Molecular Structures of $EtTiCl_3$ and $EtTiCl_3(dmpe)$ (dmpe = $Me_2PCH_2CH_2PMe_2$): New Insights into β-Agostic Bonding

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Gas-phase electron diffraction (GED) results for $EtTiCl_3$ (**1**) are consistent with a molecular model of C_s symmetry, with the bond distances (r_a in Å) Ti−C = 2.090(15), C−C = 1.526(11), and Ti−Cl = 2.195(3) and the valence angles (in deg) ∠TiCC 116.6(11) and ∠ClTiC = 104.6(4). These structural parameters give no hint of an unusual ethyl group geometry or agostic $Ti\cdots H-C_\beta$ interactions. The geometry of the EtTi fragment is conspicuously different in the diphosphine complex $EtTiCl_3(dmpe)$ (dmpe = $Me_2PCH_2CH_2PMe_2$) (**2**), the crystal structure of which has been redetermined at low temperature (105 K) by X-ray diffraction without the problems of pronounced disorder described in an earlier report. Here the TiCC valence angle at 84.57(9)° is acute, and the $Ti\cdots C_\beta$ distance at only 2.501(2) Å is strikingly short, confirming a β-agostic interaction.

Introduction

Agostic interactions are of particular consequence in organometallic chemistry since they promise to hold the key to a better understanding of important processes such as C−H activation. The term "agostic interaction", introduced in 1983 by Brookhart and Green,[1] is generally used to describe an attractive interaction between a metal atom (M) and a C−H fragment of an appended ligand which is not readily explained in terms of classical bonding concepts. Many examples of agostic interactions have been reported on the basis of structural or spectroscopic measurements or have been predicted by theoretical studies. However, the *true nature of agostic bonding* remains a matter of speculation. Brookhart and Green initially proposed the interaction to involve a three-center, two-electron covalent $M\cdots H-C$ bond. Subsequently Eisenstein et al.[2a] have suggested the presence of multiple bonding between a d^0 transition metal center and an α-methyl group which behaves like a weak π-donor via its occupied πCH_3 orbitals. This view then finds a parallel between hyperconjugative stabilization in organic systems and α-agostic interaction in organometallic chemistry.[3] Brammer et al.[4] have proposed that a distinction can be drawn between a 3c-2e $M\cdots H-C$ agostic interaction and a 3c-4e $M\cdots H-X$ hydrogen bond in which the transition metal center acts as a hydrogen bond acceptor (X = C, N, O, or S). 3c-4e $M\cdots H-X$ interactions may develop in an electronically saturated metal complex with filled d-orbitals, while 3c-2e $M\cdots H-C$ interactions require the presence of vacant (acceptor) orbitals on the metal center.

The controversy is unlikely to be allayed while the characterization of agostic bonding remains largely a matter of interpretation. Agostic interactions can be identified, it was originally suggested,[1] by the observation of significantly elongated (weakened) C−H bonds (1.13−1.19 Å), reflecting the donation of C−H bonding electrons to the Lewis acid metal center. However, the classic example of α-agostic interaction, $MeTiCl_3(dmpe)$,[5] does not reveal significantly elongated C−H

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bonds. It has been necessary therefore to turn to new definitions, for example relating α-agostic interaction to small deviations from the idealized geometry at the C_α atom brought about by tilting or flattening of the coordinated methyl groups. The well-known experimental difficulties posed by the precise location of hydrogen atoms by X-ray and gas electron diffraction (GED) studies have sometimes led to false inferences on the basis of these criteria. A case in point is the free $MeTiCl_3$ molecule, which seems, contrary to earlier reports, to display no significant agostic interactions.[6] There have been several attempts to explain why the complex $MeTiCl_3(dmpe)$ should be agostic when the parent compound $MeTiCl_3$ shows no agostic behavior.[2b,c] It is possible that the α-agostic interactions in $MeTiCl_3$ are weak and additionally hindered by the C_{3v} symmetry of the parent molecule, so that it is unsuitable as a benchmark for agostic interactions.

To discover whether agostic interactions exist in other alkyltitanium chlorides of the type R_xTiCl_{4-x} (R = alkyl) compounds, we decided to study ethyltitanium trichloride, $EtTiCl_3$ (**1**), in the gas phase and its dmpe adduct (**2**) in the solid state. These two systems offer several significant advantages as benchmarks for agostic interactions.

(a) β-agostic interactions are considered to be stronger than α-agostic interactions as a result of the reduced ring strain in the agostic M···H−C−C unit.[1] Thus, MP2 ab initio calculations focused on $EtZrCl_3$ indicate the presence of significant β-agostic interactions.[7] This in turn suggests that similar interactions may be important in the titanium analogue.

(b) $EtTiCl_3$ is sufficiently stable and volatile[8] to allow the structure of the gaseous molecule to be determined by the GED method, thereby avoiding the potential complications of crystal-packing forces and other complications peculiar to the solid state (such as crystal twinning or disorder). As yet, no agostic compound has been identified structurally in the gas phase.

(c) The risk of mistaken identification is reduced for β-agostic interactions; irrespective of the precise location of any agostic hydrogen atoms, the phenomenon is clearly signaled by an appreciable reduction of the MCC bonding angle (<100°).

(d) A survey based on the Cambridge Crystal Structure File (Release 5.10)[9] yielded only five transition metal ethyl complexes clearly manifesting β-agostic interactions. Four of these are cationic species, viz., $[EtPt\{Bu^t{}_2P(CH_2)_3PBu^t{}_2\}]^+$,[10a] valence electrons (VE) = 14, ∠PtCC = 75(1)°; $[EtNi\{Bu^t{}_2P(CH_2)_2PBu^t{}_2\}]^+$,[10b] VE = 14, ∠NiCC = 74.5(3)°; $[EtCo(\eta\text{-}Cp^*)\{P(p\text{-tolyl})_3\}]^+$ (Cp* = pentamethylcyclopentadienyl),[10c] VE = 16, ∠CoCC = 74.5(2)°; and $[EtZr(\eta\text{-}C_5H_4Me)_2(PMe_3)]^+$,[10d] VE = 16, two independent molecules in the asymmetric unit with ∠ZrCC = 84.7(5)° and 83.0(6)°, respectively. There is in addition only one *neutral* compound, viz., the 12-VE compound $EtTiCl_3(dmpe)$ (**2**), reported[5b,11] to display clear signs of a β-agostic interaction.

Here we report the molecular structure of $EtTiCl_3$ (**1**) as determined by gas electron diffraction and a more accurate determination of the crystal structure of the complex $EtTiCl_3(dmpe)$ (**2**) at low temperature. The results, together with the spectroscopic properties of the compounds, have formed the main experimental points of reference for a wider survey[12] involving extensive DFT calculations and aimed at elucidating the true nature and origins of β-agostic bonding.

Results and Discussion

Molecular Structure of $EtTiCl_3$ (1) by GED. The molecule $EtTiCl_3$ (**1**) is likely to involve *pseudo*-tetrahedral coordination of the metal atom, which with a formal VE count of only 8 is even more electron-deficient than the metal center in the complex $EtTiCl_3(dmpe)$ (**2**, VE = 12). Since the solid complex has been reported previously[5b,11] to display β-agostic interactions, the base-free molecule might be expected to develop, if anything, even more robust interactions.

In any event, structure refinements by least-squares calculations on the GED data were based on a model with C_s symmetry overall and a staggered conformation about the C−C bond of the C_2H_5Ti unit, as indicated in Figure 1a. Final refinements, including vibrational correction terms derived from a DFT force field, yielded the structure parameters listed in Table 1. Experimental and calculated molecular scattering curves are depicted in Figure 1b.

Refinements were also carried out with a C_s model having an *eclipsed* C_2H_5Ti group. This gave marginally poorer agreement between experimental and calculated intensities. The difference was, however, too small to allow us to rule out the eclipsed conformation on the basis of the GED measurements alone. We note, though, that the value obtained for the MCC angle proved independent of the conformation assumed for the C_2H_5Ti group.

DFT structure optimizations carried out without imposition of molecular symmetry converged to models

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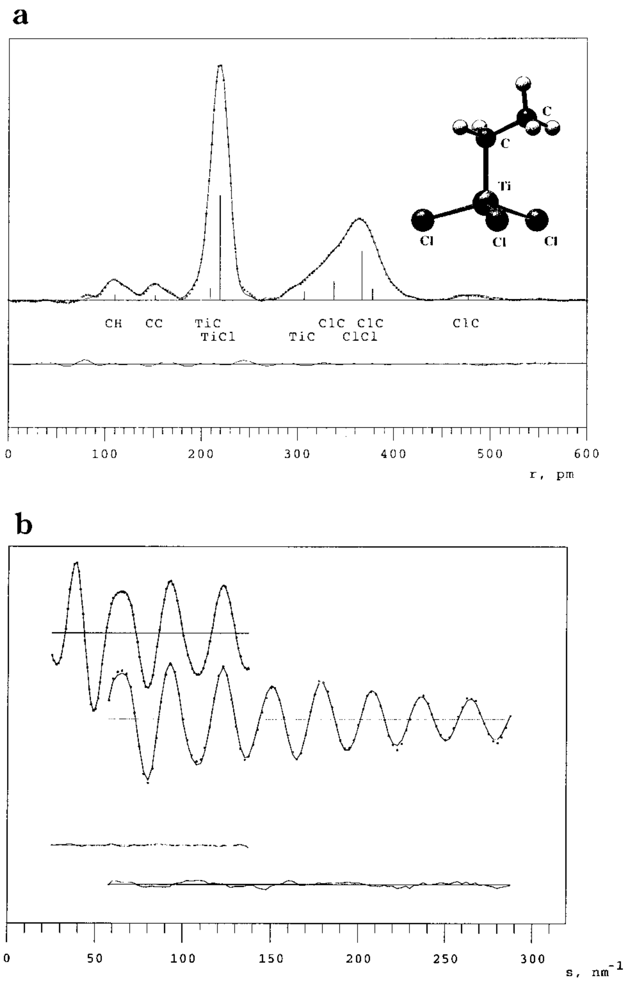

Figure 1. (a) Above: experimental (dots) and calculated (line) modified radial distribution curves for $EtTiCl_3$ (**1**). The vertical scale is arbitrary. Below: difference curve. Artificial damping constant $k = 0.0025$ Å^2. The structural refinements are based on a molecular model with C_s symmetry. (b) Comparison of experimental and calculated molecular scattering curves for gaseous $EtTiCl_3$ (**1**).

Table 1. Interatomic Distances, Valence Angles, rms Vibrational Amplitudes (l), and Vibrational Correction Terms (D) in $EtTiCl_3$ (1) by Gas Electron Diffraction (GED) and DFT Calculations[a]

parameter	r_a(GED)	r_e(DFT)	l(GED)	l(DFT)	D(DFT)
Bond Distances					
Ti−C	2.090(15)	2.052	0.076(29)	0.058	−0.006
C−C	1.526(11)	1.530	0.038(17)	0.053	−0.043
Ti−Cl	2.195(3)	2.206[b]	0.051(2)	0.049	−0.007
C−H	1.104(10)	1.103[b]	0.068(13)	0.078	−0.076
Nonbonded Distances					
Ti···C_β	3.068(17)	3.069	0.128(28)	0.114	−0.016
Cl···Cl	3.668(6)	3.683[b]	0.134(6)	0.134	−0.001
Cl···C_α	3.382(9)	3.391[b]	0.133(19)	0.132	−0.002
Cl″···C_β	3.780(25)	3.831	0.199(30)	0.261	0.004
Cl′···C_β	4.775(13)	4.826	0.144(32)	0.124	−0.007
Valence Angles					
∠Ti$C_\alpha C_\beta$	116.6(11)	117.2			
∠ClTiC_α	104.6(4)	105.5[b]			
R-factors[c]	0.018 (50 cm)		0.077 (25 cm)		0.043 (total)

[a] Distances, vibrational amplitudes, and correction terms in angstroms, angles in degrees. Estimated standard deviations of GED parameters in parentheses in units of the last digit. As refinements were carried out with diagonal weight matrixes, 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 distances were Ti−Cl′ = 2.207, Ti−Cl″ = 2.206; C_α−H = 1.107, C_β−H′ = 1.103, C_β−H″ = 1.099 Å. Individual angles were ∠CTiCl′ = 105.3, ∠CTiCl″ = 105.6; ∠CCH′ = 110.6, ∠CCH″ = 111.9°. Atoms in the symmetry plane are denoted by (′), atoms out of the symmetry plane by (″). [c] $R = [\sum w(I_{obs} - I_{calc})^2/\sum wI_{obs}{}^2]^{1/2}$.

Table 2. Comparison of the Structures of RMX_3 and R_2MX_2 Compounds (R = Me or Et; M = Ti or Re; X = Cl or O) in the Gas Phase[a]

parameter	$MeReO_3$[b]	$EtReO_3$[c]	Me_2TiCl_2[d]	$MeTiCl_3$[e]	$EtTiCl_3$[f]
r(M−C)	2.060(9)	2.095(6)	2.058(4)	2.047(6)	2.090(15)
r(M−X)	1.709(3)	1.711(2)	2.196(3)	2.185(3)	2.195(3)
r(C−H)	1.105(12)	1.106(13)	1.111(4)	1.098(6)	1.104(10)
∠CMX	106.0(2)	104.6(5)	108.9(2)	105.6(2)	104.6(4)

[a] Bond distances in angstroms and angles in degrees. [b] Reference 14a. [c] Reference 15. [d] Reference 13. [e] Reference 6b. [f] This work.

with C_s symmetry overall and with the ethyl group in a *staggered* conformation. The energy obtained by optimization of the C_s model in which the ethyl group was locked in an eclipsed conformation was 1.7 kcal mol^{-1} higher. In fact, the optimized eclipsed model corresponds not to a minimum but to a saddle point on the potential energy surface. The calculations thus favor an equilibrium structure that is staggered about the C−C bond of the C_2H_5Ti unit. Bond distances, valence angles, and some interatomic distances are listed in Table 1. We consider the agreement between the experimental and calculated structures to be satisfactory.

The value determined for the valence angle ∠TiCC = 116.6(11)° *demonstrates the absence of significant β-agostic interactions in **1***. We interpret the magnitude of the angle as furnishing evidence for repulsion between the β-methyl group and the Cl atoms in gauche positions and shall return to this point subsequently.

In Table 2 we compare the coordination geometries at the metal for $EtTiCl_3$ with those of the related alkyl compounds $MeTiCl_3$,[6b] Me_2TiCl_2,[13] $MeReO_3$,[14] and $EtReO_3$.[15] The M−C bond distances in the ethyl compounds appear to be slightly longer than in the methyl analogues, the difference possibly reflecting a weakening of the M−C bonds in the ethyl compounds. We note that the Zn−C bond distances in dimethyl- and diethylzinc, as measured by GED,[16] are 1.930(2) and 1.950(2) Å, while the Zn−C bond dissociation energies in the two compounds are reported to be 44.0 and 34.0 kcal mol^{-1}, respectively.[17]

In each of the five compounds listed in Table 2, the larger valence angles at the metal atom are those spanned by the more electronegative substituents. This

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is opposite to the trend observed for main group analogues and in apparent contradiction with a simple VSEPR model.[18] We shall return to a discussion of the structure of EtTiCl$_3$ in another context.[19] Perhaps the most striking result to emerge from the experimental and computational studies of EtTiCl$_3$ is the extreme pliability of the C$_2$H$_5$Ti moiety, as indicated by the large vibrational amplitude associated with the Ti$\cdots$C$_\beta$ nonbonded distance (Table 1) and computational evidence (DFT studies of the adiabatic TiCC bending potential).[12,20] DFT calculations suggest that an energy input of no more than 2.8 kcal mol^{-1} (i.e., an amount equal to the rotational barrier in ethane) is needed to reduce the TiCC angle by 20°.

Optimization of a model with an eclipsed ethyl group conformation and the TiCC valence angle fixed at 87°, corresponding to an agostic interaction, yields an energy 3.8 kcal mol^{-1} above that of the anagostic equilibrium structure (Figure 2). Inspection of constant probability density contours of the frontier molecular orbitals reveals that bonding interactions have been established between the Ti atom and the C$_\beta$−H′ (in plane) fragment. The nonbonded C$_\beta\cdots$Cl″ distance in the calculated equilibrium structure is 3.83 Å, slightly larger than the sum of the van der Waals radii of a methyl group and a Cl atom, viz., 3.75 Å.[21] In the agostic molecule with an eclipsed ethyl group conformation and the TiCC valence angle fixed at 87°, this distance is reduced to 3.43 Å. At the same time, the coordination geometry of the Ti atom distorts in a manner indicative of C$_\beta$H$_3\cdots$Cl″ repulsion; the two C$_\alpha$TiCl″ valence angles increase while the C$_\alpha$TiCl′ valence angle decreases. We suggest therefore that the extreme pliability of the TiCC valence angle in **1** is due to the near cancellation of two opposing forces, i.e., β-agostic attraction which favors a small angle and C$_\beta$H$_3\cdots$Cl″ repulsion which favors a large one.

Crystal Structure of EtTiCl$_3$(dmpe) (2) at Low Temperature by X-ray Diffraction. The crystal structure of the complex EtTiCl$_3$(dmpe) (**2**), as determined at room temperature, yields manifest evidence of β-agostic interaction, the valence angle ∠TiCC being 86.3(6)° and the C$_2$H$_5$Ti fragment adopting an *eclipsed* conformation.[5b,11] Accordingly, we were surprised to find no indication of similar interactions in the base-free compound EtTiCl$_3$. Since the X-ray crystal structure of **2** reported by Green and co-workers suffered from marked disorder of the dmpe ligand,[5b,11] we decided to redetermine the structure at lower temperature in the hope of gaining improved definition and so advancing our understanding of the different behaviors of **1** and **2**.[22]

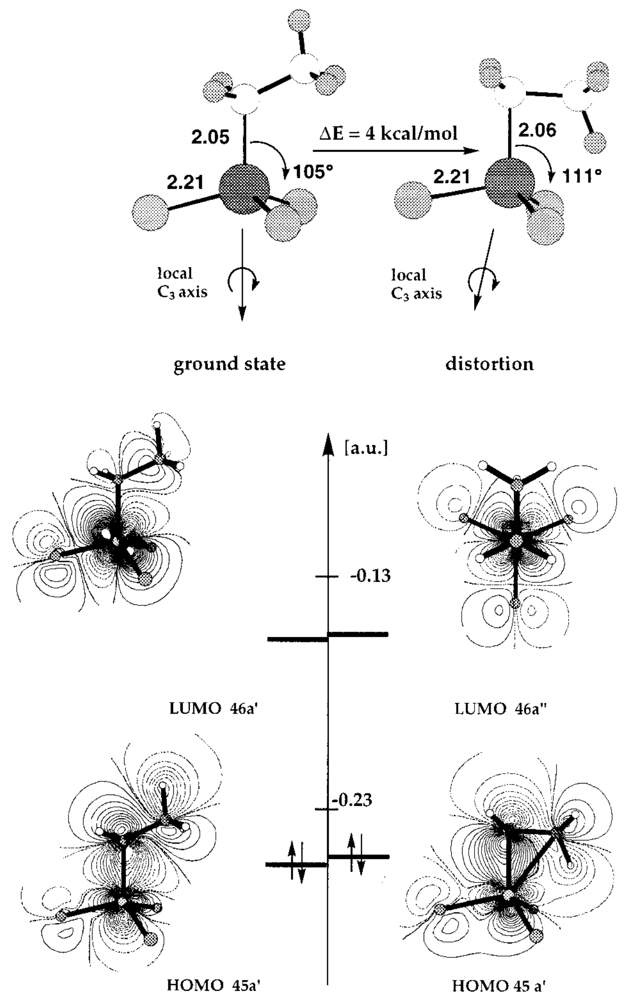

Figure 2. Contour maps of frontier MOs and coordination geometry (left) of the staggered, anagostic conformer of EtTiCl$_3$ (**1**) and (right) of the eclipsed, agostic model of EtTiCl$_3$ (**1**) (optimized with C_s symmetry contraints and ∠TiCC fixed at 87°). Distances in angstroms.

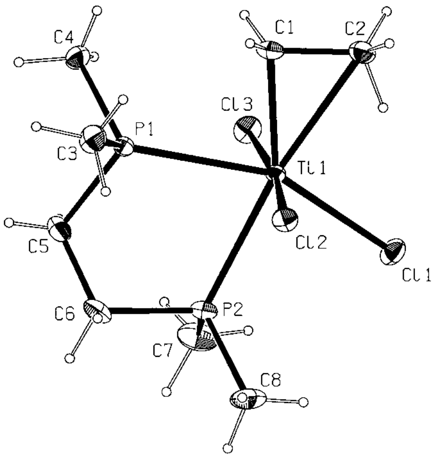

Figure 3. Molecular structure of **2** based on an X-ray study of a single crystal at 105 K. PLATON[31] drawings show the 50% probability ellipsoids.

The molecular structure deduced from X-ray diffraction measurements on a single crystal at 105 K is shown in Figure 3; the principal molecular dimensions are listed in Table 3. The Ti atom and the equatorial atoms Cl(1), P(1), P(2), C(1), and C(2) are nearly coplanar, whereas the two Ti−Cl(2) and Ti−Cl(3) bonds are

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Table 3. Relevant Structural Parameters for $EtTiCl_3(dmpe)$ (2)

	X-ray		DFT	
parameter[a]	293 K[b]	105 K[c]	eclipsed	staggered
Ti−C	2.151(9)	2.147(1)	2.170	2.151
$Ti\cdots C_\beta$	2.524(10)	2.501(2)	2.549	3.074
$C_\alpha-C_\beta$	1.467(15)	1.501(2)	1.517	1.534
$C-H_{\beta'}$	1.04(2)	1.03(2)	1.130	1.105
$C-H_{\beta''}$		0.98(2)[e]	1.100	1.101
Ti−Cl(1)	2.408(3)	2.4154(4)	2.389	2.284
Ti−Cl(2)	2.313(3)	2.3154(4)	2.330	2.338
Ti−P(1)	2.560(3)	2.5556(4)	2.585	2.638
Ti−P(2)	2.570(3)	2.5727(4)	2.586	2.638
∠TiCC	86.3(6)	84.57(9)	85.5	112.0[f]
$\angle CCH_{\beta'}$	118.9[d]	112.3(10)	114.2	110.3
∠CTiCl(1)	128.4(3)	129.61(4)	129.3	115.3
∠CTiP(1)	74.8(3)	74.84(4)	75.9	78.7
∠CTiP(2)	149.6(3)	149.53(4)	151.6	153.2
∠CTiCl(2)	90.4(3)	89.92(5)	89.7	90.4
∠Cl(2)TiCl(3)	173.0(1)	172.31(2)	167.4	162.7
∠P(1)TiP(2)	74.75(9)	74.98(1)	75.9	74.9
∠P(2)TiCl(1)	82.1(1)	80.77(1)	79.1	91.3
$\tau C_\beta C_\alpha TiCl(1)$	2.2[d]	−3.88(9)	−7.8	−20.2
$\tau H_{\beta'} C_\beta C_\alpha Ti$	7.3[d]	1.4(12)	0.1	175.8

[a] Atoms in the symmetry plane are denoted by (′), atoms out of the symmetry plane by (″); bond distances in angstroms and angles in degrees. [b] Reference 5b. [c] This work. [d] Calculated from the atomic coordinates in ref 11b. [e] Average value. [f] Constrained value.

approximately perpendicular to the equatorial plane. The coordination geometry may therefore be described as distorted octahedral, with the entire ethyl group occupying one coordination site. No significant disorder of the dmpe ligand is indicated in our structure; the twisted conformation of the dmpe backbone is normal, and the C−C bond distance in the ethylene bridge and the individual P−C bond distances are unexceptional. Thus the accuracy of all structural parameters is seen to be significantly improved. The TiCC valence angle of 84.57(9)° is in agreement with the value found in the previous study. The rather short C−C bond distance of the ethyl group, measuring 1.467(15) Å, indicated by that study, was interpreted in terms of partial olefinic character. The new value for this distance, 1.501(2) Å, appears more normal.[23] Electron density plots are in agreement with the proposed eclipsed ethyl group conformation and indicate a $Ti\cdots H_\beta$ distance of about 2.06(2) Å. This distance is about 20% longer than the Ti−H single−bond length of 1.73 Å deduced by DFT calculations on $EtTiH_3$.[24] At 2.501(2) Å, the $Ti\cdots C_\beta$ distance is no less remarkable for being only 17% longer than the bonded $Ti-C_\alpha$ distance.

DFT structure optimization of **2** was carried out without the imposition of symmetry constraints. The global energy minimum was found for a TiCC angle of 85.5° and an eclipsed C_2H_5Ti group conformation. The strength of the agostic interaction was estimated by subtracting the energy of the agostic equilibrium structure from the energy of an optimized model with the TiCC valence angle fixed at 112°: the stabilization energy, D_{112}, was thus found to be 1.84 kcal mol^{-1}.[12,25] Comparison with the structure parameters obtained by X-ray crystallography reveals good agreement between theory and experiment (see Table 3).

We have suggested that the pliability of the TiCC valence angle in **1** is due to near cancellation of agostic $M\cdots C_\beta H_3$ attraction and steric $C_\beta H_3\cdots Cl''$ repulsion. We now suggest that coordination of the diphosphine to form the adduct **2** allows the agostic attraction to prevail by reducing $C_\beta H_3\cdots Cl$ repulsions. Coordination of the diphosphine to $EtTiCl_3$ to form the adduct **2** leads to considerable changes in the Ti−C and Ti−Cl bond distances and ∠CTiCl and ∠ClTiCl valence angles. These changes are well reproduced by the calculated structures (see Tables 1 and 3). The results of the structure optimization of **2** with ∠TiCC fixed at 112° allow us to consider first the effects of diphosphine coordination with retention of an anagostic structure and second the effects of reduction of the TiCC angle. Comparison of the structure parameters of the optimized, anagostic model of **2** (∠TiCC = 112°) with the optimized structure of the base-free molecule **1** indicates that coordination with the diphosphine has increased the Ti−C bond distance by 0.1, the Ti−Cl(1) distance by 0.08, and the Ti−Cl(2) distance by 0.13 Å; the valence angle $\angle C_\alpha TiCl(1)$ has increased by 10° to 115.3°. Comparison of the optimized, anagostic model with the agostic equilibrium structure shows that the reduction of ∠TiCC from 112.0° to 85.5° is accompanied by an increase of the Ti−Cl(1) bond distance by another 0.10 Å to 2.39 Å and of the $C_\alpha TiCl(1)$ valence angle by another 14° to 129°. Both distortions serve to increase the distance $C_\beta\cdots Cl(1)$ to 3.58 Å as compared with 3.43 Å in the agostic (eclipsed) model of **1** (Figure 2). The elongation of Ti−Cl(1) is accompanied by the reduction of both Ti−P bond distances by 0.05 Å and the decrease of ∠Cl(1)TiP(2) by 12°. The two remaining angles in the equatorial belt, ∠P(1)TiP(2) and $\angle P(1)TiC_\alpha$, are less affected. We conclude that coordination of the diphosphine ligand has reduced the forces opposing the β-agostic attraction by increasing the Ti−Cl bond distances and by rendering the coordination geometry more flexible.

The more flexible nature of the framework of **2** is also indicated in the contour plot of the HOMO of the model system $EtTiCl_3(dhpe)$ (dhpe = $H_2PCH_2CH_2PH_2$) (Figure 4); the orbital displays antibonding character between the Ti and Cl(1). Thus the substantial elongation of the Ti−Cl(1) bond, by more than 0.20 Å compared with **1**, is an inherent feature of the dmpe adduct.

In parallel publications[12,20] we report the results of extensive spectroscopic and computational studies into the nature of β-agostic interactions in **2** and related compounds. In summary, these conclude that the interaction is driven largely by stabilization of the

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(23) Statistical analysis of the C−C bond distances in transition metal ethyl compounds based on 107 X-ray structures in the Cambridge Structural Database 5.10 (see ref 9a) yields an average of 1.475 Å. A referee pointed out that C−C bond distances might be systematically shortened due to the fact that librational motion is not taken into account by a simple harmonic refinement of atomic displacement parameters. However, new refinements on **2** (high-order reflection data; flexible multipole model) resulted in an even larger C−C bond distance of 1.512(1) Å. This result stresses also the need of high-order reflection data and models that account for the aspherical features of the electron density to gain accurate bond distances from X-ray data (see ref 33).

(24) Details of the Gaussian 94 DFT calculations carried out on $EtTiH_3$ are given elsewhere (see ref 12).

(25) SCF and LDF-DFT calculations on the model systems $EtTiCl_2H(PH_3)_2$ and $EtTiCl_3(PH_3)_2$ with several structure constraints have yielded higher stabilization energies. For further information see: (a) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625−4626. (b) Munakata, H.; Ebisawa, Y.; Takashima, Y.; Wrinn, M. C.; Scheiner, A. C.; Newsam, J. M. *Catal. Today* **1995**, *23*, 403−408.

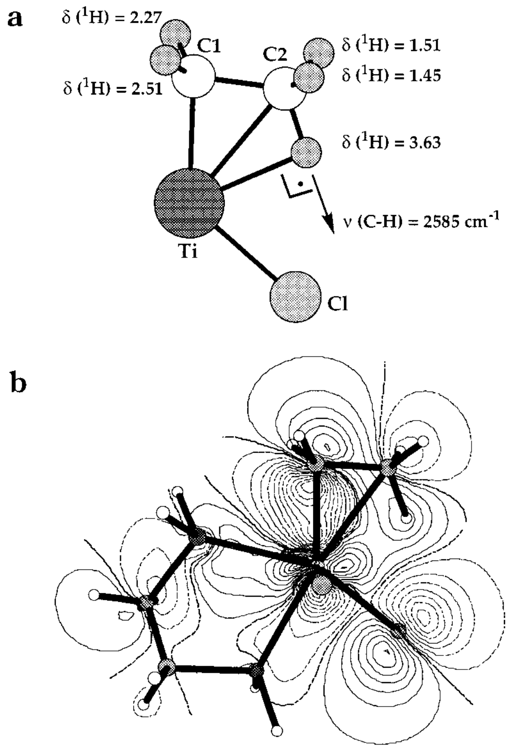

Figure 4. (a) EtTiCl$_{eq}$-unit in EtTiCl$_3$(dmpe) (**2**) based on a DFT study. Individual calculated ^{1}H NMR chemical shifts (in ppm) of **2** and the calculated directrix of the ν(C−H) stretching mode in the model system EtTiCl$_3$(dhpe) (dhpe = H$_2$PCH$_2$CH$_2$PH$_2$) are specified in the figure. (b) Contour map of the HOMO of the model system EtTiCl$_3$(dhpe).

HOMO, an M−C$_\alpha$ bonding orbital which is delocalized significantly onto C$_\beta$. As such, the total C$_2$H$_5$Ti bonding interaction is essentially a two-electron phenomenon, and any direct Ti···H interaction appears at best to be modest. This feature is exemplified by strong evidence for both eclipsed and staggered agostic conformers, with the former being marginally more stable. IR and NMR studies, in concert with force field calculations, argue strongly against the β-agostic interaction in **2** being described in terms of a Ti···H−C bridging unit, as evidenced, for example, by the nature of the C$_\beta$−H′ stretching vibration (Figure 4).

Conclusions

We have confirmed that the six-coordinated complex EtTiCl$_3$(dmpe) (**2**, VE = 12) has an unusual structure in the crystalline state with an acute TiCC bond angle [84.57(9)°], an eclipsed C$_2$H$_5$Ti unit, and a short Ti···C$_\beta$ [2.501(2) Å] as well as a Ti···H$_\beta$ [2.06(2) Å] contact. By contrast, the base-free compound EtTiCl$_3$ (**1**, VE = 8) exists in the gas phase as a four-coordinated molecule, the GED pattern of which implies a more or less normal, staggered C$_2$H$_5$Ti unit displaying no sign of β-agostic interactions. These results are consistent with the IR and NMR spectra of **1** and **2** and with the findings of DFT calculations.[12,19,20]

We suggest that the agostic interactions intimated by the structure of the dmpe adduct **2** are favored because adduct formation leads to elongation of the Ti−C bond by 0.06 Å and of the Ti−Cl bonds by up to 0.22 Å and also because it renders the EtTiCl$_3$ framework less rigid. Computational evidence indicates that the M−C$_\alpha$ bonding electrons in **2** are delocalized over the entire ethyl group[12] and that the reduction of the TiCC valence angle allows the metal atom to establish significant covalent bonding interactions with the β-C atom and perhaps to a lesser extent with its appended H atom.

In a recent publication Popelier suggests topological analysis of the electron density as a means of identifying agostic interactions.[34] A topological analysis of the experimental and calculated electron density of **2** (based on DFT calculations and multipole refinements on high-order X-ray diffraction data) reveals indeed a bond critical point between the agostic hydrogen atom and the metal center. In addition, the Ti−C bond path is significantly curved, in agreement with the assumption of a bent Ti−C bond.[12] The relevance of bond critical points between hydrogen atoms and metal centers as a criterion for an agostic interaction will be the subject of another article.[33]

Experimental Section

Synthesis of EtTiCl$_3$ and EtTiCl$_3$(dmpe). Standard Schlenk and high-vacuum techniques were used throughout to prepare EtTiCl$_3$ and EtTiCl$_3$(dmpe) by the methods described elsewhere.[12]

Gas-Phase Electron Diffraction. Electron diffraction measurements on EtTiCl$_3$ vapor were carried out with the Balzers KDG2 unit at Oslo,[26] with the sample reservoir at 268 K, the vapor being injected in the dark via an all-glass inlet system held at room temperature. Exposures were made at nozzle-to-plate distances of ca. 50 cm (4 plates) and 25 cm (5 plates). The plates were traced using a modified Joyce-Loebl microdensitometer and the data processed with a program written by T. G. Strand. Atomic scattering factors were taken from ref 27a. 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 were based on a model with C_s symmetry (see Figure 1). In keeping with the results of DFT calculations, the CTiCl$_3$ fragment was modeled on the assumption of local C_{3v} symmetry; a common C−H bond distance and a methyl group with local C_{3v} symmetry were also assumed. The geometry of the methylene group was defined by C_s symmetry, with the restriction that the CH$_2$ plane bisects the TiCC angle. In addition, identical H−C−H angles were assumed in the CH$_3$ and the CH$_2$ groups. The molecular structure was then determined by seven independent param-

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eters, viz., the bond distances Ti−C, Ti−Cl, C−C, and C−H and the valence angles ∠CTiCl, ∠TiCC, and ∠CCH(methyl). Initial refinements were carried out without corrections for thermal vibrations. Inclusion of vibrational correction terms ($D = r_\alpha - r_a$) led to a slightly improved fit but to no significant changes of the estimated geometrical parameters. Refinement of the CCH(methyl) angle led to values in the range 114−120° with large standard deviations and no significant improvement of the fit. This angle was therefore constrained to a value of 109°.

The DFT force field of **1** was used to calculate the root-mean-square (rms) vibrational amplitudes, vibrational correction terms $D = r_\alpha - r_a$, and force constants by means of the program ASYM20.[28] A single scale factor (0.966) for the theoretical force field was optimized by minimizing the rms deviations between the calculated and observed frequencies.[19]

X-ray Crystal Structure Determination for $EtTiCl_3$(dmpe). Dark red crystals were obtained by slow cooling of a toluene solution. X-ray data were collected on a STOE Imaging Plate Detector System with a rotating anode X-ray generator (Enraf-Nonius); the φ movement mode was rotation. Final cell constants were obtained by least-squares refinement of 5000 reflections with $I/\sigma(I) > 33$ ($1.5° < \varphi < 238°$, $20.5° < 2\Theta < 55.9°$) with the program CELL.[29] The data were corrected for polarization effects and anomalous dispersions. Over the duration of the measurements (32.4 h), no significant variation of the mean intensity due to degradation or absorption effects was observed. Crystal dimensions: 0.1 × 0.3 × 0.5 mm; monoclinic space group $P2_1/n$ (int. tab. No. 14); $a = 7.8095(6)$ Å, $b = 16.0799(9)$ Å, $c = 11.8014(8)$ Å, $\beta = 91.634(8)^o$, $V = 1481.4(4)$ Å^3; $T = 105(1)$ K; $Z = 4$, $F(000) = 688$, $\rho_{calc} = 1.495$ g cm^{-3}, $\mu = 13.0$ cm^{-1}. A total of 16334 reflections were collected at a detector distance of 60 mm ($3.8° < 2\Theta < 56.3°$, h (−10/10); k (−20/20); l (−14/14)); of these, 280 were systematically absent and 600 had negative intensity. A total of 15 454 reflections with $I > 0$ were merged to give 3205 independent reflections, which were used in the full-matrix refinement of 211 parameters. All atom positions were refined freely with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The structure refinement of F_{obs} data converged at shift/error < 0.0001, $R = 0.0288$, $R_w = 0.0180$, residual electron density $+0.51\ \Delta e$ Å^{-3}/$-0.41\ \Delta e$ Å^{-3}. Scattering factors and anomalous dispersion corrections were taken from ref 27b,c. All calculations were performed on a DEC Alpha/AXP workstation using the programs CRYSTALS,[30] PLATON,[31] and SCHAKAL.[32]

DFT Calculations. Details of the Gaussian 94 DFT calculations carried out on compounds **1** and **2** and related species are given elsewhere.[12]

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Supporting Information Available: A complete set of atomic parameters for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101783. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:(+44)-1223−336−033; e-mail: deposit@ccdc.cam.ac.uk). A listing (7 pages) can also be ordered from the ACS and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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