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Formation of 1:1, 2:1, and 2:2 Complexes between Carbonyl Compounds and Titanium Tetrachloride. An ab Initio Study

Vicenç Branchadell* and Antonio Oliva*

Department de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

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The complexes of formaldehyde, acetaldehyde, and acetone with titanium tetrachloride of stoichiometries 1:1, 2:1, and 2:2 have been studied with ab initio SCF−MO methods. The competition between the formation of the 2:1 and 2:2 complexes has been analyzed, and the role of the steric effects has been discussed.

Introduction

Carbonyl compounds can be activated through coordination to a Lewis acid. The formation of these complexes has important consequences in the reactivity and selectivity in many organic reactions. These include nucleophilic additions[1] and Diels−Alder reactions.[2] The knowledge of the structure and properties of such complexes is necessary to understand the mechanism of activation and to obtain information useful for the design of effective catalysts.

Crystal structures of several complexes between carbonyl compounds and Lewis acids have been determined in the last few years.[3] When the Lewis acid has several empty coordination sites, different kinds of complexes can be formed. This is the case of $TiCl_4$ and other Ti(IV) Lewis acids, which show a preference for six-coordinate complexes. The $TiCl_4$ complexes that have been characterized by X-ray diffraction are of two different types: chelate complexes with bidentate carbonyl compounds and complexes containing dimeric $TiCl_4$.[4]

Complexes between Lewis acids and carbonyl compounds have also been the object of theoretical studies.[5−18] Complexes with boron halides, aluminum halides, and alkyl halides have been studied by different authors.[5,7,8,10−16] Several studies have been devoted to late transition metal complexes of formaldehyde.[19] In these complexes, the formaldehyde molecule is generally coordinated η^2 and the main interaction between the metal and formaldehyde is the π-back-donation from the transition metal to the ligand.

We recently studied the complexes between formaldehyde and $TiCl_4$ using ab initio methods.[17] We have determined the most stable structures of $H_2CO-TiCl_4$ and $(H_2CO)_2-TiCl_4$ complexes and calculated their formation energies at several levels of calculation. The results have shown that the coordination of a second formaldehyde molecule in the 1:1 complex leads to a greater stabilization than the coordination of the first molecule. We have also discussed the formation of the dimeric complex 2:2 in which the interaction between formaldehyde and $TiCl_4$ is stronger. In this case, however, no geometry optimization was carried out. More recently, Jonas *et al.*[18] studied several chelate complexes between carbonyl compounds and $TiCl_4$.

The purpose of the present paper is to study with greater detail the formation of formaldehyde−$TiCl_4$ dimeric complexes and the competition between this process and the formation of 2:1 complexes. The role of bulky groups in the carbonyl compound molecule will be considered through calculations of acetaldehyde−$TiCl_4$ and acetone−$TiCl_4$ complexes. The nature of the interaction between carbonyl compounds and $TiCl_4$ in different complexes will be analyzed.

Computational Methods

The calculations have been done using two different types of basis sets: an all-electron basis set and a basis set containing effective core potentials. The all-electron basis set, denoted by DZ, is a double-ζ basis set. The basis set of Dunning and Hay[20] is used for H, C, O, and Cl, while for Ti the basis set of Wachters[21] with the addition of two

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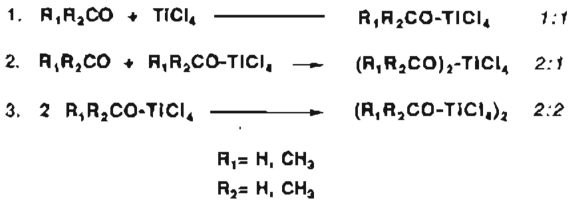
Table 1. Computed Energies[a] for H_2CO, $TiCl_4$, $H_2CO-TiCl_4$, $(H_2CO)_2-TiCl_4$, and $(H_2CO-TiCl_4)_2$

		level of calcn			
molecule	struct[b]	HF/CEP	HF/DZ	HF/CEP(d)	MP2/CEP(d)
H_2CO		−22.259 245	−113.830 712	−22.315 366	−22.600 609
$TiCl_4$		−116.410 094	−2686.449 22	−116.456 971	−117.330 751
$H_2CO-TiCl_4$		−138.695 006	−2800.309 56	−138.782 143	−139.942 818
$(H_2CO)_2-TiCl_4$		−160.985 412	−2914.173 69	−161.113 408	−162.564 491
$(H_2CO-TiCl_4)_2$	**i**	−277.400 087			
	o	−277.402 117	−5600.638 11	−277.558 086	−279.904 230

[a] In au. [b] See Figure 1.

Scheme 1



Gaussian p functions of exponents 0.03 and 0.09[22] and a d function of exponent 0.072[23] is included, so that the d shell has a triple-ζ contraction. The compact effective potential (CEP) basis set of Stevens *et al.*[24] has also been used. In this basis set, the internal electrons of Ti, Cl, C, and O are replaced by effective core potentials, while the valence shells have a double-ζ contraction. In the case of Ti, the 3s3p shell is taken in the valence space and the 3d shell is contracted triple-ζ.

The molecular geometries have been fully optimized with each basis set at the Hartree–Fock (HF) level. Calculations on open-shell systems have been done within the restricted open-shell Hartree–Fock (ROHF) formalism. Electron correlation has been taken into account through second-order Møller–Plesset perturbation theory[25] (MP2) at the Hartree–Fock geometries. In these calculations, the CEP basis set has been augmented with a set of six d polarization functions for Cl, O, and C, with exponents 0.75, 0.80, and 0.80, respectively. This basis set will be denoted by CEP(d).

The calculations have been carried out using the GAMESS,[26] GAUSSIAN-90,[27] and GAUSSIAN-92[28] programs.

Results and Discussion

As we have discussed in the Introduction, carbonyl compounds and $TiCl_4$ can form three kinds of complexes of stoichiometries 1:1, 2:1, and 2:2. The processes leading to these complexes are summarized in Scheme 1.

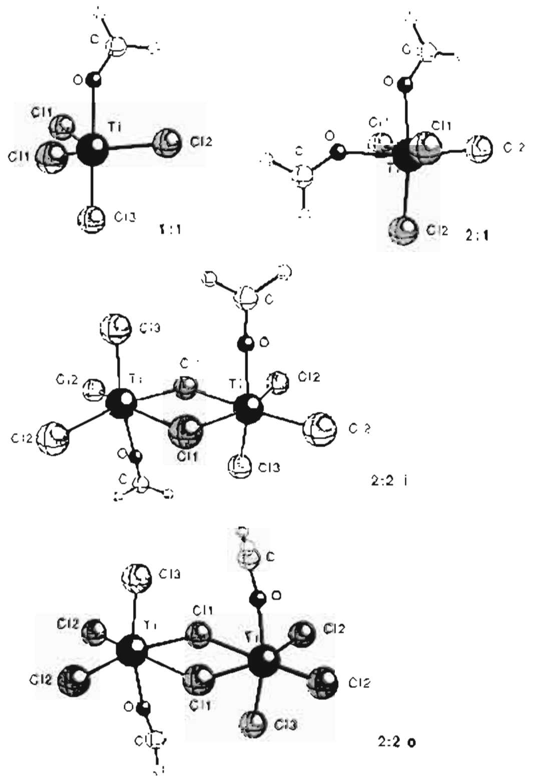


Figure 1. Structures of the complexes between formaldehyde and $TiCl_4$.

Table 2. Formation Energies[a] for the Complexes between Formaldehyde and $TiCl_4$

level of calcn	ΔE_1 (kcal/mol)	ΔE_2 (kcal/mol)	ΔE_{3i} (kcal/mol)	ΔE_{3o} (kcal/mol)
HF/CEP	−16.1	−19.5	−6.3	−7.6
HF/DZ	−18.6	−21.0		−11.9
HF/CEP(d)	−6.2	−10.0		3.9
MP2/CEP(d)	−7.2	−13.2		−11.7

[a] The subindexes 1, 2, and 3 refer to the processes represented in Scheme 1. **i** and **o** stand for the in-plane and out-of-plane structures of the 2:2 complex.

Figure 1 presents the structures of the complexes between formaldehyde and $TiCl_4$ that we have studied. For the 1:1 and 2:1 complexes we have only considered the most stable structures.[17] For the 2:2 complex we present two different structures of C_{2h} symmetry in which the two formaldehyde molecules are anti coordinated. In the first structure (**i**) both formaldehyde ligands are in the plane of the paper, while in the second one (**o**) they are in a perpendicular plane.[29]

Table 1 presents the energies of formaldehyde, $TiCl_4$, and their complexes, computed at different levels of calculation, and Table 2 presents the values of the formation energies of the

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(29) We have also considered a C_{2v} structure with the two formaldehyde ligands syn-coordinated, but its computed energy is about 20 kcal/mol higher than that of **o**.

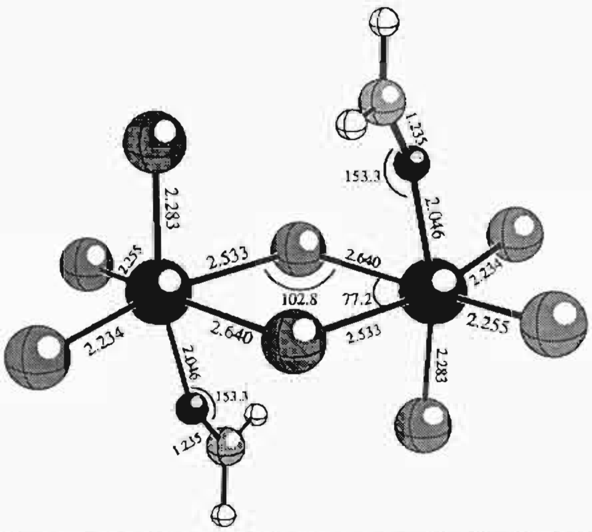

Figure 2. Geometry of the $(H_2CO-TiCl_4)_2$ complex optimized without symmetry constraints. Bond lengths in angstroms; bond angles in degrees.

complexes, corresponding to the processes represented in Scheme 1.

The comparison between the values of ΔE_1 and ΔE_2, presented in Table 2, shows that all levels of calculation the coordination of a second formaldehyde molecule produces a greater stabilization than the coordination of the first molecule.[17] The results obtained with CEP and DZ basis sets at the Hartree–Fock level are similar. The inclusion of polarization functions on C, O, and Cl has an important effect on the computed energy differences. This fact is due to the larger basis set superposition error involved when small basis sets are used. The inclusion of electron correlation has the opposite effect, producing a diminution in the values of ΔE_1, ΔE_2, and, specially, ΔE_3.

Regarding the 2:2 complex, the out-of-plane structure (**o**) is the most stable. Table 2 shows that the formation of the 2:2 complex from the 1:1 complex is energetically less favorable than the formation of the 2:1 complex. This C_{2h} structure is not an energy minimum.[30] An unconstrained geometry optimization at the HF/CEP level of the 2:2**o** structure leads to the C_i structure presented in Figure 2, which is only 1.7 kcal/mol below 2:2**o**.

Figures 3 and 4 present the structures of the complexes of acetaldehyde and acetone, respectively, with $TiCl_4$. For the 1:1, 2:1, and 2:2 complexes of acetaldehyde two different conformations have been considered. In one of them (**s**) the CH_3 group is syn with respect to the in-plane Cl atom, while in the other one (**a**) the methyl is anti.

Tables 3 and 4 present the computed energies for acetaldehyde and acetone complexes. The values of the formation energies of these complexes are presented in Table 5.

Table 3 shows that in the 1:1 and 2:1 complexes there is an important steric effect that favors one of the two possible conformations that we have considered. Steric effects are smaller in the 2:2 complexes, as shown by the relative energies of both structures of the 2:2 complex. Steric effects should also be important for acetone complexes. The structures we have considered in this case may not always be the most stable ones. In order to assess the energy variations associated with conformational changes, we have also done an unrestricted optimization at the HF/CEP level of the 2:1 complex that has lead to the C_2 structure represented in Figure 5. This structure is only 2.0 kcal/mol below the C_{2v} structure presented in Figure 4.

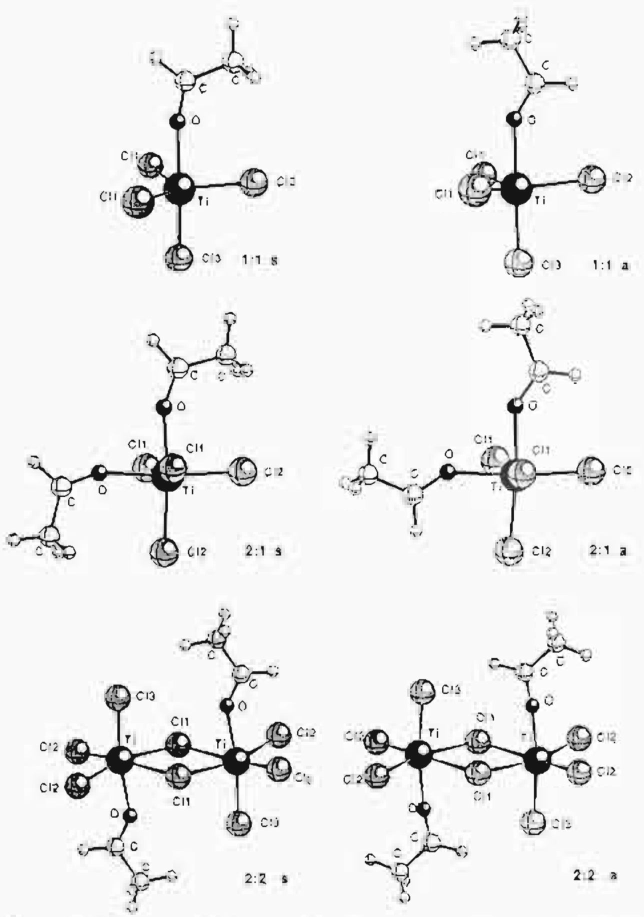

Figure 3. Structures of the complexes between acetaldehyde and $TiCl_4$.

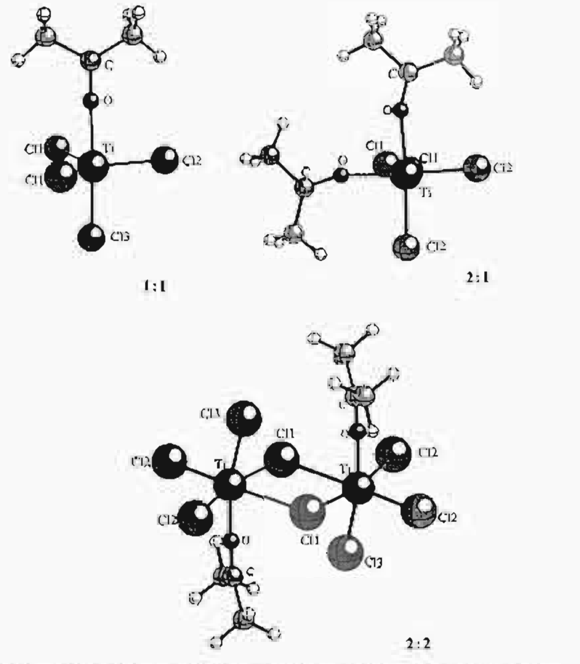

Figure 4. Structures of the complexes between acetone and $TiCl_4$.

Let us now compare the formation energies of acetaldehyde and acetone complexes (Table 5) with those of formaldehyde

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Table 3. Computed Energies[a] for Acetaldehyde and Its Complexes with $TiCl_4$

molecule	struct[b]	level of calcn HF/CEP	level of calcn MP2/CEP(d)
CH_3CHO		−28.906 260	−29.382 263
$CH_3CHO{-}TiCl_4$	s	−145.344 846 (+2.4)	
	a	−145.348 677 (0.0)	−146.728 336
$(CH_3CHO)_2{-}TiCl_4$	s	−174.283 728 (+4.5)	
	a	−174.290 864 (0.0)	−176.136 266
$(CH_3CHO{-}TiCl_4)_2$	s	−290.707 706 (+0.9)	
	a	−290.709 016 (0.0)	−293.477 808

[a] Total energies in au. The values in parentheses correspond to the energies relative to the most stable structure of each complex in kcal/mol. [b] See Figure 2.

Table 4. Computed Energies[a] for Acetone and Its Complexes with $TiCl_4$

structure[b]	level of calcn HF/CEP	level of calcn MP2/CEP(d)
$(CH_3)_2CO$	−35.564 456	−36.168 444
1:1	−151.996 357	−153.506 653
2:1	−187.581 042	−189.695 171
2:2	−304.015 444	−307.055 406

[a] Total energies in au. [b] See Figure 3.

Table 5. Formation Energies[a] for the Complexes of Acetaldehyde and Acetone with $TiCl_4$

	level of calcn	ΔE_1 (kcal/mol)	ΔE_2 (kcal/mol)	ΔE_3 (kcal/mol)
CH_3CHO	HF/CEP	−20.3	−22.5	−7.3
	MP2/CEP(d)	−9.6	−16.1	−13.3
$(CH_3)_2CO$	HF/CEP	−13.7	−12.7	−14.3
	MP2/CEP(d)	−4.7	−12.6	−26.4

[a] The subindexes 1, 2, and 3 refer to the processes represented in Scheme 1.

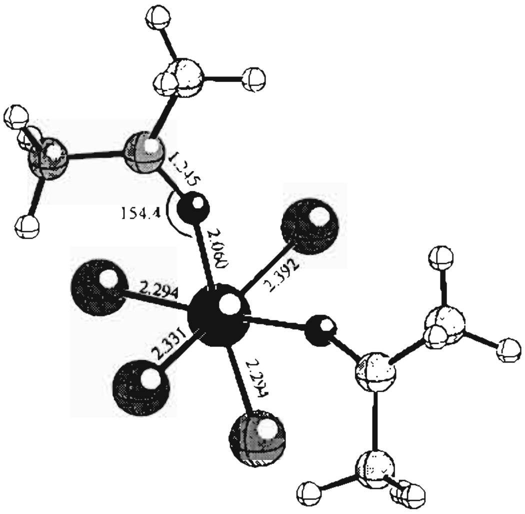

Figure 5. Geometry of the $(CH_3CHO)_2{-}TiCl_4$ complex optimized without symmetry constraints. Bond lengths in angstroms; bond angles in degrees.

complexes (Table 2). The formation of acetaldehyde complexes is in all cases more favorable than that of formaldehyde complexes. The formation of the 2:1 complex is again more favorable than the dimerization of the 1:1 complex. For acetone the situation is different. The values of ΔE_1 and ΔE_2 show that acetone complexes are less stable than those of formaldehyde and acetaldehyde. On the other hand, the value opf ΔE_3 shows that dimerization of the acetone 1:1 complex is more favorable than the formation of the 2:1 complex. The presence of methyl groups increases the steric repulsion with the Cl atoms of $TiCl_4$. This destabilizing effect can be avoided in acetaldehyde complexes, since in the most stable conformations this steric hindrance is minimized. For acetone, an important steric hindrance exists for all possible conformations of 1:1 and 2:1 complexes. This fact makes acetone 1:1 and 2:1 complexes less stable that the corresponding formaldehyde and acetaldehyde complexes.

Let us generalize the discussion to the complexes of a carbonyl compound molecule with two bulky groups, R_1 and R_2. In this case several conformations arising from the rotation around the Ti−O bond should be considered. One can assume that in all complexes the most stable conformation would be one in which the R_1 and R_2 groups are staggered with respect to the Cl atoms. Figure 6 schematically shows the staggered conformations of the complexes between R_1R_2CO and $TiCl_4$. In the 1:1 complex the dihedral angle between R_1 or R_2 and a Cl atom is only about 30°, so that the steric hindrance is still important in this conformation. In the 2:1 complex the repulsion with Cl is smaller, since the dihedral angle is 45°. However, there can be an important repulsion with the substituents of the second carbonyl compound molecule. Finally, in the 2:2 complex the steric repulsion between R_1 or R_2 and Cl is less important and there is no direct interaction between both carbonyl compound molecules. As a consequence, the formation of the 2:2 complex would be favored. In fact, the experimental structures of dimeric $TiCl_4$ complexes correspond to esters with bulky groups.[4a,d] So, the formation of 2:2 complexes between carbonyl compounds and $TiCl_4$ would be due to steric effects that destabilize both the 1:1 and 2:1 complexes. The comparison of the results corresponding to formaldehyde, acetaldehyde, and acetone confirms this argument.

Table 6 presents the values of the most important geometry parameters for formaldehyde, acetaldehyde, acetone, and $TiCl_4$. The values obtained for the C=O bond length are in good agreement with the experimental values. For $TiCl_4$, the results corresponding to the Ti−Cl bond length are within the range of values obtained by other authors[35] and are also in good agreement with the experimental value.

Table 7 presents the values of the most important geometry parameters corresponding to the formaldehyde−$TiCl_4$ complexes. We can observe that both basis sets lead to similar results for all structures. The results obtained for the 1:1 and 2:1 complexes do not change the conclusions drawn from our previous results based on calculations using smaller basis sets.[37]

Table 8 presents values of the most important geometry parameters corresponding to the complexes of acetaldehyde and acetone with $TiCl_4$. In the case of the acetaldehyde complexes, the values of the ∠TiOC bond angle noticeably change, depending on the position of the methyl group. This is the consequence of the steric repulsion with Cl atoms. For acetone 1:1 and 2:1 complexes the values of the ∠TiOC bond angles are greater than those corresponding to the formaldehyde complexes (Table 7) due to the steric repulsion.

Let us now focus our attention on the results corresponding to the 2:2 complexes. The values computed for some of the geometry parameters can be compared to experimental values corresponding to crystal structures of other 2:2 complexes. The computed values for the ∠TiOC bond angle in the 2:2 complex

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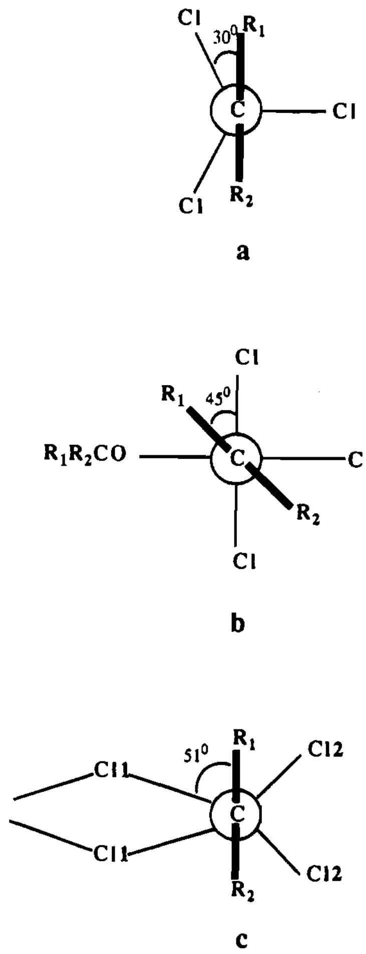

Figure 6. Newman projections of the staggered conformations of the 1:1 (a), 2:1 (b), and 2:2 (c) complexes between R_1R_2CO and $TiCl_4$. A linear Ti−O−C arrangement has been assumed in all cases.

Table 6. Geometry Parameters for Formaldehyde, Acetaldehyde, Acetone, and $TiCl_4$

molecule	basis set	R_{C-O} (Å)	R_{Ti-Cl} (Å)
H_2CO	CEP	1.224	
	DZ	1.217	
	expt[a]	1.208	
CH_3CHO	CEP	1.228	
	expt[b]	1.216	
$(CH_3)_2CO$	CEP	1.234	
	expt[c]	1.222	
$TiCl_4$	CEP		2.204
	DZ		2.217
	expt[d]		2.170

[a] Reference 31. [b] Reference 32. [c] Reference 33. [d] Reference 34.

(Tables 7 and 8) are in excellent agreement with the experimental average value. The carbonyl compound molecules are coordinated in a nearly linear arrangement, in contrast with the bent coordination obtained both for the formaldehyde and acetaldehyde 1:1 and 2:;1 complexes. The coordination mode of acetaldehyde is bent in the case of the **s** structure, due to the steric repulsion between the methyl group and the C13 atom. It has already been observed that a change from a bent to a linear coordination mode involves a small energy barrier in formaldehyde complexes.[17]

Regarding the $(TiCl_4)_2$ moiety, the computed values of the Ti−Cl bond lengths are in reasonable agreement with the average experimental values. The results corresponding to the ∠TiCl1Ti and ∠Cl1TiCl1 bond angles are also in excellent agreement with the experimental values.[36]

The comparison between the values of the Ti−O bond length in the complexes of formaldehyde, acetaldehyde, and acetone (Tables 7 and 8) shows that the strength of the interaction with $TiCl_4$ increases in the order formaldehyde < acetaldehyde < acetone. This result is in accordance with the relative values of formation energies of all formaldehyde and acetaldehyde complexes (Tables 2 and 5). For acetone this is the case only when the 2:2 complex is considered, since steric hindrance between methyl groups and Cl atoms destabilize 1:1 and 2:1 complexes.

For all the carbonyl compounds the values of the Ti−O bond lengths in the 2:2 complex are smaller than those in the 1:1 and 2:1 complexes. This indicates that the interaction between the carbonyl compound molecule and $TiCl_4$ in the 2:2 complex is stronger. This fact can also be related to the values of the C=O bond length which show a greater geometry distortion from the isolated carbonyl compound molecule in the 2:2 complexes.

These results suggest that the strength of the interaction between the carbonyl compound molecule and $TiCl_4$ increases in the order 1:1 < 2:1 < 2:2. This ordering agrees with the acceptor ability of the $TiCl_4$, $H_2CO-TiCl_4$, and $H_2CO-(TiCl_4)_2$ moieties in the 1:1, 2:1, and 2:2 complexes. These acceptor abilities can be estimated through the calculation of the electron affinities for these fragments in the geometries they have in the formaldehyde complexes. These fragments are represented in Figure 7. Table 9 presents the computed electron affinities of these fragments as well as the charge transfer to formaldehyde in each complex, computed from the Mulliken population analysis. One can observe that while electron affinity increases from $TiCl_4$ to $H_2CO-(TiCl_4)_2$, the charge transfer reaches a maximum in the case of $(H_2CO)_2-TiCl_4$. This indicates that other factors have to be taken into account.

The results presented in Tables 6 and 7 show that there is an important variation of the ∠TiOC bond angle from one complex to another. A linear arrangement of the carbonyl compound molecule favors the electrostatic interaction with the $TiCl_4$ moiety, since the dipole moment of the carbonyl compound molecule is oriented in the direction of the C=O bond.[6] On the other hand, the HOMO of the carbonyl compound molecule is centered on the O atom and it is pointing to the direction perpendicular to the C=O bond in the plane of the molecule.[14,17] This means that the overlap between this donor orbital and the acceptor orbital of the $TiCl_4$ fragment increases when the ∠TiOC bond angle becomes smaller. In the formaldehyde complexes the maximum value of charge transfer corresponds to the 2:1 complex, in which the ∠TiOC bond angle has its minimum value. In the 2:2 complexes the charge transfer is greater than that in the 1:1 complex, regardless of the linear Ti−O−C arrangement. This is due to the shorter Ti−O bond length in the 2:2 complex.

The strength in the electrostatic interaction between $TiCl_4$ and the carbonyl compound molecule in the complexes can be related to the electrostatic potential of the acceptor moiety of each complex. We have calculated the electrostatic potential created by the distorted $TiCl_4$, $H_2CO-TiCl_4$, and $H_2CO-(TiCl_4)_2$ moieties along the axis in the direction of the missing formaldehyde ligand (see Figure 7). The results obtained are presented in Figure 8. One can observe that in the region between 1.90 and 2.25 Å, which corresponds to the normal range of Ti−O bond length values, the electrostatic potential increases

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(36) The computed geometry parameters can also be compared with those corresponding to the crystal structure of $Ti_2Cl_{10}^{2-}$: Ti−Cl1 = 2.481 and 2.506 Å, ∠TiCl1Ti = 101.21°, and ∠Cl1TiCl1 = 78.78°.[37]

(37) Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1971**, *10*, 122.

Table 7. Selected Geometry Parameters[a] for the Complexes between Formaldehyde and $TiCl_4$

complex	struct	basis set	$Ti-Cl_1$	$Ti-Cl_2$	$Ti-Cl_3$	$Ti-O$	$C-O$	∠TiOC	$\angle TiCl_1Ti$	$\angle Cl_1TiCl_1$
1:1		CEP	2.250	2.276	2.236	2.151	1.231	148.0		
		DZ	2.264	2.292	2.247	2.114	1.225	147.3		
2:1		CEP	2.331	2.279		2.122	1.230	143.4		
		DZ	2.344	2.295		2.102	1.223	142.4		
2:2	**i**	CEP	2.566	2.255	2.270	2.045	1.230	177.1	102.3	77.7
	o	CEP	2.580	2.247	2.287	2.024	1.232	171.6	102.3	77.7
		DZ	2.599	2.259	2.307	1.986	1.228	169.3	101.9	78.1

[a] Bond lengths in angstroms; bond angles in degrees. See Figure 1 for numeration.

Table 8. Selected Geometry Parameters[a] for the Complexes of Acetaldehyde and Acetone with $TiCl_4$

	complex	struct	$Ti-Cl_1$	$Ti-Cl_2$	$Ti-Cl_3$	$Ti-O$	$C-O$	∠TiOC	$\angle TiCl_1Ti$	$\angle Cl_1TiCl_1$
CH_3CHO	1:1	**s**	2.266	2.271	2.244	2.082	1.237	167.2		
		a	2.257	2.280	2.243	2.106	1.238	149.0		
	2:1	**s**	2.343	2.288		2.087	1.236	157.0		
		a	2.341	2.290		2.092	1.237	143.2		
	2:2	**s**	2.548	2.272	2.257	2.058	1.241	146.5	101.8	78.2
		a	2.580	2.258	2.282	2.005	1.241	173.4	103.2	76.8
$(CH_3)_2CO$	1:1		2.277	2.268	2.249	2.042	1.244	179.4		
	2:1		2.352	2.294		2.068	1.241	162.4		
	2:2		2.584	2.262	2.296	1.966	1.251	178.2	102.1	77.9
		exp[b]	2.50	2.22	2.24	2.03		167	101	79

[a] Optimized with the CEP basis set. Bond lengths in angstroms; bond angles in degrees. See Figures 3 and 4 for numeration. [b] Average values obtained from refs 4a and 4d.

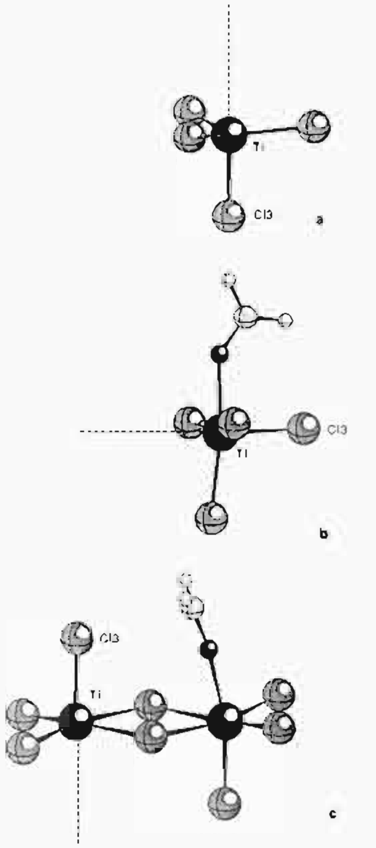

Figure 7. Acceptor moieties in the 1:1 (a), 2:1 (b), and 2:2 (c) formaldehyde$-TiCl_4$ complexes. The dashed line points to the direction of the coordination site of the missing formaldehyde ligand.

Table 9. Vertical Electron Affinity[a] of the Acceptor Moieties and Charge Transfer[b] to Formaldehyde in the Complexes between Formaldehyde and $TiCl_4$

complex	E_{ea} (kcal/mol)	t (au)
1:1	97.6	0.203
2:1	109.3	0.249
2:2	133.6	0.224

[a] Computed with the CEP basis set at the geometries corresponding to the complexes with formaldehyde. [b] Computed with the CEP basis set for the most stable structure of each complex.

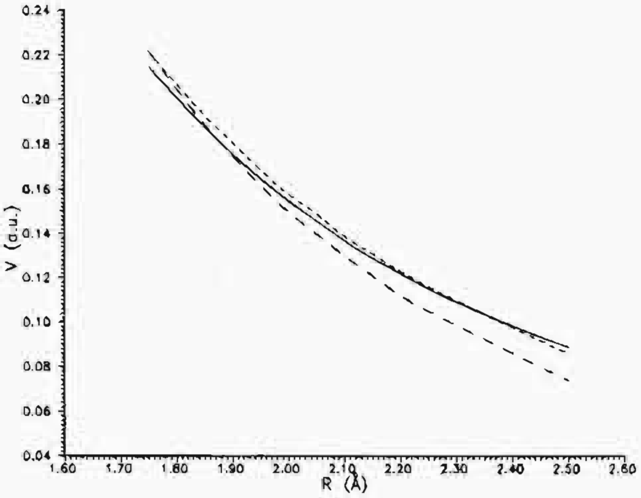

Figure 8. Variation of the electrostatic potential with the distance to the Ti atom along the axis in the direction of the missing formaldehyde ligand for the distorted $TiCl_4$ (solid line), $H_2CO-TiCl_4$ (long-dashed line), and $H_2CO-(TiCl_4)_2$ (short-dashed line) fragments.

in the order of $H_2CO-TiCl_4$ < $TiCl_4$ < $H_2CO-(TiCl_4)_2$. This result is in good agreement with the variation of the ∠TiOC bond angle in the formaldehyde$-TiCl_4$ complexes.

To confirm this analysis, we have also studied the $H_2CO-TiCl_3^+$ and $H_2CO-TiCl_5^-$ complexes. Figure 9 presents the geometries of these complexes optimized with the CEP basis set. We can see that there is an important variation of the ∠TiOC bond angle. In the $TiCl_3^+$ complex, where the interaction with formaldehyde is mainly electrostatic, the bond angle is close to 180°, while in the $TiCl_5^-$ complex, in which the electrostatic interaction is not favorable, the bond angle is much smaller.

The formation energy of the 2:2 complex (ΔE_3) can be formally decomposed into two terms: the energy necessary to distort two $R_1R_2CO-TiCl_4$ molecules from their equilibrium geometry to the geometry they have in the dimer and the interaction energy between both distorted fragments. The distortion necessary to form the 2:2 complex can also be

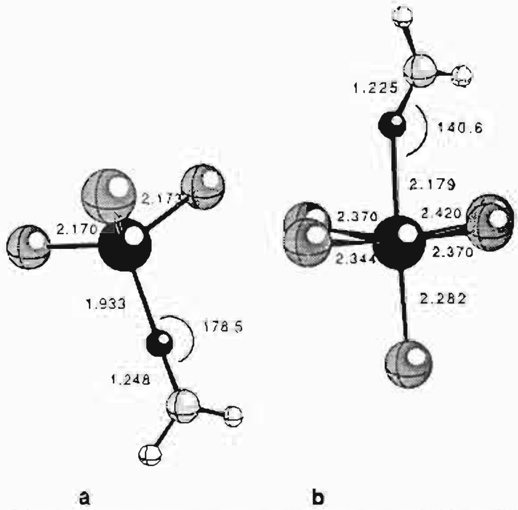

Figure 9. Geometries of the $H_2CO-TiCl_3^+$ (a) and $H_2CO-TiCl_5^-$ (b) complexes optimized with the CEP basis set. Bond lengths in angstroms bond angles in degrees.

Scheme 2

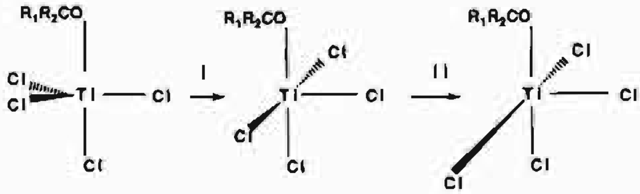

Table 10. Distortion Energies[a] for the $R_1R_2CO-TiCl_4$ Complexes in the Formation of the Dimers

R_1	R_2	ΔE_I (kcal/mol)	ΔE_{II} (kcal/mol)
H	H	11.3	11.2
CH_3	H	12.1	10.0
CH_3	CH_3	13.1	6.6

[a] See Scheme 2.

decomposed in two steps, as shown in Scheme 2. In the first one (I) the ∠ClTiCl bond angle opens to form a square pyramidal complex. This process is also involved in the formation of the 2:1 complex. The second step (II) consists of the lengthening of one of the basal Ti−Cl bonds. The computed distortion energies corresponding to the formaldehyde, acetaldehyde, and acetone complexes are presented in Table 10. One can see that the value ΔE_I slightly increases with the number of methyl groups, while the value of ΔE_{II} diminishes.

Regardless of the important geometry distortion, dimerization is energetically favorable, since the interaction energy between both distorted fragments exceeds the distortion energy. The situation is completely different if one considers the dimerization of $TiCl_4$. We have optimized the geometry of the C_{2h} structure of the $(TiCl_4)_2$ complex presented in Figure 10 with the CEP basis set. The computed dimerization energy is 20.7 kcal/mol, so that this process is energetically unfavorable. The computed distortion energy of each $TiCl_4$ moiety is 31.6 kcal/mol. The effect of the coordinated R_1R_2CO molecule is to facilitate the distortion of the $TiCl_4$ molecule involved in the dimerization. Moreover, the coordination R_1R_2CO molecule also increases the interaction energy between both monomers.

The formation of dimeric $TiCl_4$ complexes can be considered as a partial Cl^- exchange between two $TiCl_4$ moieties. The coordination of a carbonyl compound molecule increases the Cl^- donor ability of each $TiCl_4$ molecule. This fact can be related to the value of the Ti−Cl bond dissociation energy in $TiCl_4$ and $H_2CO-TiCl_4$ computed with the CEP basis set. The energy for dissociation of $TiCl_4$ into $TiCl_3^+$ and Cl^- is 222.1 kcal/mol, while that for the dissociation of $H_2CO-TiCl_4$ into $H_2CO-TiCl_3^+$ and Cl^- is 158.4 kcal/mol. On the other hand, the Cl^- acceptor ability of $TiCl_4$ is less sensitive to the coordination of a carbonyl compound. The energy for formation of $TiCl_5^-$ from $TiCl_4$ and Cl^- is −56.2 kcal/mol, computed with the CEP basis set, while the formation of $H_2CO-TiCl_5^-$ from $H_2CO-TiCl_4$ and Cl^- involves −50.6 kcal/mol. As a consequence of these facts, the energy corresponding to the complete Cl^- transfer from one $TiCl_4$ molecule to another diminishes from 165.9 to 107.9 kcal/mol due to the coordination of formaldehyde. Stronger donor carbonyl compounds and solvent molecules could favor this process in which the highly acidic $TiCl_3^+$ cation is formed.[38]

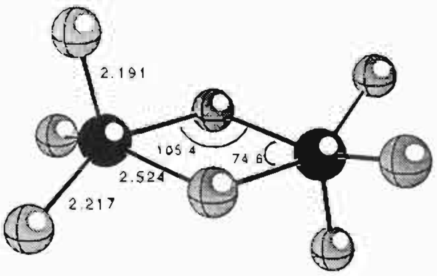

Figure 10. Geometry of the $(TiCl_4)_2$ complex optimized with the CEP basis set. Bond lengths in angstroms bond angles in degrees.

Concluding Remarks

The results obtained in this work show that formaldehyde, acetaldehyde, and acetone form 1:1, 2:1, and 2:2 complexes with $TiCl_4$.

For formaldehyde and acetaldehyde, the coordination of a second R_1R_2CO molecule in the 1:1 complex is more favorable than the formation of the 2:2 complex through dimerization of the 1:1 complex. However, the presence of two bulky groups in the carbonyl compound molecule, such as for acetone, involves important steric effects in the 1:1 and 2:1 complexes, while in the 2:2 complexes the steric hindrance is minimized. This result is in good agreement with the dimeric nature of the experimentally characterized structures corresponding to complexes with carbonyl compounds containing bulky groups.

The analysis of the formation energy of the 2:2 dimeric complexes shows that the coordination of the R_1R_2CO molecule makes the dimerization of $TiCl_4$ possible, since it increases its Cl^- donor ability.

Finally, the strength of the interaction between $TiCl_4$ and R_1R_2CO, suggested by the geometries of the complexes, increases in the order 1:1 < 2:1 < 2:2, in good agreement with the electron affinities of the acceptor moieties.

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