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Preliminary communication

On the agostic interaction in $TiCl_3CH_3$ and related compounds: A linear combination of Gaussian-type orbitals $X\alpha$ study

Peter Knappe and Notker Rösch *

Lehrstuhl für Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4,
8046 Garching (Federal Republic of Germany)

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Abstract

The geometries of $TiCl_3L$ and of $TiCl_5L^{2-}$ ($L = Cl$, CH_3) have been calculated by use of the first principles linear combination of Gaussian-type orbitals $X\alpha$ method. The calculated bond lengths and selected vibrational frequencies are generally in good agreement with experimental values, but essentially undistorted methyl groups with axial orientation have been found, at variance with conclusions from an electron diffraction study on $TiCl_3CH_3$ and from an Extended Hückel analysis of $TiH_5CH_3{}^{2-}$.

There is currently much interest in organometallic compounds with agostic interactions [1] owing to their importance for the problem of C–H bond activation [2]. In some of these complexes an obvious distortion of the ligand geometry has been observed as a consequence of the covalent bonding of a hydrogen atom simultaneously to a carbon atom and a transition metal center [1,3].

Our study was prompted by two previous investigations. First, from a molecular orbital analysis based on Extended Hückel calculations of $H_{3+n}Ti(CH_3)^{n-}$ it had been suggested [4] that agostic interaction leads to an asymmetric bending of a methyl group bound to an octahedrally coordinated titanium center ($n = 2$), but that essentially no agostic interaction should be observable at a tetrahedral titanium center ($n = 0$); the case of a symmetric methyl distortion was not treated in this molecular orbital study. Secondly, electron diffraction data suggested an unusual and (apparently [3]) rather unique agostic interaction at an α carbon atom in the case of trichloromethyltitanium(IV), $TiCl_3CH_3$ (**1**) [5]. In that study, the methyl hydrogens were found not only to be bent symmetrically towards the metal (Ti–C–H 101°) but also to exhibit substantially elongated bonds to the carbon atom (1.16 Å).

A thorough investigation of the bonding in tetrahedral and octahedral titanium compounds [4] using a first-principles all-electron method therefore seemed highly

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Table 1

Comparison of experimental and calculated geometries of various titanium compounds

	Method	Bond distances (Å)			Angles (degrees)	
		Ti–Cl	Ti–C	C–H	C–Ti–Cl	Ti–C–H
$TiCl_4$, **2**	Exp [a]	2.17				
	$X\alpha$ [b]	2.17				
$TiCl_3(CH_3)$, **1**	Exp [c]	2.19	2.04	1.16	105.2	101.0
	$X\alpha$ [b]	2.17	2.00	1.11	102.0	106.9
	GVB [d]	2.30	2.04 [e]	1.11	100.5	105.5
	CAS [d]	2.19 [e]	2.11	1.11	105.2 [e]	106.2
$TiCl_6^{2-}$, **3**	Exp [f]	2.35				
	$X\alpha$ [b]	2.35				
$TiCl_3(dmpe)(CH_3)$	Exp [g]	2.32	2.12	1.10	99.1	108.3
$TiCl_5(CH_3)^{2-}$, **4**	$X\alpha$ [b]	2.35 [e]	2.11	1.11	90.0 [e]	114.7
$TiCl_3(PH_3)_2(CH_3)$	HF [h]	2.37	2.09	1.09	–	108.0

[a] Ref. 12. [b] LCGTO-$X\alpha$, this work. [c] Ref. 5. [d] Ref. 6. [e] Fixed value. [f] Ref. 13. [g] Ref. 15. [h] Ref. 14.

desirable. While the present study was in progress an ab initio calculation raised doubts about the importance of an agostic interaction in **1** [6]. The present work supports and extends these ab initio findings by results obtained with a local density based approach.

We employed the linear combination of Gaussian-type orbitals (LCGTO) $X\alpha$ method [7,8] in its non-spin-polarized variant ($\alpha = 0.7$). Quite flexible orbital bases were used and were only rather moderately contracted (Ti: (15,11,6) contracted to [11/9/4] [9]); Cl: (12,9,1) [10] to [9/6/1]; C: (9,5,1) [11] to [6/5/1]; H: (6,1) [11] to [4/1]). The auxiliary basis sets necessary in the LCGTO-$X\alpha$ method [7] for fitting the electronic charge density and exchange potential were constructed by standard procedures [8].

For $TiCl_4$ (**2**) (in T_d symmetry) and $TiCl_6^{2-}$ (**3**) (in O_h symmetry) perfect agreement was obtained between calculated and experimental [12,13] values for the Ti–Cl bond length (see Table 1). The geometry of **1** was optimized in staggered configuration with retention of the threefold axis. For $Cl_5Ti(CH_3)^{2-}$ (**4**), only a partial geometry optimization was performed; local C_{3v} symmetry for the methyl group and a pseudo-octahedral structure for the Cl_5Ti fragment were imposed, the Ti–Cl bond length being held at the value for **3**.

The resulting geometries are reported in Table 1, together with values from other theoretical investigations [6,14] and from experiment [5,12,13,15]. As in previous LCGTO-$X\alpha$ studies [8,16], we find satisfactory agreement between calculated and experimental values for the various bond lengths, but with the well-known underestimation of the transition metal to carbon bond distance characteristic of the local density approach [8]. For **1**, essentially no distortion of the methyl group could be detected, the carbon to hydrogen bond length exhibiting a value in the usual range.

The evaluation of the results for octahedrally-coordinated titanium compounds **4** is less straightforward, since the other two systems listed in Table 1 exhibit no symmetry. Whereas the observed bond lengths are quite close to their average shown in Table 1, there is a large variation in the angles around the titanium atom [14,15], and this somewhat reduces the significance of the corresponding comparison.

Table 2

Selected vibrational frequencies (in cm^{-1}) of the methyl group in $TiCl_3CH_3$

Characteristic		Experimental [a]	Calculated	
			$X\alpha$ [b]	Ab initio [c]
$\nu(C-H)_a$	(stretching)	2980		3208
$\nu(C-H)_s$		2894	2855	3122
$\delta(C-H)_a$	(bending)	1380		1565
$\delta(C-H)_s$		1052	990	1360
$\rho(Ti-CH_3)$	(rocking)	580	625	577

[a] Ref. 5. [b] LCGTO-$X\alpha$, this work. [c] Ref. 6, results for TiH_3CH_3.

To corroborate the conclusions on the electronic structure of **1** we calculated selected vibrational frequencies without taking account of coupling between the various motions. The results for the symmetric C–H stretching mode, the symmetric bending mode, and the rocking mode of the methyl group are presented in Table 2, together with values from experiment and from the ab initio calculation [6]. The agreement between experimental and available theoretical results is very satisfactory.

In order to compare the possibility of agostic interaction at an octahedrally with that at a tetrahedrally coordinated titanium atom we also studied the methyl rocking motion in **4**, and found it at 525 cm^{-1}. Thus, in contrast to other authors [4], we did not detect a stable deviation of the methyl group from its pseudo-octahedral axial orientation, although the rocking mode is more facile than in the tetrahedral compound. Taking this mode as a criterion we agree that the agostic interaction is somewhat stronger in pseudo-octahedral coordination. Otherwise, we were able to confirm the salient features of the molecular orbital analysis [4] in both coordination geometries. The tendency for stable deformation due to agostic interaction as calculated by the Extended Hückel method [4] is weak, and may possibly be due to the use of hydrogen atoms as model ligands. A closer analysis of the orbitals found in the LCGTO-$X\alpha$ calculation [17] reveals that the chlorine atoms can certainly not be regarded as innocent, since they buffer the change in the transition metal carbon interaction when the methyl group leaves its axial orientation. The present work sheds some doubts on Extended Hückel investigations of agostic interaction [4] when these rely mainly on energy arguments without help from orbital symmetry.

Summarizing the calculated structural and vibrational data in Tables 1 and 2 we conclude in line with others [8,16,18]) that the results of a LCGTO-$X\alpha$ calculation on a transition metal compound are of a quality at least comparable to that of a Hartree–Fock calculation. For **1**, the agreement of the two rather different theoretical procedures is quite surprising. It is therefore all the more disconcerting that both of the theoretical methods (local density and ab initio) were unable to confirm the unusual geometry of the methyl ligand as deduced from an electron diffraction experiment and attributed to agostic interaction [5].

Besides electron diffraction data, the structural analysis of **1** is based on NMR [5,19] and vibrational measurements. In respect of the latter, it is noteworthy that C–H stretching frequencies exhibiting a comparable lowering have been observed in compounds without agostic interaction [20].

The electronic structure of and the extent of agostic interaction in **1** and other related compounds remains both puzzling and challenging, despite the many experimental and theoretical studies. Additional theoretical investigations are certainly necessary [17]. Most helpful for the analysis of **1** would be further direct structural information, possibly based on an augmented analysis of electron diffraction data.

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