

Molecular Structure of Dimethyldichlorotitanium(IV) by Gas-Phase Electron Diffraction, IR and NMR Spectroscopies, and Density Functional Theory Calculations. Unexpected Distortion from Tetrahedral Coordination Geometry

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The molecular structure of $(\text{CH}_3)_2\text{TiCl}_2$ has been determined by gas-phase electron diffraction. The bond distances are $\text{Ti}-\text{C} = 205.8(4)$ pm and $\text{Ti}-\text{Cl} = 219.6(3)$ pm, and the valence angles are $\text{Cl}-\text{Ti}-\text{Cl} = 117.3(3)^\circ$, $\text{Cl}-\text{Ti}-\text{C} = 108.9(2)^\circ$, and $\text{C}-\text{Ti}-\text{C} = 102.8(9)^\circ$. The larger valence angles at Ti are thus those spanned by the more electronegative substituents. This is opposite to the trend observed in the main group analogues $(\text{CH}_3)_2\text{ECl}_2$, $\text{E} = \text{Si}, \text{Ge}, \text{or Sn}$. Density functional theory (DFT) calculations with a triple- ζ basis yield an optimal structure in good agreement with experiment. There is nothing in the gas-phase electron diffraction structure, DFT calculations, gas-phase IR spectra, or the NMR spectra of $(\text{CH}_2\text{D})_2\text{TiCl}_2$ hinting at unusual methyl group geometries or agostic $\text{Ti}\cdots\text{H}-\text{C}$ interactions.

Introduction

The molecular structures of mixed methylhalogeno derivatives of the group 14 elements silicon, germanium, and tin, $(\text{CH}_3)_n\text{MX}_{4-n}$ ($\text{M} = \text{Si}, \text{Ge}, \text{or Sn}$; $\text{X} = \text{F}, \text{Cl}, \text{or Br}$; $n = 1, 2, \text{ or } 3$), have been extensively studied, and the deviations from ideal tetrahedral valence angles at the central atom M are well documented: the larger valence angles are spanned by the more electropositive substituents.^{1–3} In contrast, the structural information on monomeric and base-free mixed methylhalogeno derivatives of the group 4 metals titanium, zirconium, and hafnium is largely limited to one member of the family, *viz.* CH_3TiCl_3 . The structure of this compound has been determined experimentally by gas-phase electron diffraction (GED)^{4,5} and computationally by structure optimization at high levels, first by Williamson and Hall,⁶ later by other groups.^{7–10} CH_3TiCl_3 has also been studied by IR¹¹ and NMR^{10,12} spectroscopies.

Methyltrichlorotitanium(IV) has also occupied a central position in the study of so-called agostic interactions¹³ between transition-metal atoms and C–H bonds in coordinated organic units. In 1986, Berry *et al.* suggested that the methyl group in the monomeric, base-free CH_3TiCl_3 is significantly flattened as a result of α -agostic $\text{M}\cdots\text{H}-\text{C}$ interactions,⁴ but the evidence cited in support of this suggestion has since been refuted or reinterpreted.^{5,6,10–12} While it now appears to be generally accepted that the methyl group geometry in the monomeric, base-free molecule is unexceptional, X-ray and neutron diffraction investigations of the complex with $\text{dmpe} = (\text{CH}_3)_2\text{PCH}_2\text{-CH}_2\text{P}(\text{CH}_3)_2$ indicate that the CH_3-Ti group is here canted in a manner suggesting strong interaction between the metal atom and one of the C–H bonds.¹⁴ An X-ray crystallographic study of CH_3TiCl_3 shows that the compound forms dimers in the solid phase. The positions of the hydrogen atoms were, however, not determined with sufficient accuracy to allow firm conclusions to be drawn with regard to the methyl group geometry.¹⁵

Two additional members of the $(\text{CH}_3)_n\text{MX}_{4-n}$ family ($\text{M} = \text{Ti}, \text{Zr}, \text{ or Hf}$), *viz.* $(\text{CH}_3)_2\text{TiCl}_2$ and $(\text{CH}_3)_3\text{TiCl}$, have been studied by ^1H , ^{13}C , and $^{47,49}\text{Ti}$ NMR spectroscopies,⁹ and their

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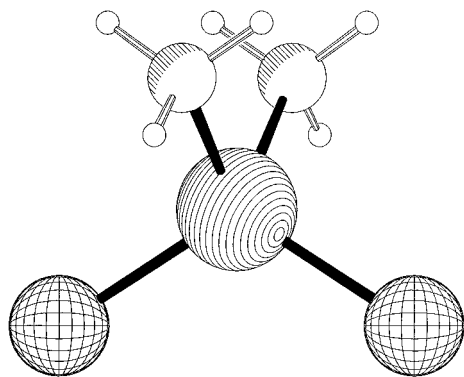


Figure 1. Molecular model of $(\text{CH}_3)_2\text{TiCl}_2$, symmetry C_{2v} .

molecular structures have been optimized at the Hartree–Fock and MP2 levels by effective core potential and all-electron calculations.^{9,10} In this article, we report the molecular structure of the dichloride as determined experimentally by GED, NMR studies of the deuterated species $(\text{CH}_2\text{D})_2\text{TiCl}_2$, and IR studies of different isotopomers of the molecule.

Computational Methods

Density Functional Theory (DFT) Calculations. The molecular structure of $(\text{CH}_3)_2\text{TiCl}_2$ was optimized and the molecular force field determined by DFT calculations using the program system Gaussian 94.¹⁶ The calculations were carried out with the aid of the BPW91 density functional program with the gradient correction of Becke¹⁷ for exchange and of Perdew–Wang¹⁸ for correlation. The force field was calculated using analytical derivative methods.¹⁹

The calculations made use of standard 6-311G(d) bases for H and C²⁰ and the chlorine basis set of McLean and Chandler²¹ (13s,10p,1d contracted to 6s,5p,1d; the exponent of the polarization function was 0.75). The primitive Gaussian basis set for titanium suggested by Wachters²² has been slightly modified by adding two diffuse p orbitals with exponents 0.156 and 0.0611 and one diffuse d orbital with exponent 0.0743. The resulting 14s,11p,6d basis set was contracted to 10s,8p,3d.

The optimization proceeded under the assumption of C_{2v} molecular symmetry, as in Figure 1. The resulting bond distances and valence angles are listed in Table 1.

The DFT force field was used to calculate the root-mean-square (rms) vibrational amplitudes and vibrational correction terms $D = r_\alpha - r_a$ by means of the program ASYM20.²³ The vibrational amplitudes and correction terms thus obtained are listed in Table 1.

Hartree–Fock calculations, Foster–Boys localization,²⁴ and Mulliken population analysis were effected with the program system GAMESS-UK.²⁵ Calculations employed single- ζ (SZ) (STO4G)^{25,26} and double- ζ (DZ)^{25,27} basis sets.

Table 1. Bond Distances and Valence Angles, rms Vibrational Amplitudes (l), and Vibrational Correction Terms (D) in $(\text{CH}_3)_2\text{TiCl}_2$ Determined by Density Functional Theory (DFT) Calculations and Interatomic Distances, Valence Angles, and Vibrational Amplitudes Determined by Gas-Phase Electron Diffraction (GED)^a

	$r_c(\text{DFT})$	$l(\text{DFT})$	$D(\text{DFT})$	$r_a(\text{GED})$	$l(\text{GED})$
Bond Distances					
C–H	110.3 ^b	7.8	–23.5	111.1(4)	7.2(6)
Ti–C	205.9	5.8	–0.8	205.8(4)	9.0(5)
Ti–Cl	221.6	5.0	–0.6	219.6(3)	5.4(2)
Nonbonded Distances					
Ti···H	15.3	–10.0		256.7(12)	16.0(10)
C···C	14.4	–0.2		320.6(22)	13.0(5)
Cl···C	14.2	0.0		345.1(5)	13.0(5) ^c
Cl···Cl	14.3	0.2		373.8(7)	11.8(7) ^c
Valence Angles					
Ti–C–H	109.9 ^b			108.1(10)	
C–Ti–C	106.1			102.8(9)	
Cl–Ti–C	108.4			108.9(2)	
Cl–Ti–Cl	116.7			117.3(3)	
R factors ^d	0.021 (50 cm)	0.057 (25 cm)		0.032 (total)	

^a Distances, vibrational amplitudes, and correction terms in pm and angles in deg. Estimated standard deviations of GED parameters in parentheses in units of the last digit. As refinements were carried out with diagonal weight matrices, the esd's have been doubled to reflect the added uncertainty due to data correlation and further expanded to include an estimated scale uncertainty of 0.1%. ^b Average values. Individual C–H bond distances were 110.2 (two) and 110.3 pm (four). Individual Ti–C–H valence angles were 109.6° (four) and 110.3° (two). ^c These amplitudes were assumed equal. ^d $R = [\sum w(I_{\text{obs}} - I_{\text{calc}})^2 / \sum I_{\text{obs}}^2]^{1/2}$.

Experimental Section

Synthesis, Characterization, and Spectroscopy. Dimethyldichlorotitanium(IV) was prepared by the reaction of titanium tetrachloride with an excess of dimethylzinc in pentane and purified by fractional condensation *in vacuo* in an all-glass apparatus. In a typical preparation, 1.0 g (5.3 mmol) of TiCl_4 was dissolved in pentane (*ca.* 10 mL), and $(\text{CH}_3)_2\text{Zn}$ (1.5 g; 15.8 mmol) was cocondensed with the solution at 77 K. The mixture was warmed to 250 K and stirred for several minutes. Repeated fractional condensation of the volatile materials afforded $(\text{CH}_3)_2\text{TiCl}_2$ in a trap held at 210 K. The purity was assessed by reference to the ¹H NMR^{10,28} and IR^{29,30} spectra of the sample and by chemical analysis.³¹ The high reactivity, thermal frailty, and photosensitivity of the compound necessitated the performance of control experiments to confirm the integrity of the sample under the conditions of the electron-diffraction experiment.

Dimethylzinc was prepared by reduction of CH_3I with a zinc/copper couple.³² Isotopically labeled samples of $(\text{CH}_3)_2\text{TiCl}_2$ were obtained by the gas-phase reaction between TiCl_4 and the appropriate isotopomer of $(\text{CH}_3)_2\text{Zn}$,^{11,30} synthesized from the corresponding iodomethane which

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was prepared by literature methods.^{33,34} NMR spectra were recorded using a Brüker AM 500 MHz spectrometer. Gas-phase infrared spectra were measured using a Mattson "Galaxy" FTIR spectrometer at a resolution of 1 cm^{-1} .

Electron Diffraction. Gas-electron-diffraction data were recorded on the Balzers KDG2 unit at Oslo³⁵ with the sample reservoir at 273 K, the vapor being injected in the dark *via* an all-glass inlet system at room temperature. Exposures were made at nozzle-to-plate distances of *ca.* 50 cm (3 plates) and 25 cm (4 plates) with an electron wavelength of 5.867 pm. The plates were traced with a modified Joyce-Loebl microdensitometer, and the data were processed with a program written by T. G. Strand. Atomic scattering factors were taken from ref 36. Backgrounds were drawn as least-squares-adjusted polynomials to the difference between the total experimental and the calculated molecular scattering intensities. Structure refinements were carried out with the program KCED26, written by G. Gundersen, S. Samdal, H. M. Seip and T. G. Strand.

Structure Refinements. Structure refinements of $(\text{CH}_3)_2\text{TiCl}_2$ were based on a molecular model of C_{2v} symmetry (see Figure 1). The DFT calculations indicate that individual C-H bond distances differ by less than 0.1 pm and Ti-C-H angles by less than 1° (see footnote to Table 1). Ti-CH₃ fragments were therefore modeled on the assumption of C_{3v} local symmetry. The molecular structure is then determined by six independent parameters, *viz.* the bond distances C-H, Ti-C, and Ti-Cl and the valence angles Ti-C-H, C-Ti-C, and Cl-Ti-Cl.

Initial refinements were carried out without corrections for thermal vibration. These refinements led to unremarkable values for the three bond distances, but to abnormal values for the valence angles Ti-C-H (102.6°), C-Ti-C (104.1°), and Cl-Ti-Cl (116.8°). Inclusion of vibrational correction terms ($D = r_\alpha - r_a$) led to an improvement of the fit and an increase of the Ti-C-H valence angle by 5.5° , while the valence angles at Ti changed by about 1° .

Several refinements of the six structure parameters and eight rms vibrational amplitudes were carried out with starting values of the angle C-Ti-C ranging from 100 to 120° while starting values for Cl-Ti-Cl ranged from 120 to 100° . All these refinements converged to yield the best values listed in Table 1. The largest element in the correlation matrix was $\rho[r(\text{Ti-Cl})/(\text{Ti-C})] = -0.74$.

Experimental and calculated molecular intensity curves are compared in Figure 2, while experimental and calculated radial distribution curves are compared in Figure 3. The agreement between experimental and calculated curves is satisfactory.

Discussion

Structure of the $C_2\text{TiCl}_2$ Framework. The structure parameters for $(\text{CH}_3)_2\text{TiCl}_2$ obtained by the DFT calculations and by gas-phase electron diffraction are listed in Table 1. The experimental dimensions are seen to be in good agreement with the calculated DFT values, as well as with the results of *ab initio* calculations previously published by Frenking and co-workers.^{9,10} In the following discussion, we shall refer to the experimental values since these are accompanied by error estimates.

The Ti-C and Ti-Cl bond distances are unremarkable: the Ti-Cl distances in $(\text{CH}_3)_2\text{TiCl}_2$, CH_3TiCl_3 ,⁵ and TiCl_4 ³⁷ appear to decrease in the sequence $219.6(3) > 218.5(3) > 217.0(2)$ pm. Similarly the Ti-CH₃ bond distances in $(\text{CH}_3)_3\text{Ti}(\eta^5\text{-C}_5\text{-Me}_5)$,³⁸ $(\text{CH}_3)_2\text{TiCl}_2$, and CH_3TiCl_3 appear to decrease in the

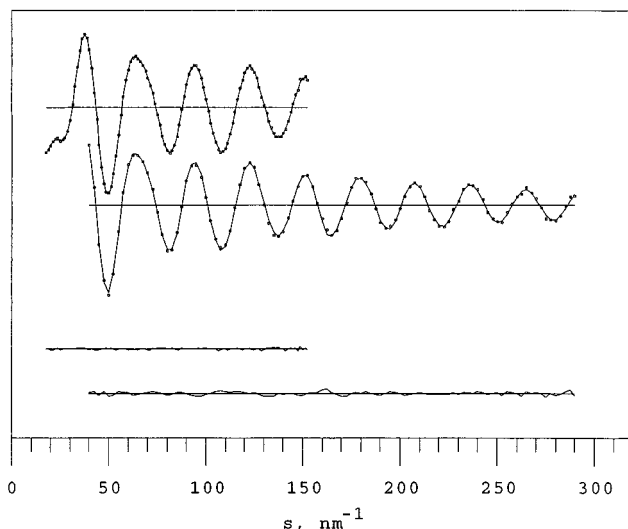


Figure 2. Top: modified intensity curves for $(\text{CH}_3)_2\text{TiCl}_2$, experimental (dots) and calculated (full lines). The vertical scale is arbitrary. Bottom: difference curves.

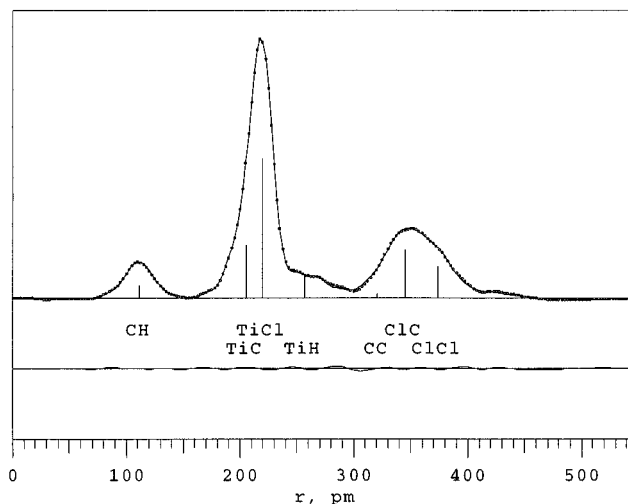


Figure 3. Top: radial distribution curves for $(\text{CH}_3)_2\text{TiCl}_2$, experimental (dots) and calculated (full lines). The vertical scale is arbitrary. Bottom: difference curve. The artificial damping constant $k = 25$ pm.

sequence $210.7(5) > 205.8(4) > 204.7(6)$ pm. This systematic shortening of the bond distances with increasing number of electronegative substituents is commonly observed in similar derivatives of group 14 elements.¹

The valence angles at the Ti atom are found to decrease in the sequence $\text{Cl-Ti-Cl} = 117.3(3) > \text{Cl-Ti-C} = 108.9(2) > \text{C-Ti-C} = 102.8(9)^\circ$. The larger valence angles are therefore those spanned by the more electronegative substituents. The same trend is found in CH_3TiCl_3 , where $\text{Cl-Ti-Cl} = 113.0(2) > \text{C-Ti-Cl} = 105.6(2)^\circ$.⁵

This trend is exactly opposite to that established for mixed methylgeno derivatives of the group 14 elements Si, Ge, or Sn: in these main group compounds, the larger valence angles at the central atom are invariably those which are spanned by the more electropositive substituents.¹⁻³ Thus, in $(\text{CH}_3)_2\text{SiCl}_2$ the valence angles increase in the order $\text{Cl-Si-Cl} = 107.5(1) < \text{C-Si-Cl} = 108.7(2) < \text{C-Si-C} = 114.2(2)^\circ$ ^{2,3} and in $\text{CH}_3\text{-SiCl}_3$ the valence angles are $\text{Cl-Si-Cl} = 106.9(3) < \text{C-Si-Cl} = 111.9(3)^\circ$.³⁹ It remains to be seen whether the valence angles at the central atom in other molecules of the type $(\text{CH}_3)_n\text{MX}_{4-n}$ in the titanium family ($M = \text{Ti, Zr, or Hf}$) will

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Scheme 1

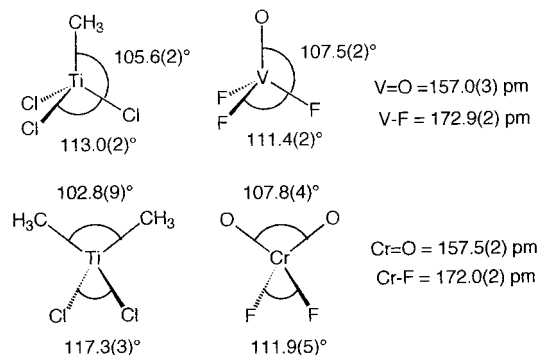


exhibit the same trend as the two Ti compounds studied to date exhibit.

In the following account, we briefly explore possible rationalizations of the unexpected angles in terms of repulsion between the ligands, valence shell electron pair repulsion (VSEPR),⁴⁰ multiple metal-to-ligand bonding, and hybridization.

(i) Repulsion between the Ligands. The unusual angles in the Ti derivatives can hardly be explained by *steric* repulsions between the ligands since the cone angles cited for methyl and chlorine ligands in transition-metal complexes at 90 and 102°, respectively, are considerably smaller than tetrahedral.⁴¹ The Ti–C and Ti–Cl bonds in (CH₃)₂TiCl₂ are, moreover, significantly longer than Si/Ge–C or Si/Ge–Cl bonds in the main group counterparts. Steric repulsions between the ligands should therefore be greater in the Si or Ge analog. We note, however, that since Ti is significantly more electropositive than Si, Ge, or Sn, the *Coulombic* repulsion between electronegative ligands carrying substantial negative charge may be considerably larger in the Ti derivatives.

(ii) Valence Shell Electron Pair Repulsion. The observed trend in valence angles at the group 14 elements Si, Ge, and Sn has been rationalized in two ways. The first rationalization evokes the VSEPR model: polarization of bonding electrons in the direction of electronegative ligands reduces their spatial requirements on the surface of the central atom, and the angles between such bonds are consequently reduced. Application of the VSEPR model to a group 4 analog would obviously lead to the prediction of similar behavior.

(iii) Multiple Metal–Ligand Bonding. The structures of CH₃TiCl₃ and (CH₃)₂TiCl₂ would be in agreement with the predictions of the VSEPR model if the Ti–Cl bonds are assumed to possess significant multiple bond character. In Scheme 1, however, we compare valence angles in the two titanium compounds with those of the molecules F₃VO and F₂CrO₂.^{42,43} The bond distances indicate that the M–O bonds have more multiple bond character than the M–F bonds; nevertheless, the larger angles are those spanned by the more electronegative F atoms. It seems that the VSEPR tenet that the spatial requirement of a multiple bond is greater than the spatial requirement of a single bond is invalid for tetrahedral d⁰ transition-metal compounds, although the high electronegativities of *both* substituents in these two molecules may complicate the issue.

(iv) Hybridization. The second simple approach that has been used to rationalize the coordination geometries of the group 14 compounds is a hybridization model. According to “Bent’s

rule”, the atomic s character tends to concentrate in hybrid orbitals that are directed toward the more electropositive groups:⁴⁴ increasing the s character of two of four sp³ hybrids increases the angle between them. At the same time, the s character of the remaining hybrids must be reduced if the hybrids are to remain orthogonal, and the angle between them will close. Similarly, increasing the s character of one hybrid of four will lead to a decrease of the angle between the remaining three.

Freking and co-workers⁴⁵ have explored a similar model for the superficially analogous situation involving sdⁿ hybridization. While the angle between two equivalent spⁿ hybrids is uniquely determined by their s character, this is not true for the angle between two equivalent sdⁿ hybrids, which also depends on the nature of the d orbitals involved: thus, sd² hybrids formed from the d_{xz} and d_{yz} orbitals are trigonal *pyramidal*, while sd² hybrids formed from the d_{x²-y²} and d_{xy} orbitals are trigonal *planar*. Similarly, while the angle between two equivalent spⁿ hybrids increases monotonically with increasing s character, the angle between two equivalent sdⁿ hybrids may increase or decrease depending on the nature of the d orbitals involved. The implications of Bent’s rule for sdⁿ hybridization must therefore be worked out specifically for each coordination geometry.

Tetrahedral sd³ hybrids may be formed from the s, d_{xz}, d_{yz}, and d_{x²-y²} atomic orbitals. Increasing the s character of two of four hybrids decreases the angle between them,⁴⁶ and increasing the s character of one hybrid of four will lead to an opening of the angle between the remaining three. The observed structures of CH₃TiCl₃ and (CH₃)₂TiCl₂ might therefore be rationalized by application of Bent’s rule to sd³ hybridization.

In order to obtain clues to the hybridization of atomic orbitals at the Ti atom, Berger and co-workers have analyzed the wave function of (CH₃)₂TiCl₂ obtained by structure optimization at the MP2 level with an effective core potential at Ti,¹⁰ using the natural bond orbital (NBO) partitioning scheme for the electron density.⁴⁷ Analysis of the electron density assigned to localized Ti–C and Ti–Cl *bonding* orbitals indicates that the s character of the hybrids directed toward the C atoms, h(C), is smaller than the s character of the hybrids pointing toward the Cl atoms, h(Cl).¹⁰ This trend is opposite to that predicted by the simple hybridization argument outlined above. The trend would be

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(46) We first assume the valence angles to be exactly tetrahedral and define a Cartesian coordinate system with Ti at the origin, the z axis coinciding with the 2-fold symmetry axis, the C atoms in the xz plane at positive z, and the Cl atoms in the yz plane at negative z. The four equivalent sd³ hybrids pointing toward the four ligands are then uniquely determined as

$$h(C) = s/2 \pm d_{xz}/\sqrt{2} + d_{x^2-y^2}/2$$

and

$$h(Cl) = s/2 \pm d_{yz}/\sqrt{2} + d_{x^2-y^2}/2$$

where h(C) denotes the two hybrid orbitals pointing toward the C and h(Cl) denotes the hybrids pointing toward the Cl atoms. If the s character of the h(C) hybrids is increased, the contribution from d_{x²-y²} must be decreased in order to maintain normalization and the angle between the two hybrid orbitals will be reduced, in the limit of sd_{xz} hybridization to 90°. If the s character of the h(C) hybrids is increased, the s character of the h(Cl) hybrids must be reduced in order to maintain orthogonality. This condition in turn implies that the contribution to h(Cl) from d_{x²-y²} must be increased and the angle between the two hybrids will increase, in the limit of d_{yz}d_{x²-y²} hybridization to 117°. The reduction of the angle between the h(C) hybrids will presumably provide a driving force for the closing up of the C–Ti–C valence angle from 109.5° and the increase of the angles between the h(Cl) hybrids for a corresponding opening out of Cl–Ti–Cl. Once the valence angles deviate from the ideal tetrahedral value, the d_{z²} orbital is no longer excluded by symmetry and the situation becomes intractable.

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Table 2. Population Parameters Given by Mulliken Population Analysis of Ti–Cl and Ti–C Bond Orbitals Obtained by Foster–Boys Localization of HF Wave Functions of $(\text{CH}_3)_2\text{TiCl}_2^a$

valence angles (basis set)	Ti–Cl				Ti–C			
	Ti(e)	s(%)	p(%)	d(%)	Ti(e)	s(%)	p(%)	d(%)
tetrahedral (SZ)	0.232	27	35	38	0.396	30	29	42
GED (SZ)	0.230	27	36	37	0.403	29	27	44
tetrahedral (DZ)	0.155	17	23	60	0.352	13	15	72
GED (DZ)	0.153	17	25	58	0.379	14	14	72

^a Ti(e) is the total occupancy of Ti atomic orbitals (in electrons); s(%), p(%), and d(%) give the distribution of the total between Ti s, p, and d orbitals.

reversed, however, if the d(Ti) electron density assigned to the Ti–Cl bonding orbitals was increased by less than 0.07. We have repeated the calculations of Berger and co-workers and find that the NBO partitioning leads to the assignment of more than 0.68 Ti d electron to formally vacant *antibonding* Ti–C and Ti–Cl orbitals. Under these circumstances we do not believe that much significance can be assigned to small differences obtained by analysis of the bonding orbitals by the NBO procedure. A rather more satisfactory approach is to analyze the populations of localized molecular orbitals obtained by the Foster–Boys procedure,²⁴ since this leads to localization without allocating electron density to formally vacant antibonding orbitals.

Since the sd^3 hybridization model presented above rests on simple symmetry and orthonormality arguments, one might hope that the conclusions would be reflected in population analysis of wave functions obtained by Hartree–Fock (HF) calculations with relatively small bases. Following the receipt of results of calculations performed at the HF level using a triple- ζ (TZ) base, in the course of a wider study of deviations from tetrahedral symmetry,⁴⁸ we repeated these for $(\text{CH}_3)_2\text{TiCl}_2$ with single- ζ (SZ) and double- ζ (DZ) bases. These were carried out with the valence angles at the Ti atom constrained to both tetrahedral and the experimentally determined values; the results are summarized in Table 2.

As is usually the case, the Mulliken population parameters are found to be very basis-set dependent. For what they are worth, however, the parameters are inconsistent with the sd^3 hybridization model. First, the numbers indicate that the Ti p orbital populations are as large as, or larger than, the Ti s orbital populations. Second, while the SZ calculations indicate that the s character of the h(C) hybrids is essentially equal to the s character of the h(Cl) hybrids, the DZ calculations indicate that the s character of the h(Cl) hybrids is larger.

An alternative approach would allow for the ionic contribution, which is likely to be much larger for the Ti–Cl than for the Ti–C bonds. This model can adequately account for the observed valence angles at Ti, but is also at odds with the population analyses presented in Table 2.⁴⁹ We do not believe it worthwhile to investigate further the dependence of the Mulliken population parameters on basis sets or to look for basis sets which lead to population parameters in better agreement with the hybridization model, but prefer to let the matter rest here. No simple model seems able as yet to provide a consistent and rational explanation of the skeletal geometry assumed by d^0 molecules such as $(\text{CH}_3)_2\text{TiCl}_2$.

Methyl Group Geometries. There is no shortage of reported sightings of agostic $\text{M}\cdots\text{H}-\text{C}$ interactions,¹³ but it is far from easy to pin down precisely the geometry of methyl substituents coordinated to metal atoms. Apart from the low cross sections of the H atoms with respect to the scattering of X-rays or

electrons, there are two other major snags. First, there is the question of sample purity. Much care is needed to produce samples of compounds such as CH_3TiCl_3 and $(\text{CH}_3)_2\text{TiCl}_2$ which are free from contamination, particularly by decomposition or reaction byproducts and by other members of the family $(\text{CH}_3)_n\text{TiCl}_{4-n}$ ($n = 0-2$). In practice, this calls for techniques similar to the ones used for the preparation and manipulation of gallium hydrides⁵⁰ and for scrupulous spectroscopic monitoring of the purity of the products. The second problem concerns the unusually low frequencies and large amplitudes of $\rho(\text{CH}_3)$ fundamentals in compounds such as CH_3TiCl_3 ¹¹ and $(\text{CH}_3)_2\text{TiCl}_2$ ³⁰ which are liable to lead to appreciable shrinkage effects. Hence, the vibrationally averaged r_a C–H and Ti–H distances deduced directly from the electron-diffraction pattern of the gaseous molecule are somewhat longer than the corresponding r_c distances. As a result, the valence angle Ti–C–H is more narrow in the r_a structure (102.6°) than in the equilibrium structure. Our best estimates of vibrational correction terms imply in fact that Ti–C–H does not depart significantly from the tetrahedral value in the equilibrium structure, a conclusion consistent with the results of our own and earlier¹⁰ DFT calculations.

NMR studies of CH_3TiCl_3 and other molecules have exploited the lower symmetry of CH_2D isotopomers in seeking evidence for agostic interactions by determining the magnitude and sign of the coupling constant $^2J(\text{H},\text{D})$ and/or by determining the change in chemical shift on deuteration and the temperature dependence of this “Shapley shift”.^{13,33,51} The proton-detected $^1\text{H}-^{13}\text{C}$ heteronuclear shift correlation spectrum of a sample containing $(\text{CH}_2\text{D})_2\text{TiCl}_2$ in CD_2Cl_2 solution at 253 K was measured, and $^2J(\text{H},\text{D})$ was found to be -1.54 Hz, giving $^2J(\text{H},\text{H}) = -10.02$ Hz. The compounds $\text{CH}_2\text{DTiCl}_3$ and $(\text{CH}_2\text{D})_2\text{TiCl}_2$ are therefore very similar in both the magnitude and sign of $^2J(\text{H},\text{H})$, implying H–C–H angles close to 108° . As noted previously, however, the correlation with $^2J(\text{H},\text{H})$ is not particularly reliable for estimating the methyl group geometry.³³ Variable temperature studies on the same sample gave for $(\text{CH}_2\text{D})_2\text{TiCl}_2$ at 293 K an isotope shift of 0.042 relative to the nondeuterated species; at 243 K the isotope shift altered only slightly to 0.044. The magnitudes of the shift and of its temperature dependence are too small to be ascribed to $\text{Ti}\cdots\text{H}-\text{C}$ interactions of any consequence, although the absence of a Shapley shift does not exclude the possibility of symmetrical agostic interactions involving all three bonds in both methyl groups.

The IR spectra of gaseous samples and harmonic local mode (energy-factored force field) calculations⁵² on the internal modes of methyl groups in the species $(\text{CH}_m\text{D}_{3-m})_2\text{TiCl}_2$ ($m = 0-3$),

(49) If the Ti–C bonds are considered to be essentially covalent and the Ti–Cl bonds largely ionic, the bonding can be thought of as deriving from the interaction between $[\text{TiMe}_2]^{2+}$ and two chloride anions. The Ti–C bonds in the cation would be formed from two sd hybrid orbitals on the Ti atom (bond angle 90°), with the Cl^- ions initially diametrically opposed about this cation in order to minimize Coulombic repulsion between the two negative charges and occupying pseudoaxial positions in a sawhorse arrangement. Introduction of a degree of covalent character into the Ti–Cl bonds will lead to greater use of the valence orbitals at the Ti atom and the incorporation of further d character into all Ti–X bonds. Consequently, the Cl–Ti–Cl angle will close down and the C–Ti–C angle will open up from 90° until the combined covalent and electrostatic interactions reach a minimum on the potential energy surface. Such a model makes qualitative sense of the observed valence angles, but suffers from the drawback that Ti s character is again concentrated in the Ti–C bonds, a conclusion at odds with the population analyses we have performed.

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along with the wavenumbers of the “isolated” $\nu(\text{C-H})$ fundamentals of the isotopomer $(\text{CHD}_2)_2\text{TiCl}_2$, lead to the prediction of 109.8 pm for the $r_0(\text{C-H})$ bond distance and 109.1° for the Ti-C-H valence angle. A full account of the IR spectroscopy and force field calculations will be published separately.³⁰

Thus, gas-phase electron diffraction, DFT calculations, and NMR and IR spectroscopies all indicate perfectly normal methyl group geometries with no significant α -agostic $\text{Ti}\cdots\text{H-C}$ interactions.

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