MCSCF Study of Multiple Bonding between Ti and the Main-Group Elements C, Si, N, and P

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The nature of the multiple bonding of $H_2Ti{=}EH_2$ (E = C, Si) and $H_2Ti{=}EH$ (E = N, P) molecules has been investigated with the multiconfiguration SCF (MCSCF) method. It is shown that the Ti−C and Ti−P bond lengths decrease with bond rotation, whereas the Ti−Si bond length increases. MCSCF geometry optimization shows that Ti−N has triple-bond character with a linear Ti−N−H bond angle that results from strong back-bonding from the N lone pair into the empty Ti d orbitals. The rotation barrier and bond dissociation energy for Ti=E are estimated with the MCSCF + multireference second-order perturbation theory (MRMP2) method. The singlet rotation barriers in Ti=C, Ti=Si, and Ti=P are estimated to be 15.9, 8.6, and 9.3 kcal/mol, respectively. The Ti=C and Ti=Si bond dissociation energies are estimated to be 83.4 and 56.9 kcal/mol, respectively. The Ti≡N triple-bond energy is about 30 kcal/mol larger than that of the carbon species, whereas the energy of the Ti=P bond is about 8 kcal/mol smaller than that of the silicon species.

Introduction

The nature of chemical bonds connecting main-group with transition-metal atoms is fundamental to a variety of processes, such as chemical vapor deposition and catalysis.[1] In the past several decades, there has been considerable progress in the development of experimental and theoretical analysis of the nature of transition-metal compounds.[2−5] Nevertheless, this area of study is challenging due to the complexity of transition metals, such as many low-lying electronic states that lead to a variety of geometries, spin states, and oxidation states.

To understand the chemistry of transition-metal complexes, it is necessary to consider the fundamental nature of the chemical bonding between the transition-metal and main-group elements. In the last few decades, there have been several reports about transition-metal−main-group bonds.[2,6−19] However, there have been few quantitative studies of the nature of multiple bonds between transition-metal and main-group elements. The multiple bonds between transition-metal and main-group elements are of interest in many important chemical and industrial processes. There have been some theoretical reports about transition-metal−main-group double bonds, such as alkylidene (M=C),[8,9] silylidene (M=Si),[10] imido (M=N),[11] and phosphinidine (M=P)[12] complexes. Although the overall features of transition-metal−main-group double bonds are qualitatively similar to those of main-group−main-group double bonds (i.e., one σ and one π bond), their bonding results from the interactions between the five metal d and three main-group p orbitals. This is quite different from the main-group−main-group p orbital interactions. Previous studies have also illustrated the need for a reliable wave function for elucidating metal−main-group bonds.

Recently, there has been considerable interest in titanium compounds as advanced materials, catalysts. and electronic and magnetic devices.[20−22] Because of these important applications, it is useful to determine precise information about the bonding between Ti and main-group elements. Since Ti is electron deficient in many of its common molecular environments, the

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chemical behavior of titanium-containing molecules is frequently somewhat different from that of the molecules containing lighter man-group or other transition-metal elements.[19] As a result, it is frequently difficult to describe Ti compounds with a single electronic configuration. That is, a single Lewis structure generally does not present an adequate picture of many Ti compounds, especially those that may be described as "unsaturated".[19] For this reason, the quantum-mechanical description of such species often requires a multiconfigurational wave function, such as the multiconfiguration SCF (MCSCF)[23] method. Several previous theoretical studies[9−14,19] of unsaturated titanium compounds have illustrated that the MCSCF approach is crucial for understanding their chemical behavior as well as the nature of their electronic structure.

In this paper, the nature of multiple bonding between Ti and the main-group elements E = C, Si, N, P is analyzed using MCSCF-based wave functions. The nature of π bonding is assessed, on the basis of the bond dissociation energies and the barriers to internal rotation.

Computational Details

All calculations were performed using the GAMESS[24] electronic structure program. The molecular structures of the lowest singlet and triplet states for $H_2Ti{=}CH_2$, $H_2Ti{=}SiH_2$, $H_2Ti{=}NH$, and $H_2Ti{=}PH$ were optimized at the MCSCF level with the SBKJC[25,26] effective core potential (ECP) and triple-ζ with polarization (TZVP)[27,28] basis sets. The bond rotation process was used for analyzing the Ti=E π bonding of these species, while the bond dissociation process was used for estimating their total bond energies.

The complete active space (CAS)SCF active space must consistently describe the Ti=E bond as it rotates from planar ($\phi = 0°$) to perpendicular ($\phi = 90°$). For E = C, Si, this requires at least the three p orbitals plus two electrons for E and three d orbitals ($\sigma + \pi$) plus two electrons for Ti. Therefore, the simplest adequate active space is (4,6), four electrons in six orbitals. To obtain more accurate energies, an (8,10) active space has been used. The additional four electrons and four orbitals arise from the two Ti−H bonding orbitals whose natural orbital occupation numbers (NOON) are smaller than 1.97 and two Ti−H antibonding orbitals whose NOON are larger than about 0.03. Further increases in the active space do not have any significant effect on the electronic structure. The active spaces used for E = N, P are discussed below.

To achieve a more reliable energy comparison, MRMP2[29] single-point energy calculations were performed with the ECP and TZVP basis sets at the MCSCF geometries.

Results and Discussion

Ti=C vs Ti=Si. The MCSCF geometric parameters for planar and twisted $H_2Ti{=}CH_2$ and $H_2Ti{=}SiH_2$ are summarized in Table 1. For these two species, the planar structure has a singlet ground state. However, the twisted structure has a singlet ground state in the carbon species and a triplet ground state in the silicon species. The Ti−C bond length in $H_2Ti{=}CH_2$ is shorter than that of its silicon analogue, as expected. It is interesting that the Ti−C bond length in the planar structure is somewhat longer than that in the twisted one. Generally, when a molecule with a double bond is internally rotated, the bond length increases, since the π bond is broken by the bond rotation. This is the behavior observed for E = Si (Table 1).

Table 1. Computed Geometrical Parameters for the $H_2Ti{=}CH_2$ and $H_2Ti{=}SiH_2$ Molecules at the MCSCF(8,10)/TZVP Level of Theory (Distances in Å and Angles in deg)

geometric params	$H_2Ti{=}CH_2$ planar	$H_2Ti{=}CH_2$ twisted	$H_2Ti{=}SiH_2$ planar	$H_2Ti{=}SiH_2$ twisted[a]
R(Ti-E)	1.937	1.901	2.501	2.579
R(Ti−H)	1.817	1.831	1.790	1.767
R(E−H)	1.083	1.102	1.487	1.485
∠(H−Ti−H)	128.0	143.9	124.1	123.2
∠(H−E−H)	113.7	115.7	106.0	106.5

[a] Triplet state.

The origin of the behavior of the Ti=C bond may be understood from the natural orbital occupation numbers (NOON). Normally, the π and π^* NOON in a double-bond species change from about 2.0 and 0.0, respectively, to about 1.0 and 1.0 as the π bond is broken, reflecting the fact the a diradical has been formed. However, the MCSCF calculation reveals that the π orbital NOON in planar $H_2Ti{=}CH_2$ increases from 1.74 to 1.88 as the rotation occurs. This is consistent with the calculated bond length decrease and suggests only modest diradical character.

Both the Ti−H and C−H bond lengths in the planar structure are somewhat shorter than those in the twisted molecule. There is a considerable increase in the H−Ti−H bond angle when the molecule is twisted. This bond angle in the planar structure is about 15° smaller that that in the twisted one. The behavior of the Ti d_{xy} orbital in the Ti=E species may be responsible for the geometric parameter changes around the Ti atom. In the planar structures, this orbital mainly participates in Ti−H bonding. However, this orbital makes a contribution to the π bond, as well as to the Ti−H bond, in the twisted structure. In this manner, the π bonding is largely preserved as the molecule rotates, and little or no π bond strength is lost.

The nature of the bonding in the silicon species is considerably different from that of the carbon species. The Ti−Si bond length increases upon bond rotation. When the planar silicon species is rotated, the NOON for the π bonding orbital decreases from about 1.6 to 1.0. This means the π bonding in the planar structure is essentially broken as the molecule is rotated; thus, the species is now essentially a diradical. This difference is very likely related to the weaker π-bonding ability of Si compared to that of C. There are no significant changes in the Ti−H and Si−H bond lengths when the bond rotation occurs. The H−Ti−H bond angle of the planar structure decreases by about 4° upon the rotation.

The shapes of the potential energy surfaces for E = C, Si as a function of the Ti=E bond rotation at the

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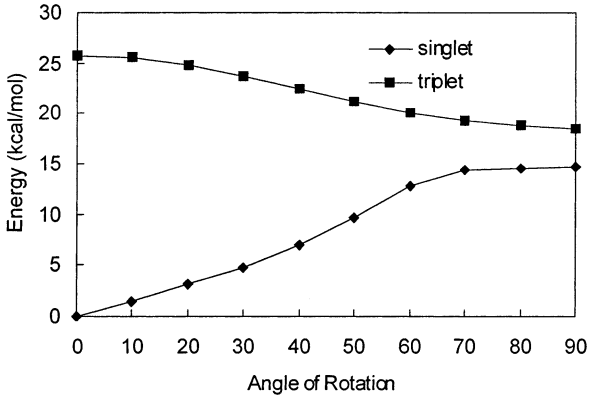

Figure 1. Change in MCSCF(8,10)/TZVP energy with respect to the Ti=C bond rotation in $H_2Ti{=}CH_2$.

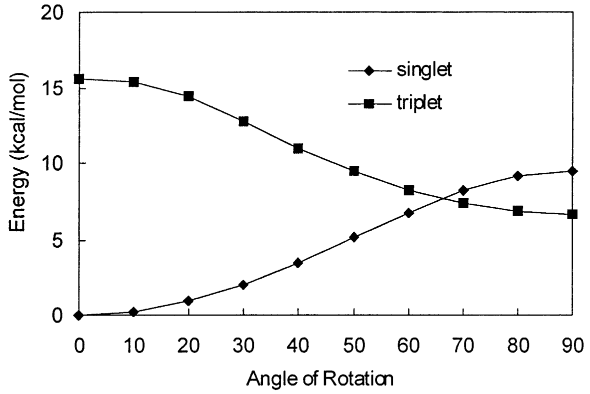

Figure 2. Change in MCSCF(8,10)/TZVP energy with respect to the Ti=Si bond rotation in $H_2Ti{=}SiH_2$.

MCSCF(8,10)/TZVP level are illustrated in Figures 1 and 2. In these two figures, the planar structure has a rotation angle (ϕ) of 0°, while $\phi = 90°$ corresponds to the twisted structure. For $H_2Ti{=}CH_2$ the singlet surface is always lower in energy than the triplet surface. The planar structure is the global minimum for the singlet state, whereas the triplet state minimum is at the twisted structure. In the planar structure, the triplet state lies about 25 kcal/mol above the singlet state. This singlet−triplet energy difference is about 5 kcal/mol in the twisted structure.

The relative shapes of the $H_2Ti{=}SiH_2$ internal rotation energy curves are somewhat different from those of the carbon analogue (Figure 2), although the qualitative trend of the two curves is similar to the carbon case. The singlet and triplet curves cross around $\phi = 65°$. The singlet state lies about 15 kcal/mol below the triplet state in the planar structure. However, the triplet state is lower in energy than the singlet state in the twisted structure. The highest level of theory, MRMP2/TZVP, predicts the singlet−triplet energy gaps for the planar carbon and silicon species to be 28.6 and 14.3 kcal/mol, respectively (Table 2).

The rotation barriers for $TiH_2{=}EH_2$, E = C, Si, are summarized in Table 2 together with their planar singlet−triplet energy gaps. As can be seen in this table, the computed energy barriers are not very sensitive to the theoretical level. In the carbon species, the highest level of theory, MRMP2/TZVP, predicts the singlet and triplet energy barriers to be 15.9 and −7.2 kcal/mol, respectively. For silicon, the singlet barrier is estimated to be about half of the carbon value, whereas the carbon and silicon triplet barriers are similar. Although the rotation barriers cannot rigorously be equated with the π bond energies, the *relative* rotation barriers, as well as the NOONs discussed above, suggest that the π bond in Ti=C is stronger than that of Ti=Si.

The MCSCF Ti=E bond dissociation energies for E = C, Si are summarized in Table 3. The Ti=C and Ti=Si bond energies are computed to be 61.3 and 37.1 kcal/mol at the MCSCF(4,6)/SBKJC level, respectively. Increasing the size of the active space to MCSCF(8,10)/SBKJC scarcely affects these values. When dynamic correlation is taken into account at the MRMP2//MCSCF(8,10)/SBKJC level, the predicted bond dissociation energies increase to 77.5 and 50.3 kcal/mol, respectively. At the highest level of theory, MRMP2/TZVP, the dissociation energies for Ti=C and Ti=Si bond are 83.4 and 56.9 kcal/mol, respectively. Therefore, there are significant basis set and electron correlation effects on the computed dissociation energies.

Ti=N and Ti=P Bonds. One might suspect that the nature of Ti=N and Ti=P bonding differs from that of Ti=C and Ti=Si, since the tricoordinate N and P atoms have nonbonding electron pairs. Both RHF and MCSCF geometry optimizations predict the Ti−N−H bond angle in $H_2Ti{=}NH$ to be linear, whereas the Ti−P−H bond angle in the phosphorus analogue is bent. Previous reports of linear M−N−H bond angles[2,15] suggest this may be due to strong back-donation from the nitrogen lone pair into the empty M d orbitals.

The linear Ti−N−H bond angle means that the Ti−N bond has triple-bond character similar to that of the acetylene molecule (two π bonds and one σ bond). These features suggest an active space composed of six electrons in three bonding and three antibonding orbitals, CASSCF(6,6), in $H_2Ti{=}NH$ with a linear Ti−N−H angle. This active space is increased (10,10) for more accurate calculations, in which the two Ti−H bonding orbitals and their four electrons and two Ti−H antibonding orbitals are added to the (6,6) active space. The phosphorus species with a bent Ti−P−H angle has one nonbonding orbital on P. Therefore, two more lone-pair electrons and one more nonbonding orbital is added to the active space for the Ti=P species. Thus, the basic active spaces for studying the Ti=P bond are designated as (6,7). The largest active spaces used for the Ti=P species in this study are (10,11), in which two Ti−H bonding orbitals and their four electrons and two Ti−H antibonding orbitals are included.

The MCSCF geometric parameters for $H_2Ti{=}NH$ and $H_2Ti{=}PH$ are summarized in Table 4. As discussed above, the Ti−N−H bond angle is 180°, whereas $H_2Ti{=}PH$ is a planar structure with a Ti−P−H bond angle of 64.8°. The Ti−N bond length is computed to be 1.698 Å, ~0.24 Å shorter than the Ti=C bond. The NOON for the σ bonding orbital of the Ti−N bond is 1.97, while those for the two π bonding orbitals are ~1.90. The Ti=P bond length in the planar structure is longer than that of the rotated structure. This behavior is similar to that discussed above for the Ti=C compound. The computed Ti=P bond length is somewhat shorter than the Ti=Si bond length, but the internal rotation barrier about the Ti=P bond is similar to that

Table 2. Internal Rotation Energy Barriers (kcal/mol) for $H_2Ti{=}CH_2$ and $H_2Ti{=}SiH_2$ at Various Levels of Theory

	Ti═C			Ti═Si		
calculational level	singlet	triplet	ΔE^a	singlet	triplet	ΔE^a
MCSCF(4,6)/SBK	15.6	−8.0	25.0	8.8	−8.8	14.6
MCSCF(8,10)/SBK	17.0	−8.0	27.3	9.3	−7.4	14.4
MRMP2//MCSCF(4,6)/SBK	14.2	−8.5	28.5	9.5	−9.8	15.7
MRMP2//MCSCF(8,10)/SBK	16.7	−8.6	28.8	9.0	−8.1	14.2
MCSCF(4,6)/TZVP	15.9	−7.5	23.6	9.3	−11.1	17.4
MCSCF(8,10)/TZVP	14.6	−7.3	25.8	9.5	−9.0	15.6
MRMPT2//MCSCF(4,6)/TZVP	16.6	−6.0	29.1	9.2	−12.2	16.9
MRMP2//MCSCF(8,10)/TZVP	15.9	−7.2	28.6	8.6	−8.7	14.3

[a] Singlet−triplet energy gap in the planar structure.

Table 3. Bond Dissociation Energies (kcal/mol) for for $H_2Ti{=}CH_2$ and $H_2Ti{=}SiH_2$ at Various Levels of Theory

calculational level	Ti═C	Ti═Si
MCSCF(4,4)/SBK	61.3	37.1
MCSCF(8,8)/SBK	62.0	40.0
MRMP2//MCSCF(4,4)/SBK	76.6	48.8
MRMP2//MCSCF(8,8)/SBK	77.5	50.3
MCSCF(4,4)/TZVP	61.8	39.1
MCSCF(8,8)/TZVP	62.7	42.0
MRMP2//MCSCF(4,4)/TZVP	82.0	54.7
MRMP2//MCSCF(8,8)/TZVP	83.4	56.9

Table 4. Computed MCSCF Geometric Parameters for $H_2Ti{=}NH$ and $H_2Ti{=}PH$ (Distances in Å and Angles in deg)

		$H_2Ti{=}PH^b$	
geometric params	$H_2Ti{=}NH^a$	planar	twisted
R(Ti−E)	1.698	2.273	2.255
R(Ti−H)	1.810	1.791	1.806
R(E−H)	0.997	1.488	1.502
∠(H−Ti−H)	133.4	127.4	134.9
∠(Ti-E−H)	180.0	64.8	59.1

[a] MCSCF(10,10)/TZVP. [b] MCSCF(10,11)/TZVP.

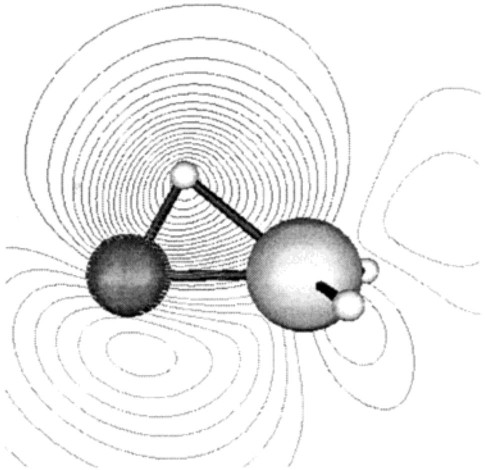

Figure 3. Localized molecular orbital contour diagram for P- -H- -Ti bonding of the $H_2Ti{=}PH$ molecule with the twisted structure.

of the Ti═Si species, despite the apparently rather different electronic structures. When the planar $H_2Ti{=}PH$ is internally rotated, the NOON of the σ bonding orbital decreases from 1.91 to 1.87, whereas the NOON of the π orbital increases from 1.77 to 1.86. Thus, the diradical character is modest in the TiN and TiP species and changes only slightly upon internal rotation. At the highest level of theory, MRMP2/TZVP//MCSCF(10,11)/TZVP, the internal rotation barrier in singlet $H_2Ti{=}PH$ is estimated to be 9.3 kcal/mol, as compared with 8.6 kcal/mol in the Si analogue.

Table 5. Bond Dissociation Energies (kcal/mol) for $H_2Ti{=}NH$ and $H_2Ti{=}PH$ at Various Levels of Theory

calculational level	Ti═N^a	Ti═P^b
MCSCF/SBK	90.4	28.0
MCSCF/TZVP	99.7	33.3
MRMP2//MCSCF/SBK	109.1	49.7
MRMP2//MCSCF/TZVP	116.5	48.1

[a] (10,10) active space. [b] (10,11) active space.

The Ti−H bond length in rotated $H_2Ti{=}PH$ is somewhat longer than that in the planar structure. The Ti−P−H bond angle of 64.8° in the planar structure decreases by about 6° when the molecule is rotated. In fact, the hydrogen attached to the P atom (H_p) gets closer to the Ti atom as the Ti═P bond is rotated. In the rotated structure, the Ti- - -H_p distance is estimated to be 1.965 Å. This means that there is considerable interaction between the Ti and H_p atoms in the twisted structure. The localized orbital analysis (Figure 3) shows that the H- - -Ti- - -H_p interaction is similar to the three-center bonding in B_2H_6.

The bond dissociation energies of $H_2Ti{=}NH$ and $H_2Ti{=}PH$ are summarized in Table 5. At the best level of theory, MRMP2 with the TZVP basis set, the Ti≡N bond dissociation energy is estimated to be 116.5 kcal/mol. This value is about 30 kcal/mol larger than that of Ti═C. On the other hand, the estimated Ti═P bond strength is 48.1 kcal/mol, which is about 8 kcal/mol smaller than that of the Ti═Si bond.

Conclusion

The nature of multiple bonding between Ti and four main-group elements, C, N, Si, and P, has been investigated using multireference wave functions. The π bonding properties are examined using the bond rotation about the M−E bond, while complete bond dissociation is used to examine the total bond energy. It is found that the Ti−C bond length decreases upon bond rotation, whereas the Ti−Si bond length increases. The bonding may be understood using the MCSCF natural orbital occupation numbers (NOON). The singlet $H_2Ti{=}CH_2$ and $H_2Ti{=}SiH_2$ internal rotation barriers are estimated to be 15.9 and 8.6 kcal/mol, respectively, whereas the triplet barrier is about 8 kcal/mol for both species. The Ti−N−H bond angle is predicted to be linear, whereas the Ti−P−H bond angle is bent. The linear nature in the nitrogen compound may be understood in terms of significant Ti−N triple-bond character caused by strong back-bonding from the N lone pair into the Ti empty d orbitals. The Ti═P singlet rotation barrier is estimated to be about 9 kcal/mol.

The bond dissociation energies for these four species were examined using MRMP2 with the TZVP basis set. The Ti═C and Ti═Si bond dissociation energies are estimated to be 83.5 and 56.9 kcal/mol, respectively. The Ti≡N bond energy is predicted to be about 30 kcal/mol larger than that of the carbon species, whereas the Ti═P bond energy is about 8 kcal/mol smaller than that of the silicon species.

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