In examining the infrared harmonic vibrational frequencies of each isomer, we note a few high-intensity modes as characteristic of one isomer or another. For the (2, 3, 1) structure, identifying modes would include the $(H_t)_2Ti$ bend at 325 cm^{-1} and two bridged-bending modes at 971 and 1004 cm^{-1}. In the (2, 2, 2) neutral isomer, the $(H_t)_2Ti$ bending mode is located at 289 cm^{-1}, significantly lower that the mode in the (2, 3, 1) isomer. Other unmistakable high-intensity modes lie at 726, 1211, 1334, and 1468 cm^{-1}. The (3, 3, 0) isomer should be easily recognized by the pattern of modes that arise from the C_{3v} symmetry. In particular the grouping at 1736 cm^{-1} and the degenerate pair at 1692 cm^{-1} should be characteristic.

For the $TiGaH_6$ neutral isomer identification, IR harmonic vibrational frequencies are again illustrative. The (2, 3, 1) isomer should be easily recognizable by the $(H_t)_2Ti$ bending mode at 342 cm^{-1} and the very high-intensity mode at 1046 cm^{-1}. The (2, 2, 2) isomer has its $(H_t)_2Ti$ bending mode redshifted in comparison to the (2, 3, 1) isomer, falling at 285 cm^{-1}, and should otherwise be recognizable by the four modes located in the range from 1207 to 1430 cm^{-1} where neither of the other two isomers have any vibrational modes. Of course the (3, 3, 0) isomer would be charaterized by its symmetry and the three Ti−Ht stretching modes (1690 cm^{-1} (×2) and 1735 cm^{-1}).

4. Conclusions

The isomers of both neutral and negative $(TiXH_6)^{0/-}$, X = B, Al, Ga, systems have been studied using density functional theory for the potential energy surface scan and coupled-cluster theory including single and double excitations, with sufficiently flexible basis sets, for the energies.

For the neutral $(TiXH_6)^0$, X = B, Al, Ga, systems, structures of C_s symmetry and signature (2, 3, 1) have been found to be stable on the B3LYP/A potential energy surfaces. In addition,- for X = Al, Ga, two more isomers of C_{2v} and C_{3v} symmetry and signatures (2, 2, 2) and (3, 3, 0), respectively, have also been characterized as stable structures.

The (3, 3, 0) isomer is predicted to lie more than 30 kcal/mol higher in energy than the (2, 3, 1) and (2, 2, 2) isomers for the neutral $(TiXH_6)^0$, X = Al, Ga systems, with the latter isomers being almost isoenergetic, i.e., the (2, 3, 1) is only 1.27 kcal/mol more stable than the (2, 2, 2) for X = Al and 0.75 kcal/mol for X = Ga.

For the negative $(TiXH_6)^-$systems, isomers of C_s symmetry exist also. However their signatures are (3, 2, 1) as opposed to the (2, 3, 1) found for both positive and neutral $(TiXH_6)^{+,0}$ systems. The transformation of the (2, 3, 1) structure to the (3, 2, 1) structure for the anionic species is due to the fact that one Ti−H σ bond and a Ti−X bent bond are energetically more stable than a combination of one (2e, 3c) bond and a lone pair on Ti. The structural analogues to the neutral C_{2v} (2, 2, 2) and C_{3v} (3, 3, 0) isomers do also exist for the negative systems. Additionally, one more isomer of C_{2v} (2, 2, 2) type but planar at Ti has been found for X = Al and another of C_{3v} symmetry and (3, 0, 3) signature for both X = Al and X = Ga.

Although in the case of X = B there is only one stable structure (3, 2, 1), the additional stable structures involving bridging bonds for X = Al and X = Ga cases lie very close in energy. In the case of X = Al, the (2, 2, 2) structure is the global minimum for the singlet anion with the (3, 3, 0) structure lying only 0.06 kcal/mol and the (3, 2, 1) structure 0.31 kcal/mol higher. When X = Ga, the (3, 3, 0) structure is found to be the global minimum. The (3, 2, 1) structure lies only 0.58 kcal/mol higher, but the (2, 2, 2) structure is 5.96 kcal/mol less stable. Both (3, 0, 3) structures lie significantly higher.

All the isomers studied, except the (3, 0, 3) open structure, have very strong (2e, 3c) hydrogen bridging bonds. Also most of the considered structures do not have Ti−X bonding interactions, which reinforces earlier evidence of the skeletal character of hydrogen bridging bonds for this kind of compound. However, it is worth noting that the negative (3, 2, 1) isomers of X = B, Al, and Ga all have one T−X bent bond formed through a combination of the Ti d_{z^2} orbital and a p_z orbital on the X atom. The anionic (2, 2, 2) isomer does show some σ bonding in the case of X = Ga because of the improved overlap of Ti and Ga atomic orbitals. Naturally, the open structure (3, 0, 3) isomers of X = Al and Ga have a Ti−X single bond, though for these isomers this bonding interaction has a substantial electrostatic character.

For the negative $(TiXH_6)^-$, X = Al, Ga systems, all their isomers with hydrogen bridge bonds lie very close in energy, namely, within 5.80 kcal/mol for X = Al and within 5.96 kcal/mol for X = Ga. The open structures lie much higher in energy.

Acknowledgment. This research has been supported by the University of the Basque Country (Euskal Herriko Unibertsitatea) and the Basque Government (Eusko Jaurlaritza), Grant No. GV/203.215-49/94. A.G. thanks the Spanish Agencia de Cooperación Iberoamericana (AECI) for a grant, and J.E.F. thanks the Basque Government for a postdoctoral grant.

Supporting Information Available: Tables giving Cartesian coordinates and bonding properties for the $(TiXH_6)^0$ and $(TiXH_6)^-$ isomers and IR frequencies and intensities for the $(TiXH_6)^-$ isomers (14 pages). Ordering and accessing information is given on any current masthead page.

References and Notes

(1) Dain, C. J.; Downs, A. J.; Goode, M. J.; Evans, D. G.; Nicholls, K. T.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1991**, 967.

(2) Kudo, T.; Gordon, M. S. *J. Phys. Chem.* **1995**, *99*, 9340.

(3) García, A.; Ugalde J. M. *J. Phys. Chem.* **1996**, *100*, 12277.

(4) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(5) Switkes, E.; Stevens, R. M.; Lipscomb, W. N.; Newton, M. D. *J. Chem. Phys.* **1969**, *51*, 2085.

(6) Xu, Z.; Lin, Z. *J. Coord. Chem. Rev.* **1996**, *156*, 139 and references therein.

(7) Demachy, I.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; Maseras, F.; Oro, L. A.; Valero, C.; Volatron, F. *J. Am. Chem. Soc.* **1996**, *118*, 8388.

(8) Volatron, F.; Duran, M.; Lledos, A.; Jean, Y. *Inorg. Chem.* **1993**, *32*, 951.

(9) García, A.; Mercero, J. M.; Ugalde, J. M. *J. Phys. Chem. A* **1997**, *101*, 5953.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(11) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(12) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(13) (a) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081. (b) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193.

(14) Ignacio, E. W.; Schlegel, H. B. *J. Comput. Chem.* **1991**, *12*, 751.

(15) Hay, P. J. *J. Chem. Phys.* **1971**, *66*, 4377.

(16) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062.

(17) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J Chem Phys.* **1980**, *72*, 650.

(18) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(19) (a) Scuseria, G. E.; Jansen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1988**, *89*, 7382 (b) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(20) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(21) Frish, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Croslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision A.1);* Gaussian, Inc.: Pittsburgh, PA, 1995.

(22) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(23) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

(24) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1980**, *27*, 1924.

(25) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

(26) Porterfield, W. W.; *Inorganic Chemistry*; Addison-Wesley Publishing Company: New York, 1984.