Structure, Bonding, and Heats of Formation of Silatitanacyclobutanes

Vassiliki-Alexandra Glezakou and Mark S. Gordon*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

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The MP2/TZVP geometries and the standard heats of formation at 0 and 298.15 K of 1,2- and 1,3-silatitanacyclobutanes and a number of smaller Ti- and/or Si-containing alkanes are calculated using the G2 model. The G2 procedure was suitably modified to allow for treatment of first-row transition elements and was directly applied to the reference compounds, which were subsequently connected to the two rings via the appropriate homodesmic reactions. The expected accuracy should be on the order of 3 kcal mol^{-1}. Bonding and structural characteristics are discussed in terms of Boys localized orbitals and Bader density analysis.

Introduction

Metallacyclobutanes[1] are known for a wide variety of reactivities with both organic and inorganic reagents, playing a key role in a wide spectrum of important reactions including methylene transfer to organic carbonyls,[2,3a] formation of enolates,[2b,3] electron transfer from activated halides,[4] olefin metathesis,[5] ring-opening polymerization,[6] and complexation with metal halides.[7] Their reactivity is influenced by both kinetic and thermodynamic factors, the metal center and its ligands, and the substituents.[8] Correlated photoelectron spectroscopy (PES)[9] is often employed to address electronic structure related questions.

Unfortunately, metallacyclobutanes are not particularly stable for high-quality PES studies. On the other hand, the analogous silametallacyclobutanes show considerable thermal stability and have been chemically, structurally, and spectroscopically characterized for a number of transition metals[9] (M = Ti, Zr, Nb, and Mo) and Th.[10] From the early transition metals, only Ti has been characterized by X-ray diffraction, while tetravalent Zr, Nb, and Mo offer more stable analogues for study. They all crystallize in a monoclinic unit cell of $P2_1/m$ symmetry.

We are interested in the thermochemical properties as well as the reaction behavior (ring opening) of these cyclic systems. As a first step, and given the lack of thermochemical data, the MP2 structures and heats of formation obtained using homodesmic reactions[11] are reported for the 1-sila-2- and 1-sila-3-metallacyclobutanes. In principle, reliable heats of formation could be directly calculated using a basis of triple-ζ quality with extra diffuse and polarization functions at a high level of theory to account for correlation, for example, using higher orders of perturbation theory or extensive configuration interaction methods. Calculations at this level become very expensive. Instead, the heats of formation of a number of smaller Ti-containing alkane and silane reference compounds were calculated, using the Gaussian-2 model;[12a] these were subsequently combined in the homodesmic reactions from which the estimated G2 heats of formation of the cyclic systems were finally obtained.

Computational Details

The heats of formation of 1-sila-2- and 1-sila-3-titanacyclobutane were calculated from the appropriate homodesmic reactions (vide infra) involving two and three heavy atom fragments. A modified G2 procedure was employed for the direct evaluation of the heats of formation of these smaller molecules.

TABLE 1: Modified G2 Procedure to Include Transition Metals

original G2	modified G2
(H, C, Si)	(Ti)
HF geometries, frequencies/6-31G(d,p)	
MP2(FU) geometries/6-31G(d,p)	MP2(FZC) geometries, frequencies/H, C, Si, Ti, TZVP
The following calculations refer to single-point frozen core energies at MP2(FZC) geometries	
MP4SDTQ/6-311G(d,p)	MP4SDTQ/Ti, TZV(f)
MP4SDTQ/6-311+G(d,p)	MP4SDTQ/Ti, TZV + (f)
MP4SDTQ/6-311G(2df,p)	MP4SDTQ/Ti, TZV(2fg)
QCISD(T)/6-311G(d,p)	QCISD(T)/Ti, TZV(f)
higher level correction (HLC)	HLC
MP2/6-311+G(3df,2p)	MP2/Ti, TZV + (3fg)

Three ab initio progams were employed for our calculations:

The **GAMESS** suite of programs[13] was used to perform self-consistent-field (SCF) geometry optimizations and to obtain Boys localized molecular orbitals[14] using the built-in triple-ζ[15a] plus polarization[15b] (TZVP) basis set. GAMESS was also used for exponent optimization for the higher order polarization functions on Ti.

The diffuse s, p, and d polarization functions for Ti were extracted from the standard TZV basis in an even-tempered fashion; the resulting exponents are

$$\alpha_s = 0.0350; \quad \alpha_p = 0.0239; \quad \alpha_d = 0.0207$$

The f and g polarization functions were obtained by individual exponent optimizations on the ground ^3F state of Ti atom. These optimizations were performed with a singles and doubles configuration interaction (CISD) from a restricted Hartee−Fock (ROHF) wave function, in which only the $(4s)^2$ $(3d)^2$ electrons were correlated. The optimized exponents are

$$\alpha_f = 0.591; \quad \alpha_g = 0.390$$

The (2f) and (3f) polarization sets were obtained following the even-scaling rule,[17a] according to which atomic basis

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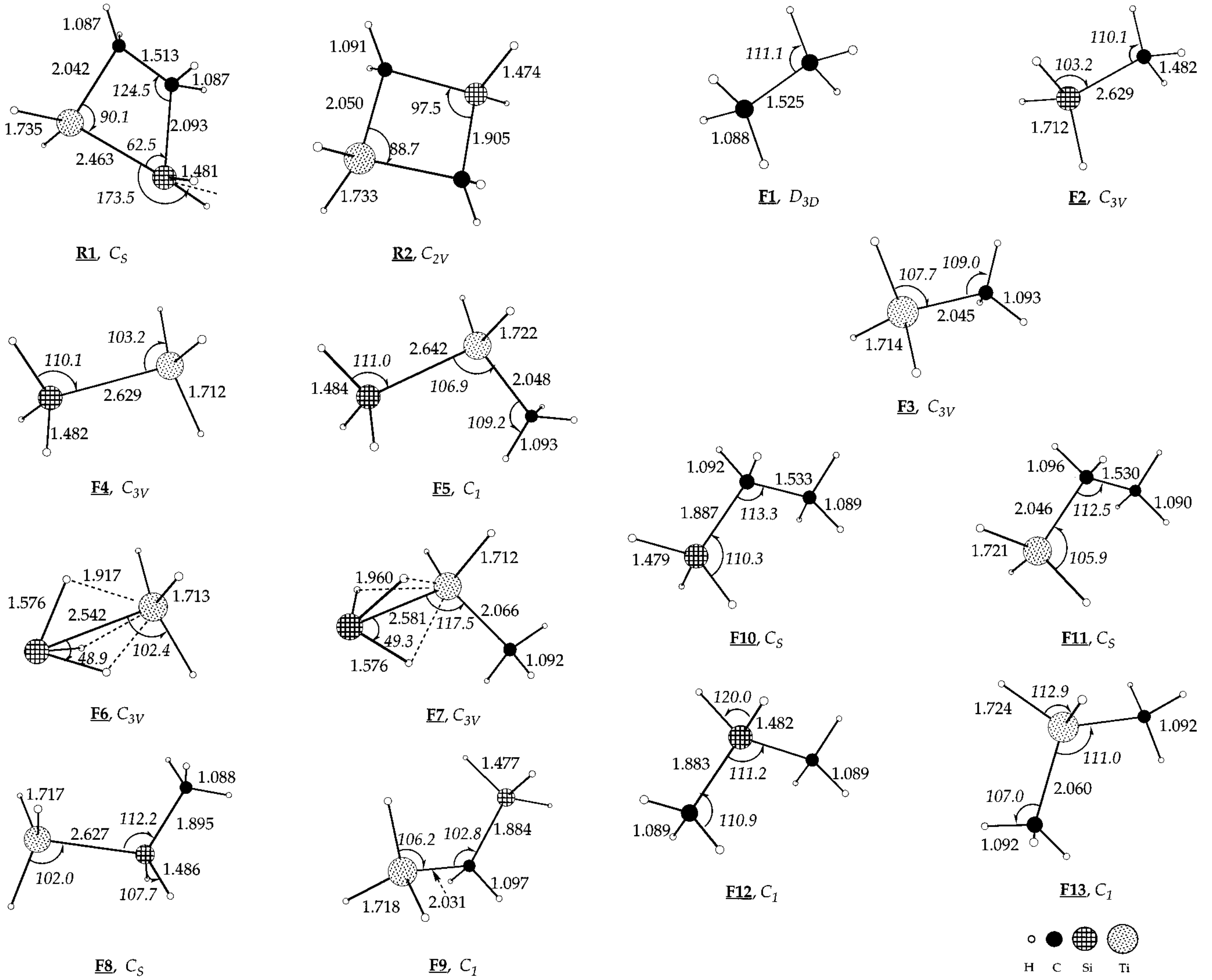


Figure 1. MP2/TZVP geometries of the silatitanacyclobutanes (R1 and R2) and the reference compounds (F1−F13). For C_1 symmetries, the average bond distances are given.

functions with the same angular momentum should have exponents in a geometric progression:

$$(2f) = (1/2\ f_o,\ 2f_o)^{17b} \quad \text{and} \quad (3f) = (1/4\ f_o,\ 1f_o,\ 4f_o)^{17b}$$

where f_o refers to the original single f-exponent.

The **Gaussian 92** program[18] was used for second-order perturbation theory (MP2) geometry optimizations[19] and analytic Hessians[20] (second derivatives of the energy) to locate the potential energy minima for the rings and smaller systems. Gaussian 92 was also employed for the majority of the G2 steps (single-point calculations using second-order perturbation theory with extended and diffuse polarization basis sets (MP2) and fourth-order perturbation theory with corrections from single, double, triple, and quadruple excitations (MP4SDTQ);[21] single-point energies using quadratic configuration interaction including contributions from singles, doubles, and triples (QCISD(T)).

HONDO 8.4[23] was used for the MP2 and MP4SDTQ single-point calculations where basis sets with g polarization functions were involved.

All MP2 and MP4 single-point calculations were done at the MP2 (frozen core)/TZVP optimized geometries.

Modifications of the original G2 scheme were made in order to handle Ti. To date, the procedure has been applied only to main group elements with an accuracy of 2−3 kcal mol^{-1}. In our modified scheme, we kept the originally proposed basis sets for H, C, and Si (ref 12a and refs therein) and used a TZV plus polarization (TZVP) basis set on Ti, expanding with higher angular momentum polarization functions to be consistent with the main group elements. This TZVP basis set was used throughout the MP2 optimization and Hessian runs. Table 1 summarizes the additions/changes made. For clarity, only Ti is listed in the column of modifications, but it is understood that the basis sets listed in column "Original G2" were still used for H, C, and Si.

Results and Discussion

Theoretical prediction[24] of heats of formation generally involves the computation of bond dissociation energies, atomization energies, and heats of reactions, and one can combine theoretical as well as experimental data for this purpose. Because more than one step is usually involved, care should be taken to minimize the systematic errors, while almost always empirical corrections are made for chemical accuracy. Even high-quality calculations may lead to erroneous predictions, unless the appropriate reactions are considered. Large basis sets and treatment for electron correlation are the most important factors, both of which are computationally expensive. Because of the size of the ring compounds, in terms of numbers of electrons and basis functions, direct application of the G2 model

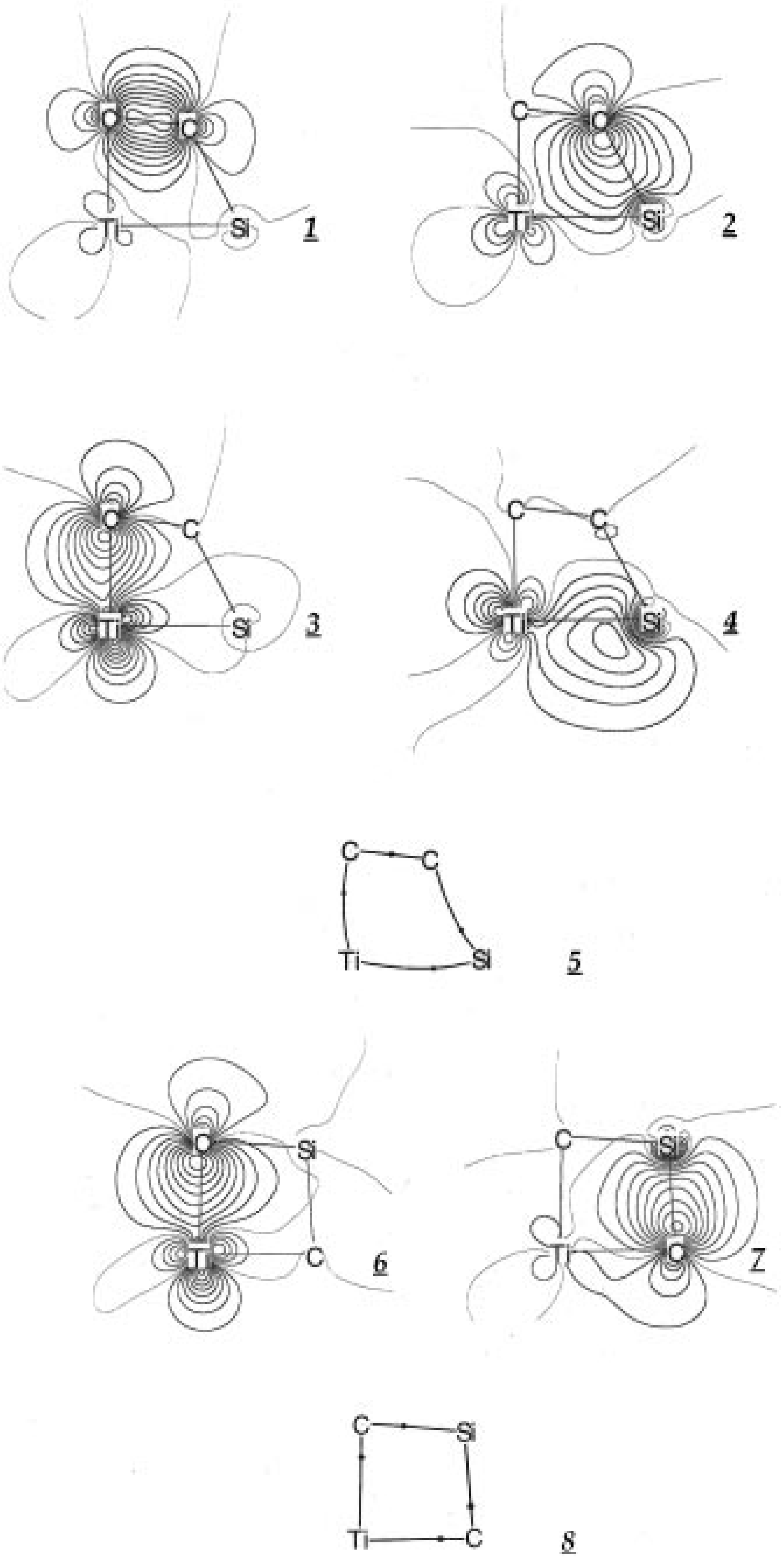
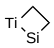


Figure 2. Boys localized orbitals for 1-sila-3-titanacyclobutane (**1**−**4**) and 1-sila-2-titanacyclobutane (**6**, **7**). **5** and **6** show the real bond path and the bond critical points from the Bader analysis. Red (+) and blue (−) correspond to opposite signs of the wave function.

on the cyclic compounds would be too demanding; therefore, in this study, we employ homodesmic reactions to optimize the cancellation of systematic errors, while the G2 procedure isapplied directly to the smaller reference compounds to obtain their heats of formation.

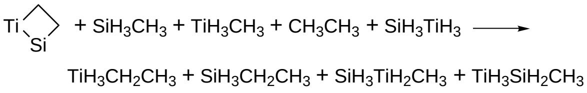
I. Homodesmic Reactions.[11] In this type of reaction, entire chemical groups are conserved upon going from reactants to products. Homodesmic reactions are expected to minimize the contribution to the heat of formation from electron correlation and basis set effects by forcing a cancellation of such errors.

TABLE 2: Zero-Point MP2, G1, and G2 Energies and Standard Heats of Formation

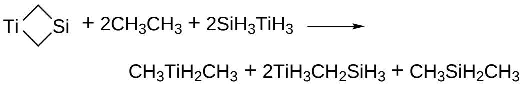
molecule	E_0(MP2)[a]	ZPE[b]	E_0(G1)[a]	E_0(G2)[a]	$\Delta H°_{f,0K}$[c]	$\Delta H°_{f,298.15K}$[c]	experiments
H	−0.499 81		−0.500 00	−0.500 00	+51.6[d]	+52.1[d]	
C	−37.746 84		−37.784 64	−37.784 20	+170.0[d]	+171.3[d]	
Si	−288.895 87		−288.933 78	−288.933 25	+106.6[d]	+107.6[d]	
Ti	−848.417 85		−848.464 11	−848.462 59	+112.6[d]	+113.2[d]	
CH_3CH_3	−79.501 96	72.02	−79.625 58	−79.630 01	−16.4	−20.2	−20.24 ± 0.05[e]
SiH_3CH_3	−330.518 65	59.12	−330.654 29	−330.656 82	−3.1	−7.0	−6.9 ± 1.0[e]
TiH_3CH_3	−889.912 47	48.43	−890.061 44	−890.062 64	+80.4	+77.9	
SiH_3TiH_3	−1140.904 69	41.44	−1141.068 31	−1141.067 12	+107.7	+103.7	
$SiH_3CH_2CH_3$	−369.683 42	86.90	−369.873 42	−369.877 14	−3.5	−8.9	−34.2[f]
$CH_3SiH_2CH_3$	−369.701 92	87.00	−369.892 12	−369.896 98	−16.0	−21.1	−22.6 ± 1.0[e]
$TiH_3CH_2CH_3$	−929.077 40	76.25	−929.280 54	−929.283 09	+79.9	+75.4	
$CH_3TiH_2CH_3$	−929.105 86	75.74	−929.307 92	−929.310 29	+62.8	+58.8	
$SiH_3TiH_2CH_3$	−1180.099 09	68.01	−1180.31819	−1180.31826	+88.0	+83.1	
$TiH_3SiH_2CH_3$	−1180.084 33	67.06	−1180.300 94	−1180.302 34	+97.9	+93.5	
$TiH_3CH_2SiH_3$	−1180.103 58	64.53	−1180.318 84	−1180.318 28	+87.9	+83.1	
	−1218.102 34	76.80			+96.3	+91.3	
	−1218.139 53	73.94			+79.0	+74.3	

[a] Energies in Hartrees. [b] Vibrational zero-point energies in mHartrees, scaled by 0.943. [c] Heats of formation in kcal mol^{-1}. [d] Reference 28. [e] Reference 32. [f] Reference 30.

For the cyclic systems of interest the following homodesmic reactions were used:



(1)



(2)

The heats of formation of the cyclic systems can be calculated from the heats of reactions 1 and 2, once the heats of formation are known for the smaller reference species.

II. Geometries.[25] In Figure 1, the MP2/TZVP geometries of the cyclic systems (R1, R2) and of the fragments (F1−F13) are shown. For geometries of C_1 symmetry, a bond distance average value is given; the local symmetry of XH_3 groups (X = C, Si, or Ti) is essentially C_{3v}.

Of the two silatitanacyclobutanes (R1, R2), the 1,3−isomer is more stable by 21.5 kcal mol^{-1} at the MP2/TZVP level of theory, in agreement with the experimental evidence accompanying the synthesis of analogous systems.[9]

At the same level of theory, structures F4, F6 and F5, F7 constitute two conformational pairs. As also reported before,[26] SiH_3TiH_3 shows two close-lying minima, both of C_{3v} symmetry (structures F4, F6), differing by only 2.7 kcal mol^{-1}. In the lowest energy minimum (F6), the hydrogens on Si are inverted toward Ti, forming three hydrogen bridges. As a result, the Si−Ti bond shortens by 0.077 Å compared to the “conventional”, ethane−like structure (F4). The anlogous effect is observed in the $SiH_3TiH_2CH_3$ isomers (F5, F7), but the minima here are almost degenerate, F7 being more stable by only 1.4 kcal mol^{-1}.[25] Structures R1 and F8 also have Si directly bonded to Ti and Si−Ti bond distances similar to those in F4 and F5. Nonetheless, no bridging minima were found for either of these species. It seems essential to have a SiH_3− unit rather than $-SiH_2-$ for any bridging to occur. This conclusion was further supported by an effort to use the CH_3 group for bridging in $TiH_3SiH_2CH_3$. The resulting minimum lies 4.6 kcal mol^{-1} higher than F8.

In calculating the heats of formation, only the lowest minima were considered.

III. G2 Energies and Heats of Formation. The zero-point G2 energy is given by the formula[12]

$$E_0(\mathrm{G2}) = E_0(\mathrm{G1}) + \Delta_1 + \Delta_2 + 1.14 \times 10^{-3}\, n_{\mathrm{pair}} \quad (\mathrm{III.1})$$

E_0(G1)[12b] is the calculated G1 energy, computed at the MP4 and QCI levels of theory, and includes the vibrational zero-point energy corrections, as well as an empirical correction (HLC). The following formulas are the ones used for the G1/G2 energies, adjusted to our basis set modifications. In the adopted notation for the basis set, “triple-ζ” is equivalent to 6-311G for H, C, and Si and TZV for Ti suitably extended with polarization functions:

$$\begin{aligned} E_0(\mathrm{G1}) = {} & E(\mathrm{MP4/triple\text{-}}\zeta\mathrm{(f,d,p)}) + \\ & [E(\mathrm{MP4/triple\text{-}}\zeta\mathrm{+(f,d,p)}) - E(\mathrm{MP4/triple\text{-}}\zeta\ \mathrm{(f,d,p)})] + \\ & [E(\mathrm{MP4/triple\text{-}}\zeta\mathrm{(2fg,2df,p)}) - E(\mathrm{MP4/triple\text{-}}\zeta\mathrm{(f,d,p)})] + \\ & [E(\mathrm{QCISD(T)/triple\text{-}}\zeta\mathrm{(f,d,p)}) - E(\mathrm{MP4/triple\text{-}}\zeta\mathrm{(f,d,p)})] + \\ & \mathrm{HLC} + \mathrm{ZPE} \quad (\mathrm{III.2}) \end{aligned}$$

where HLC is an empirical correction and ZPE is the MP2 vibrational zero-point energy scaled by 0.943.[27]

$$\begin{aligned} \Delta_1 = {} & [E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{+(3fg,3df,2p)}) - \\ & E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{(f,d,p)})] - [E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{+(f,d,p)}) - \\ & E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{(f,d,p)})] - [E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{(2fg,2df,p)}) - \\ & E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{(f,g,p)})] \quad (\mathrm{III.3}) \end{aligned}$$

$$\begin{aligned} \Delta_2 = {} & [E(\mathrm{MP2/triple\text{-}}\zeta\mathrm{+G(3fg,3df,2p)}) - \\ & E(\mathrm{MP2/triple\text{-}}\zeta\ \mathrm{G(f,d,p)})] \quad (\mathrm{III.4}) \end{aligned}$$

The corrections (III.2, III.3, III.4) made on top of G1 (III.1) account for additivity assumptions of the diffuse and higher order polarization functions, while the last term readjusts the higher level correction.

The heats of reaction (ΔH_r) for the homodesmic reactions 1 and 2 were calculated at the MP2/TZVP level from the E_0(MP2) energies. The standard heats of formation, $\Delta H_{f,0K}$, for each of the fragments were calculated using the experimental energies of atomization.[28] The standard heats of formation at 298.15 K were then calculated by adding the thermal corrections for vibrations, rotations, and translations. Table 2 summarizes the results of our calculations. Both cyclic systems appear to be higly reactive. The calculated heats of formation at 298.15 K are 91.3 and 74.3 kcal mol^{-1} for the 1,2- and 1,3-silatitanacyclobutane, respectively. The 1,3-isomer is more stable by 17.0

kcal mol^{-1} and therefore should be a better candidate for synthesis and isolation, especially if bulkier substituents are used, which might further enhance this energy differrence. All the Ti-containing reference compounds also feature high heats of formation, which are reported for the first time. The calculated values for CH_3CH_3, SiH_3CH_3, and $CH_3SiH_2CH_3$ are in excellent agreement with experiment and certainly within the error of the method. For $SiH_3CH_2CH_3$, the G2 result is in very good accordance with previously reported theoretical results using MP2 isodesmic reactions.[29] This earlier work noted that the experimental value[30] for this molecule should be revisited.

IV. Boys Localization and Bader Analysis[31]. In Figure 2 we show the Boys localized orbitals, **1**−**4** for the 1,2-ring and **6**−**7** for the 1,3-ring. These reveal some very interesting features, especially for the first system. The C−C bond in the first system is typical, but the others are indicative of considerable ring-strain. The Ti−Si and Ti−C bonds are bent outward, as one would expect for a strained system. Especially noteworthy is the observation that the C−Si bond is bent toward the interior of the ring, an unusual feature for a neutral molecule. We therefore employed a Bader analysis of the localized orbitals to determine the actual bond path and bonding in these cyclic systems. This type of density analysis is discussed in full detail in ref 31 and especially in ref 31d. We are interested in *critical points* of the electron density, e.g. points where the gradient of the density is zero, $\nabla\rho(\mathbf{r}) = 0$. A *bond critical point* is a point at which the Hessian of the density has one positive and two negative eigenvalues. This implies that there is a bond path connecting the two atoms, and they are considered to be bonded. Bond critical points are indicated by the black dots in **5** and **8**. A *ring critical point* is a point at which the Hessian has two positive and only one negative eigenvalues. According to this definition, both systems are rings with formal two-center bonds.

The ring-strain of the 1,2-isomer is obvious in both the curved path of the contour plots of the localized orbitals (**2**−**4**) and the bond path from the density analysis (**5**). As noted above, the Si−C bond is curved inward toward the interior of the ring. The corresponding Si−C localized orbital shows considerable delocalization (back-bonding) on Ti: nearly 10% of the two electrons in this LMO are located on Ti. The Mulliken atomic populations in this orbital are 0.168 on Ti, 0.612 on Si, and 1.33 on C. This may explain the unusual location of the bond critical point of the Si−C bond, closer to the less electronegative center (Si).

The increase in the length of the most strained bonds, measured by the length of the electron density bond path, as compared to the geometrical distances is on the order of 1−2%. The Ti−Si bond is increased by 0.0489 Å, Si−C by 0.044 Å, and Ti−C by 0.017 Å (only 0.8%). The C−C bond remains essentially unchanged. In the 1,3-isomer, the geometric and bond path lengths are essentially the same.

Conclusions

In the present work, the MP2/TZVP geometries and the standard heats of formation at 0 and 298.15 K of 1-sila-2- and 1-sila-3-titanacyclobutanes obtained from the G2 energies and the appropriate homodesmic reactions are reported. A G2 procedure modified to include first-row transition metals has been used. Species that contain directly bonded Si and Ti exist in more than one close-lying minima and favor geometries with the hydrogens on Si inverted toward Ti. All the Ti-containing fragments have high enthalpies of formation, which are tabulated here for the first time. The 1-sila-3-titanacyclobutane is more stable than the 1,2-isomer by 17.0 kcal mol^{-1} and with bulkier substituents would be easier to isolate. Boys localization and Bader analysis show considerable ring-strain in the 1,2-isomer and delocalization of the Si−C bond onto Ti.

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