

# Articles

## Molecular Structures for Azatitanatranes

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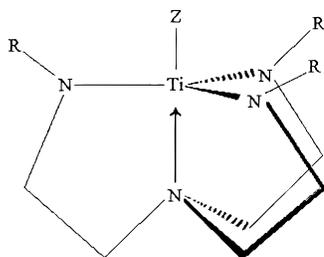
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*Ab initio* geometry optimizations for a series of azatitanatranes,  $ZTi[-NR(CH_2)_2-]_3N$ , where  $Z = CH_3, NH_2, OH, F,$  and  $N(CH_3)_2$  and  $R = H$  and  $CH_3$ , have been performed using a triple- $\zeta$  basis set for Ti and a 6-31G(d) basis set for all other atoms. An analysis of the transannular Ti–N interaction indicates that it is significantly stronger than that found in the analogous azasilatranes. In addition there is reasonable agreement between the calculated structure and the available X-ray data for  $Z = N(CH_3)_2$  and  $R = CH_3$ . Of special significance in this calculation is the fact that theory correctly predicts that the axial Ti–N bond is shorter than the equatorial Ti–N bonds.

### Introduction

Our group has recently published *ab initio* studies on a series of azaphosphatranes<sup>1</sup> and silicon atranes.<sup>2</sup> Key elements in these investigations are the nature of the P–N and Si–N transannular interaction. The purpose of the present study is to compare the transannular interaction in the group IVA element Si with the group IVB element Ti. To this end we report *ab initio* geometry optimizations for a series of azatitanatranes,  $ZTi[-NR(CH_2)_2-]_3N$ , where  $R = H, Z = CH_3, NH_2, OH, F,$  and  $N(CH_3)_2$  and, for  $R = CH_3, Z = CH_3, F,$  and  $N(CH_3)_2$ .



There is a vast literature available on the chemistry of the atranes, and the recent experimental progress in this field has been reviewed by Verkade.<sup>3</sup> Relevant to our study, the groups of Schrock<sup>4,5</sup> and Verkade<sup>6,7</sup> have reported interesting results on a series of azatitanatranes. Azatitanatranes are of particular interest to

industrial and synthetic chemists because of their potential use in the metal organic chemical vapor deposition (MOCVD) of titanium nitride, TiN, thin films.<sup>6</sup> The metallic properties, hardness, and chemical inertness of TiN make it a suitable candidate for a wide variety of practical applications. Clearly, a better understanding of the electronic structure of the azatitanatranes should contribute to the realization of these desirable applications.

### Computational Methods

The geometry optimizations were carried out at the RHF level of theory using the GAMESS electronic structure program. Several of the calculations required the parallel implementation of GAMESS which has previously been described in the literature.<sup>8</sup> The calculations employed a triple- $\zeta$  basis set for titanium<sup>9</sup> and a 6-31G(d)<sup>10</sup> basis set for the other elements. Pulay's group coordinates<sup>11</sup> were used in all calculations to accelerate convergence. The convergence criterion for all cases studied was that the root mean square of the gradient was less than 0.0001 hartree/bohr and that the maximum gradient was less than one-third of this value. While we were doing the computations it became apparent that the TiN transannular bond has a deeper potential well than we have found in silatranes and that RHF structures agree very well with experimental measurements. Therefore we have not explored the influence of electron correlation on the titanatranes structures. To facilitate analysis of the transan-

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(3) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483–489.

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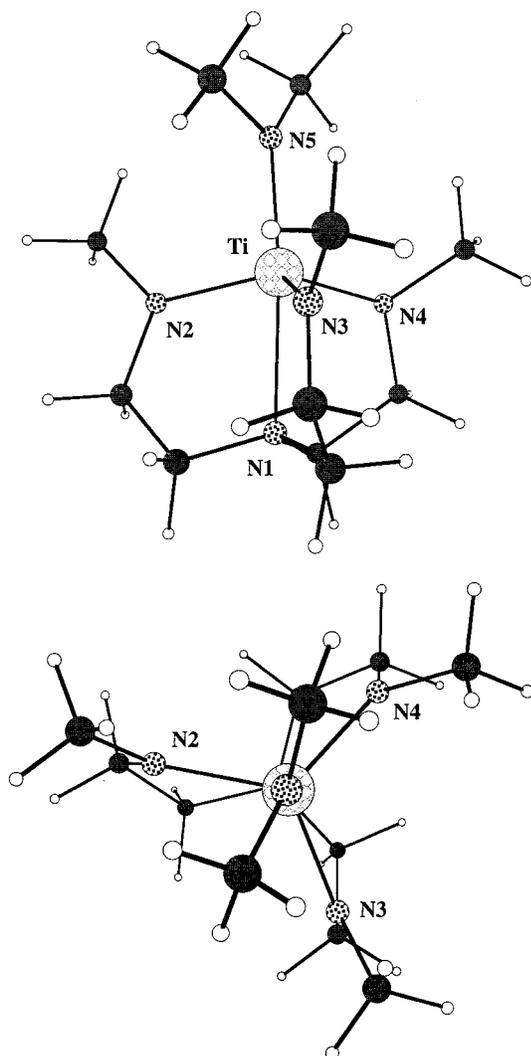
(7) Duan, Z.; Naiini, A. A.; Lee, J.-H.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 5477–5482.

(8) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(9) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033–1036. This has been extended to triple- $\zeta$  quality by using d functions (developed by: Rappe, A. K.; Smedley, T. A.; Goodard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 2607–2611), deleting Wachters' most diffuse s function  $\zeta = 0.0333$ , adding an s function with  $\zeta = 0.209$  to better describe the 3s–4s region, and adding two p functions  $\zeta = 0.1506$  and  $0.0611$  to allow for a 4p.

(10) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1981**, *85*, 2607–2611. (b) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163–168. (c) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213–222.

(11) (a) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550–2560. (b) Fogarasi, G.; Zhou, X.; Taylor, P. W.; Pulay, P. *J. Am. Chem. Soc.* **1992**, *114*, 8191–8201.



**Figure 1.** Two views of the calculated equilibrium gas-phase structure for  $R = \text{CH}_3$  and  $Z = \text{N}(\text{CH}_3)_2$ .

nular bond the RHF molecular orbitals were localized using the Pipek–Mezey algorithm,<sup>12</sup> since that method yields  $\sigma$  and  $\pi$  orbitals rather than forming banana bonds.

## Results and Discussion

Of the eight azatitanatranes considered in this study only  $(\text{CH}_3)_2\text{NTi}[-\text{NCH}_3(\text{CH}_2)_2-]_3\text{N}$  has been structurally characterized.<sup>3</sup> The molecular orientations for the calculated structures shown in Figure 1 reveal a distorted trigonal bipyramidal geometry around the titanium. The comparison of X-ray bond lengths and bond angles with their calculated values provided in Table 1 indicates that the agreement between the experimental and calculated structure is quite good. This is evidence that a reliable level of theory has been used in this study. Note, in particular, that theory correctly predicts the axial Ti–N(5) distance to be shorter than the equatorial Ti–N bonds. We will comment at greater length on this unusual result below.

Given that the transannular interaction is of prime interest, the calculated results for the Ti–N transannular distance are shown in Table 2 for the series of azatitanatranes considered. For purposes of comparison

**Table 1.** Comparison of Experimental and Calculated Bond Lengths (Å) and Bond Angles (deg) for  $R = \text{CH}_3$  and  $Z = \text{N}(\text{CH}_3)_2$

	bond lengths		bond angles		
	exptl	calcd	exptl	calcd	
Ti–N(1)	2.257	2.301	N(1)–Ti–N(5)	174.0	174.5
Ti–N(5)	1.921	1.934	N(2)–Ti–N(5)	98.7	98.7
Ti–N(2)	1.961	1.977	N(1)–Ti–N(2)	75.6	75.8
Ti–N(3)	1.947	1.965	N(1)–Ti–N(3)	78.6	78.1
Ti–N(4)	1.940	1.961	N(1)–Ti–N(4)	77.2	77.7
			N(2)–Ti–N(3)	118.7	118.6
			N(2)–Ti–N(4)	116.6	117.3
			N(3)–Ti–N(5)	106.0	105.3
			N(3)–Ti–N(4)	110.1	109.7
			N(4)–Ti–N(5)	104.3	104.9

**Table 2.** Transannular Distances (Å) as a Function of R and Z for Ti and Si Compounds

R (Ti or Si)	Z				
	CH <sub>3</sub>	NH <sub>2</sub>	OH	F	N(CH <sub>3</sub> ) <sub>2</sub>
H (Ti)	2.305	2.335	2.325	2.308	2.339
H (Si)	2.385	2.363	2.287	2.208	
CH <sub>3</sub> (Ti)	2.302			2.270	2.301
CH <sub>3</sub> (Si)	2.261		2.181	2.127	

the values for the transannular distances for the analogous silicon compounds<sup>2</sup> are also included in the table.

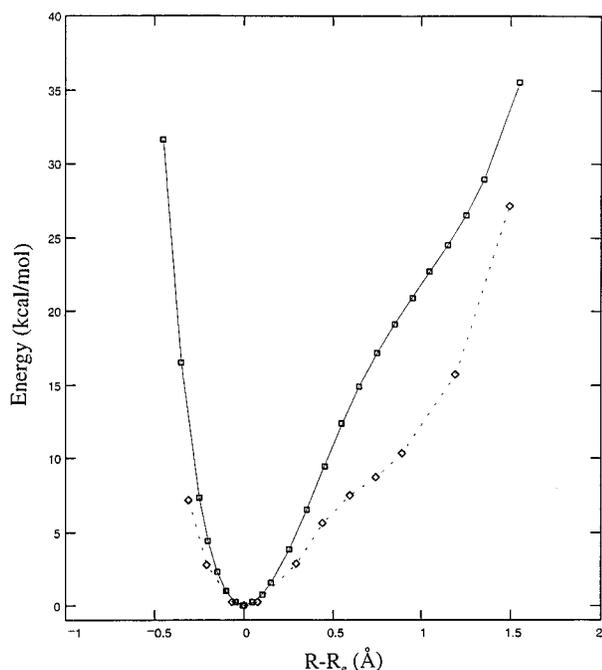
Internuclear distance is, of course, an important criterion for the existence of a chemical bond. The results in Table 2 show that for the azatitanatranes the Ti–N transannular distance is on average 14% greater than the sum of the covalent radii (2.02 Å) for Ti and N. For the azasilatranes the Si–N transannular distance is 21% greater than the sum of the covalent radii (1.87 Å).<sup>13</sup> Given that most observers consider the Si–N interactions to be weak, these data support the idea that the transannular interaction is stronger in the azatitanatranes than in their silicon counterparts.

It is also clear from the results presented in Table 2 that the transannular bond in the azatitanatranes is much more resistant to change due to variations in substituents R and Z than is the Si–N bond in the analogous silicon compounds. The standard deviation for these distances is 0.021 Å for titanium and 0.087 Å for silicon. The much higher resistance of the Ti–N transannular distance to distortion as R and Z are changed is additional evidence that the transannular bond is significantly stronger in the azatitanatranes than in the analogous azasilatranes.

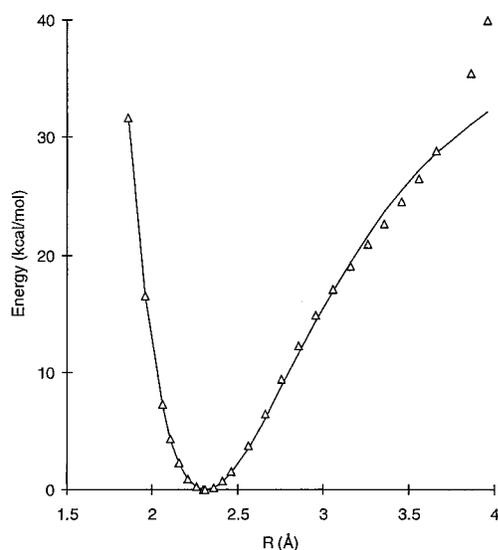
This conclusion is further strengthened by a comparison of the stretching potential for  $\text{FTi}[-\text{NH}(\text{CH}_2)_2-]_3\text{N}$  and  $\text{FSi}[-\text{NH}(\text{CH}_2)_2-]_3\text{N}$  which is shown in Figure 2. This figure shows that approximately 10 kcal/mol is required to stretch the Si–N transannular bond by 1 Å from its equilibrium value, while twice that value is required for the Ti–N bond. The stretching potential was calculated by increasing and decreasing the Ti–N transannular distance from the equilibrium value, followed by reoptimization of the rest of the molecule. Because the stretching potential for the titanium compound has a much greater curvature, we expect the titanatranes structures to be less sensitive to computational level (such as basis set or electron correlation) than the silatranes.<sup>2</sup>

(12) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916–4926.

(13) Atomic radii were taken from: Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, U.K., 1991.



**Figure 2.** Comparison of stretching potentials for FTi[-NH(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N, □, and FSi[-NH(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N, ◇.



**Figure 3.** Morse fit for the FTi[-NH(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N stretching potential.

A more quantitative analysis of the stretching potentials was performed by fitting Morse,  $V = D[1 - \exp(-\beta(R - R_e))]^2$ , and cubic spline functions to the data shown in Figure 2. The Morse fit provides both the well depth ( $\approx$  bond energy) and the force constant ( $k = 2\beta^2 D$ ). The cubic spline fit yields the force constant at the equilibrium internuclear distance. The results of this analysis are summarized in Table 3. Both determinations of the force constants clearly indicate that the Ti-N transannular bond is twice as strong as the Si-N transannular bond.

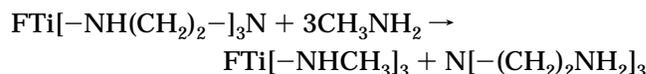
The bond strength of the transannular bond is difficult to define, since stretching this bond to the dissociation limit will require high energy due to the eventual stretching of the side chains. For example, the Morse fit for FTi[-NH(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N is shown in Figure 3. The sharp rise in the stretching potential in the neighborhood of 4 Å is a reflection of the onset of

**Table 3.** Summary of Morse and Cubic Split Fits for Ti and Si Stretching Potentials

	FTi[NH(CH <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub> N	FSi[NH(CH <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub> N
Morse $D$ (kcal/mol)	39.1	18.7
Morse $k$ (N/m)	111	64.9
Morse $\beta/\text{Å}^{-1}$	1.43	1.59
Cspline $k$ (N/m)	121	66.6

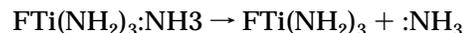
stretching the side chains. Accordingly, the last 6 data points are omitted from the Morse fit. The fits to just that part of the potential which is attributed to the transannular stretch give a value of 18.7 kcal/mol for Si-N and just over twice this for Ti-N, 39.1 kcal/mol. Again, this supports the conclusion that the Ti-N interaction is much stronger. While we do not claim that the Morse fit's dissociation energy is truly the bond energy, it does offer some quantitative idea of the strength of this interaction. It is interesting to note that the Morse dissociation energy for Si-N is within the range (13–22 kcal/mol) previously suggested for this bond from silatrane ionization potentials.<sup>14</sup>

Another way to estimate the strength of the transannular interaction is to calculate the energy of the following isodesmic reaction:



The  $\Delta E$  for this reaction is the transannular bond energy plus any difference in strain energy between products and reactants:  $\Delta E_{\text{isodesmic}} = \Delta E_{\text{transannular}} + \Delta E_{\text{strain}}$ .  $\Delta E_{\text{isodesmic}}$  was calculated to be 14.6 kcal/mol, and thus, we find that  $\Delta E_{\text{transannular}} = 14.6 \text{ kcal/mol} - \Delta E_{\text{strain}}$ . Since  $\Delta E_{\text{strain}}$  is clearly negative for this reaction, this calculation is not in qualitative disagreement with the Morse potential determination of the transannular bond strength discussed above. In other words, the energy change for the isodesmic reaction provides a lower limit for the strength of the Ti-N transannular interaction.

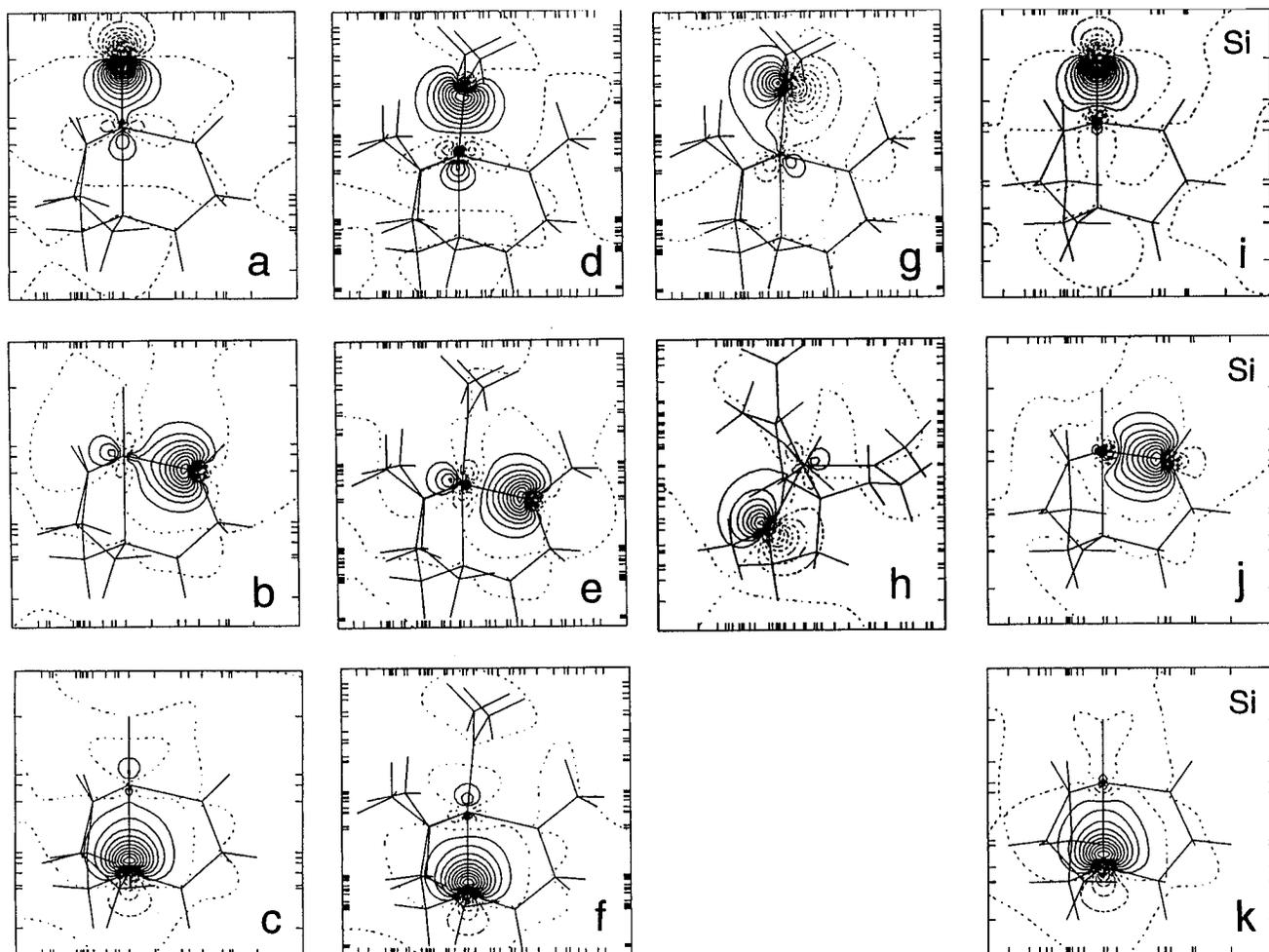
Another assessment of the dative Ti-N bond strength in the absence of ring strain can be obtained from the reaction



The calculated endothermicity of this reaction is 11.0 kcal/mol. This suggests that some additional stability in the TiN interaction is attained in the atrane and that the ring strain may be small.

Figure 4 displays the localized molecular orbitals for several related titanium and silicon compounds. Parts a–c and d–f show the axial, equatorial, and transannular bonds in FTi[-NH(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N and (CH<sub>3</sub>)<sub>2</sub>NTi[-NCH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N, respectively. For purposes of comparison the same bonding orbitals for FSi[-NH(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N are shown in parts i–k. Axial orbitals a, d, and i and equatorial orbitals b, e, and j show the electron density polarized toward the more electronegative N or F, indicating a polar bond to the Ti or Si. The transannular bonds c, f, and k are clearly even more polarized to the base nitrogen than the more covalent equatorial bonds. Further support for this conclusion can be seen by a comparison of orbitals a and b with c

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**Figure 4.** Localized molecular orbitals for the following: (a) axial, (b) equatorial, and (c) transannular Ti bonds in  $\text{FTi}[-\text{NH}(\text{CH}_2)_2-]_3\text{N}$ ; (d) axial, (e) equatorial, and (f) transannular Ti bonds in  $(\text{CH}_3)_2\text{NTi}[-\text{NCH}_3(\text{CH}_2)_2-]_3\text{N}$ ; (g) axial back-bonding and (h) equatorial back-bonding in  $(\text{CH}_3)_2\text{NTi}[-\text{NCH}_3(\text{CH}_2)_2-]_3\text{N}$ ; (i) axial, (j) equatorial, and (k) transannular Si bonds in  $\text{FSi}[-\text{NH}(\text{CH}_2)_2-]_3\text{N}$ . The increment between contours is  $0.05 \text{ bohr}^{-3/2}$ , and the atomic projections are shown as tick marks on the sides of the figure. All plots are in the plane containing  $\text{Z}-\text{Ti}(\text{Si})-\text{N}_{\text{eq}}$  except (h), which is in the plane  $\text{N}_{\text{eq}}-\text{Ti}-\text{N}_{\text{eq}}$ .

**Table 4. Comparison of Ti-Z Bond Lengths (Å) for  $\text{ZTi}[\text{NH}(\text{CH}_2)_2]_3\text{N}$  with Model Compounds,  $\text{ZTi}(\text{NH}_2)_3$**

Z	R = H	model	Z	R = H	model
$\text{CH}_3$	2.130	2.100	$\text{OH}$	1.825	1.819
$\text{NH}_2$	1.936	1.913	$\text{F}$	1.795	1.781

and orbitals d and e with f. The polar covalent orbitals (a, b, d, and e) show twice the number of contours on the titanium as do the respective transannular orbitals (c and f).

Previously the Si-N bonding<sup>2</sup> was described as a mainly dative interaction with evidence for some three center character. The evidence for the three center bonding was a small, but noticeable, elongation of the axial Si-Z bond when compared to silane model compounds. We have carried out geometry optimizations on the model series  $\text{ZTi}(\text{NH}_2)_3$ , where  $\text{Z} = \text{CH}_3, \text{NH}_2, \text{OH},$  and  $\text{F}$ , at the same level of theory as described earlier. The Ti-Z bond lengths of these model compounds are compared with those for  $\text{ZTi}[-\text{NH}(\text{CH}_2)_2-]_3\text{N}$  in Table 4. The average elongation of the Ti-Z bond in the azatitanatranes for this series is  $0.018 \text{ \AA}$ , as compared with a value of  $0.025 \text{ \AA}$  for the Si-Z bond in the analogous silatranes compounds.<sup>2</sup> Thus we conclude that three center-four electron bonding is even

**Table 5. Comparison of Ti-Z and Ti-N<sub>eq</sub> Distances (Å)**

R	Z				
	$\text{CH}_3$	$\text{NH}_2$	$\text{OH}$	$\text{F}$	$\text{N}(\text{CH}_2)_3$
	Ti-Z				
H	2.130	1.936	1.825	1.795	1.927
$\text{CH}_3$	2.139			1.801	1.934
	Ti-N <sub>eq</sub>				
H	1.939	1.943	1.939	1.930	1.947
$\text{CH}_3$	1.957			1.942	1.968

less important in the azatitanatranes than it is in the azasilatranes.

Further evidence that 3c-4e bonding is not significant in the azatitanatranes is shown in Table 5, where the Ti-Z and the average Ti-N equatorial distances are listed as a function of R and Z. For those structures in which nitrogen occupies all of the trigonal bipyramidal positions ( $\text{Z} = \text{NH}_2$  or  $\text{N}(\text{CH}_3)_2$ ), the average Ti-N<sub>ax</sub> distance is  $1.932 \text{ \AA}$ , while for Ti-N<sub>eq</sub> it is  $1.953 \text{ \AA}$ . Although this average Ti-N<sub>ax</sub> value is a bit longer than in the model compound  $\text{Ti}(\text{NH}_2)_4$ ,  $1.913 \text{ \AA}$ , it is surprising result that the Ti-N<sub>ax</sub> is shorter than the Ti-N<sub>eq</sub> distance. This computational result, which is in agreement with an experimental structure,<sup>3</sup> further

**Table 6. Axial–Equatorial Bond Length (Å) Summary for Pentacoordinated Silicon and Titanium Clusters**

	ax	eq
TiF <sub>5</sub> <sup>-</sup>	1.845	1.805
Ti(NH <sub>2</sub> ) <sub>5</sub> <sup>-</sup>	2.040	1.990
	2.037	1.977
		1.967
Si(NH <sub>2</sub> ) <sub>5</sub> <sup>-</sup>	1.893	1.786
	1.896	1.795
		1.803
NH <sub>3</sub> Ti(NH <sub>2</sub> ) <sub>4</sub>	1.920	1.930
	2.398	1.941
		1.941
NH <sub>3</sub> Si(NH <sub>2</sub> ) <sub>4</sub>	1.725	1.716
	3.996	1.729
		1.740
Me <sub>2</sub> NTi[-NMe(CH <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub> N	1.921	1.961
	2.257	1.947
		1.940

supports the conclusion that the transannular bond is mainly dative with little three center interaction.

An explanation for the short axial Ti–N bond in the existing azatitanatranes can be found in orbitals d and g of Figure 4. Taken together these show a predominantly polar covalent  $\sigma$  interaction (d) supplemented by nitrogen lone-pair back-bonding (g) to vacant titanium valence orbitals for the axial bond. Back-bonding from the equatorial nitrogens to Ti is present (h) but to a smaller extent than for the axial nitrogen, as can be seen by a comparison of orbitals (h) and (g). It is this greater axial back-bonding which is responsible for the axial bond being slightly shorter than the equatorial bonds. We note that stronger Ti–N interactions than we have found here have been observed for other systems. For example, Petersen et al. have recently reported Ti–N distances in the range 1.865–2.077 Å.<sup>15</sup>

To explore further the nature of the transannular interaction we performed RHF/6-31(d) geometry opti-

(15) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572–1581.

mizations on the pentacoordinated titanium and silicon clusters shown in Table 6. The anions give the expected result with the axial distance somewhat longer than the equatorials. However, for neutral (NH<sub>2</sub>)<sub>4</sub>TiNH<sub>3</sub> the axial Ti–NH<sub>2</sub> distance is shorter than the equatorial bonds and the Ti–NH<sub>3</sub> distance is about the same as the transannular distance in (CH<sub>3</sub>)<sub>2</sub>NTi[-NCH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N. In the analogous silicon cluster the Si–NH<sub>3</sub> distance clearly shows only a van der Waals type interaction.

### Summary

By comparing the results of *ab initio* geometry optimizations on a series of azatitanatranes with those performed earlier on the analogous azasilatranes, we conclude that the transannular interaction is significantly stronger in the titanium compounds. However, we also conclude that the bonding in both cases is mainly a dative contribution from the nitrogen lone pair with evidence for only very modest three center bonding. The extent of the bonding interaction in the titanatranes is small. The net bonding interaction, including any contribution from strain, is estimated to be 14.6 kcal/mol using an isodesmic reaction. In addition, we interpret the surprisingly short Ti–N axial bond in (CH<sub>3</sub>)<sub>2</sub>NTi[-NCH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N as due to back-bonding of the nitrogen lone pair to available titanium valence orbitals.<sup>16</sup>

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(16) Optimized atomic coordinates for (CH<sub>3</sub>)<sub>2</sub>NTi[-NCH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>N or any of the other compounds considered in this study are available by e-mail from frioux@csbsju.edu.