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Molecular and Electronic Structures of TiH3X Compounds

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Abstract

Electronic structure calculations, with a triple zeta plus polarization basis set and second-order perturbation theory, are used to predict the molecular and electronic structures for TiH3X compounds, with X = CH3, NH2, OH, SiH3, PHz, and SH. It is found that for the second-period substituents CH3, NHz, and OH the structures are similar to those of the corresponding silicon compounds. On the other hand, the S, P, and Si substituents show an increasing propensity to form bridging structures when an appropriate level of electron correlation is included in the geometry optimizations.

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Molecular and Electronic Structures of TiH3X Compounds

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Electronic structure calculations, with a triple zeta plus polarization basis set and second-order perturbation theory, are used to predict the molecular and electronic structures for TiH3X compounds, with X = CH3, NH2, OH, SiH3, PH2, and SH. It is found that for the second-period substituents CH3, NH2, and OH the structures are similar to those of the corresponding silicon compounds. On the other hand, the S, P, and Si substituents show an increasing propensity to form bridging structures when an appropriate level of electron correlation is included in the geometry optimizations.

Introduction

Titanium compounds are important as catalysts in a wide variety of organometallic reactions, including, for example, the hydrosilation[1] and silane polymerization[2] reactions. The simplest prototypical Ti compounds are the hydrides TiH3X, where X = CH3, NH2, OH, SiH3, PH2, or SH. Such compounds provide a baseline understanding of the fundamentals of bonding and structure against which more complex substituents can be assessed. While there have been a few theoretical studies of the role of Ti compounds as catalysts,[3,4] there has to our knowledge been no systematic study of the titanium hydrides.

There have been two previous computational papers on TiH3-CH3. Dobbs and Hehre[5] performed partially constrained restricted Hartree–Fock (RHF) 3-21G[6] geometry optimizations on several saturated and unsaturated TiC compounds. Williamson and Hall[7] performed both RHF and seven pair generalized valence bond (GVB) geometry optimizations with several basis sets and found no evidence of the "agostic" bonding suggesting by the 101° HCTi angle determined by a previous electron diffraction study.[8] The HCTi angle found by Williamson and Hall was consistently around 107°.

The electronic structure of titanium and the compounds it forms is intriguing, since it is the simplest group IVB analog of the well-studied group IVA elements C and Si. Surprisingly little seems to be known about the impact of the fundamental differences between the s^2p^2 electronic configuration in group IVA and s^2d^2 electronic configuration in group IVB. In the present paper we report the results of geometry optimizations for TiH3X compounds as the first step in a series of investigations of titanium chemistry.

Computational Methods

Geometries were optimized at both the RHF and second-order perturbation theory (MP2[9]) levels of theory. The basis sets used in this work are 6-311G(d,p)[10] for the main group elements combined with the Ti triple zeta plus polarization basis set developed by Wachters[11] and Goddard.[12] In the following, this basis set will be referred to as TZVP. All stationary points were characterized as minima or transition states by calculating and diagonalizing the hessian (matrix of energy second derivatives), using the analytic hessian methods in the electronic structure codes GAMESS[13] and GAUSSIAN92.[14] Final energetic comparisons are made with fourth-order perturbation theory (MP4[15]) using the same basis sets. Localized orbital
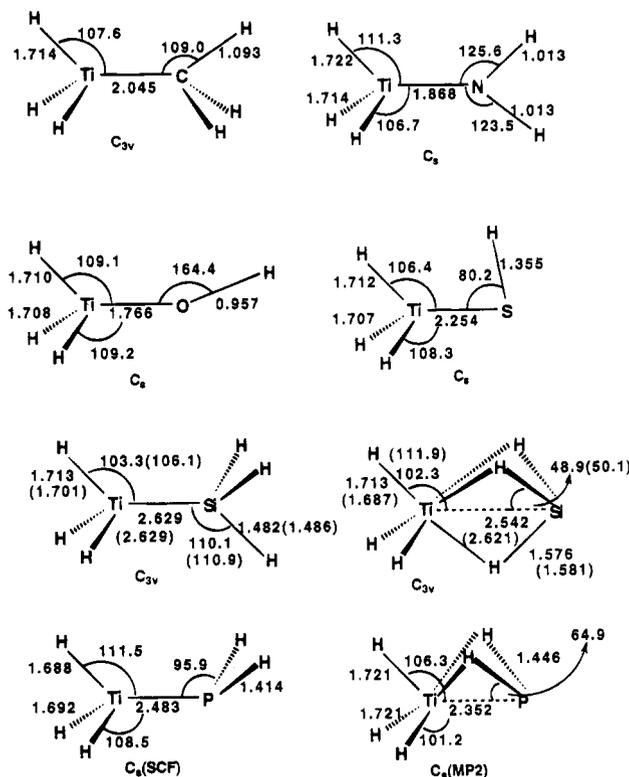
Figure 1. MP2/6-31G(d) structures, with SCF geometries in parentheses. Bond lengths are given in Å, bond angles in deg.

calculations[16] and total density plots have been used to aid in the interpretation of the results.

Results and Discussion

The MP2-optimized structures for each of the six compounds of interest here are summarized in Figure 1. These structures and related wave functions and energetics are discussed in the following subsections.

TiH3CH3. This is the only species investigated in this work that has been the subject of previous *ab initio* calculations. The MP2/TZVP structure predicted in the present work is in good agreement with that found earlier by Williamson and Hall. As noted by those authors, the H–C–Ti angle is close to tetrahedral, and there is no evidence for "agostic" bonding between Ti and the geminal hydrogens. Note also that the global minimum for this compound is found to be eclipsed, rather than the usual staggered arrangement expected for analogous silicon

(a)

(b)

(c)

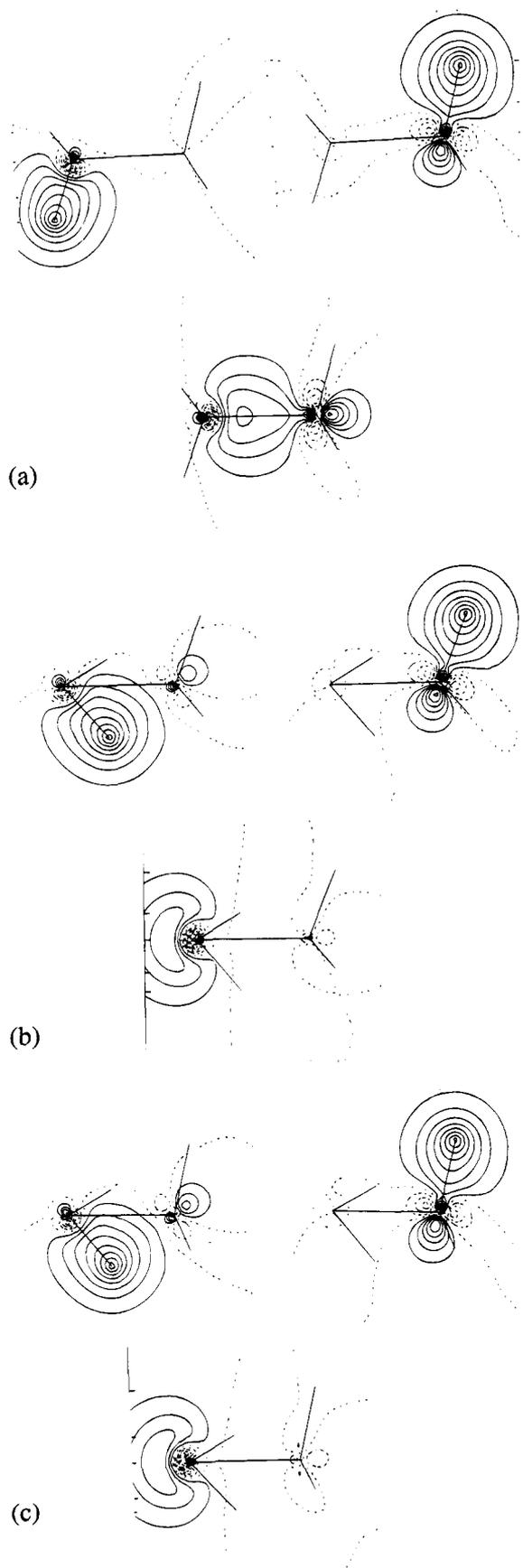**Figure 2.** Contour plots (each contour is separated by 0.05 bohr$^{-3/2}$) of LMO's in TiH₃SiH₃. Si is on the left; Ti is on the right. In each case, the SiH bond LMO is shown in the upper left; the TiH bond LMO is shown in the upper right; and the SiTi bond (Si lone pair) LMO is shown in the lower middle: (a, top) open structure at the SCF geometry; (b, middle) bridged structure at the SCF geometry; (c, bottom) bridged structure at the MP2 geometry.
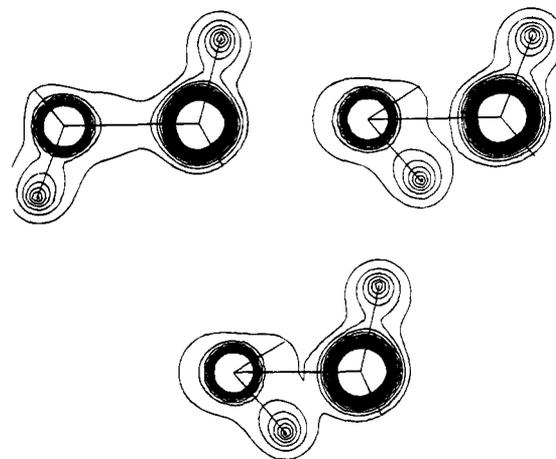

Figure 3. Contour plots (each contour is separated by 0.05 bohr$^{-3/2}$) for the total electron density for TiH₃SiH₃. The open structure at the SCF geometry is shown at the upper left; the bridged structure at the SCF geometry is shown at the upper right; and the bridged structure at the MP2 geometry is shown in the lower middle.

and carbon compounds, at the MP2/TZVP level of theory. However, TiH₃CH₃ should be thought of as having essentially free internal rotation, since the internal rotation barrier is on the order of 0.1 kcal/mol. At the SCF level of theory with the same basis set, the staggered structure is predicted to be slightly lower than eclipsed.

TiH₃SiH₃. Two minima are found on the ground state potential energy surface for this compound (Figure 1). One of these minima is an open, staggered structure, with HTiC and HCTi angles of 103.2° and 110.1°, respectively. The internal rotation barrier to the eclipsed rotamer from this structure is again a very small 0.4 kcal/mol. More interesting is the discovery of an isomer of the staggered structure in which the three Si hydrogens turn inside, with HSiTi angles of 48.9°, to form an apparent triple bridge structure. At the SCF/TZVP level of theory, both structures are found to be minima on the potential energy surface, with the bridged structure lying 9.9 kcal/mol *higher* in energy than the staggered form. These relative stabilities are reversed at the MP2/TZVP level, with the bridged isomer lying 2.7 kcal/mol *lower* in energy. The use of higher order perturbation theory (i.e., MP4) increases the relative stability of the bridged structure to 7.3 kcal/mol. So, it is clear that correlation plays a major role in stabilizing this bridge structure.[17] At the MP2 level of theory, the Ti- - -H distance between titanium and the silicon hydrogens is 1.916 Å. This is about 0.2 Å longer than the "direct" TiH bond lengths. Interestingly, the TiSi distance is 0.08 Å *shorter* in the bridged structure.

Some insight into the nature of the bonding in these structures can be gained by examining the localized molecular orbital (LMO) contour diagrams shown in Figure 2 and the total density contour maps shown in Figure 3. The key localized orbitals are those corresponding to the TiH, SiH, and TiSi bonds. These are shown for the open (staggered) structure, the bridged structure at the SCF geometry, and the bridged structure at the MP2 geometry. The LMO's for the open structure (Figure 2a) are those one would expect, on the basis of experience with ethane or methylsilane: three equivalent TiH bond LMO's, three equivalent SiH bond LMO's, and a TiSi σ bond. This set of LMO's gives rise to the unsurprising total density map shown in Figure 3. At the SCF geometry, the LMO's for the bridged structure are rather different (except for the three equivalent TiH bond LMO's that are essentially the same for all three geometries). The most striking difference is that the bridged structure has no LMO that corresponds to a TiSi bond. Rather, there is a Si lone pair and three SiH bond LMO's that have

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some delocalization onto Ti. As a result, the total electron density between Ti and Si (Figure 3) is much less than that in the open structure. Relaxation of the geometry of the bridged structure from the SCF (Figure 2b) to the MP2 geometry (Figure 2c) has important consequences. The Si lone pair remains essentially the same, but the delocalization of the SiH bonds onto Ti clearly increases. This manifests itself into the more obvious three-center Si—H—Ti bonds that appear in the total density shown in Figure 3. So, correlation corrections clearly play an important role in determining the electronic structure of this molecule.

Due to the discovery of the bridged structure, attempts were made to identify analogous species for the carbon analog; however, no such structures were found. In addition, the alternative bridging arrangement, in which the hydrogens on Ti, rather than those on Si, are bent in, returns to the open structure in Figure 2 with no intervening barrier. Presumably, this means that Ti is better able to participate in three-center bridged bonding in a neutral environment than is Si. Finally, attempts to find structures that have just one or two bridging hydrogens on either the Ti or Si end were not successful.

TiH₃NH₃. The geometry of this compound may be described as an essentially tetrahedral TiH₃ bonded to an essentially planar NH₂. This is similar to the analogous silylamines, in which N also tends to planarity due to π backbonding.[18] As noted above, this molecule also exhibits essentially free internal rotation.

TiH₃PH₂. Both the SCF/TZVP and MP2/TZVP geometries for this compound are shown in Figure 1. The SCF level of theory finds only an open, staggered structure, with TiPH angles of 95.9°. No bridged structure is found on the SCF surface. Indeed, geometry optimizations at the GVB level[19] (TCSCF) (the highest occupied and lowest empty molecular orbitals are correlated), as well as the eight-electron, seven-orbital MCSCF level[20] (all but the TiH bonds are correlated), yield essentially the same results as the SCF calculation. On the other hand, optimization of the geometry of this molecule at the MP2 level of theory detects only the bridged structure shown in Figure 1. Reoptimization of the MP2 structure using MP4(SDTQ)/TZVP predicts a more strongly bridged geometry, with TiPH angles of 57.8°, as compared with 64.9° predicted using MP2. The MP2 nonbonded Ti- - -H distances are 2.178 Å, nearly 0.3 Å longer than the corresponding distances in TiH₃SiH₃. These Ti- - -H distances decrease to 2.034 Å at the MP4 geometries. So, once again, correlation plays an important role in determining the molecular and electronic structure. The latter may be examined further using the LMO's (Figure 4) and total densities (Figure 5). Unlike the LMO's in TiH₃SiH₃, those in bridged TiH₃PH₂ are more like those which one would expect, since TiH, SiH, and TiP bonds and a P lone pair are found. Also, note that the delocalization of the PH bonds onto Ti is much smaller than was found for the SiH bonds. As a result, the total SCF density in bridged TiH₃PH₂ looks more like two-center bonding than three-center bonding. However, since the SCF and MP2 structures are dramatically different, the SCF density is not likely to be definitive.

TiH₃OH. As shown in Figure 1, the TiOH angle is nearly linear in this compound. Indeed, at the SCF level of theory, the linear structure is the only minimum on the potential energy surface. Using MP2, the barrier to linearity is still only 0.05 kcal/mol, and this value remains essentially the same at the MP4(SDTQ) level of theory. The eclipsed rotamer is predicted to be very slightly (0.01 kcal/mol) lower in energy than the staggered one.

TiH₃SH. Both the SCF and MP2 levels predict the eclipsed structure to be slightly lower than staggered, 0.06 kcal/mol at the MP2 level of theory. Using MP4, the relative stabilities
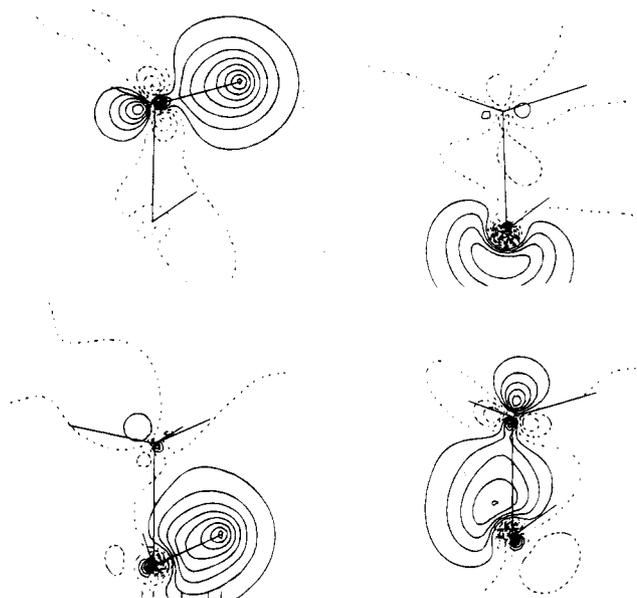

Figure 4. Contour plots (each contour is separated by 0.05 bohr⁻³/²) of LMO's in TiH₃PH₂. A PH bond LMO is shown in the upper left; a TiH bond LMO is shown in the upper right; the PTi bond LMO is shown in the lower left; and the P lone pair LMO is shown in the lower right.
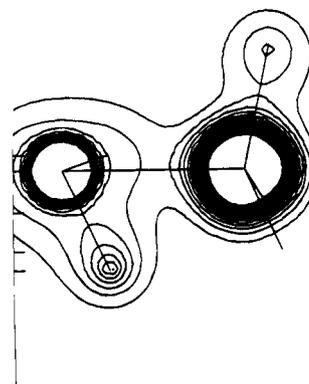

Figure 5. Contour plot (each contour is separated by 0.05 bohr⁻³/²) for the total electron density for TiH₃PH₂.

are reversed, with staggered lower by a similarly small amount (0.07 kcal/mol). As has been noted in previous paragraphs, MP2 predicts the H on the third-period main group atom to bend in toward Ti. In this case the difference between the predictions of SCF and MP2 is small with TiSiH angles of 93.9° and 80.2° predicted at the SCF and MP2 levels of theory, respectively. So, one cannot think of the structure of this compound as bridged.

Summary and Conclusions

The molecular structures for TiH₃X, where X = CH₃, NH₂, or OH, are similar to those one would expect, on basis of analogy with the corresponding SiH₃X compounds. The long TiX bond lengths lead to virtually free internal rotation, planar N, and almost linear O. In contrast, proceeding right to left in the third period of the periodic table, the XH bonds are found to have an increasing propensity to form bridging three-center Ti- - -H- - -X bonds. This is a reflection of both the ability of Ti to accommodate more than the main group complement of four ligands and the electrostatic attraction between the negative H and the positive Ti and X centers. The electron density around H certainly increases in the order of X = S < P < Si, and this must play an important role in the ultimate molecular structures. In contrast, the hydrogens attached to the second-

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period atoms have positive partial charges and shorter bond lengths. Both of these factors will mitigate against the formation of bridged structures. On the other hand, an important factor that contributes to the formation of bridged structures is the fact that in these TiH₃X compounds Ti is formally coordinatively unsaturated. Therefore, replacement of the titanium hydrogens with substituents that have the capability to donate more electrons to Ti (e.g., cyclopentadienyl) may decrease the propensity to form bridged structures.

It is noteworthy that the bridged structure is the global minimum on the TiH₃SiH₃ potential energy surface only when dynamic correlation is included in the calculation, via second- or fourth-order perturbation theory. Similarly, TiH₃PH₂ is predicted to have an open structure at the SCF and MCSCF levels of theory, but geometry optimizations that include dynamic correlation find only the bridged structure. So, electron correlation plays a critical role in determining these molecular geometries.

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