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Complexes between Formaldehyde and Titanium Tetrachloride. An ab Initio Study

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Abstract: The complexes of titanium tetrachloride with one or two molecules of formaldehyde have been studied with ab initio SCF-MO methods. Several structures of the $H_2CO–TiCl_4$, $(H_2CO)_2–TiCl_4$, and $(H_2CO–TiCl_4)_2$ complexes have been considered, and the rearrangements between them have been discussed. The interaction between formaldehyde and $TiCl_4$ has been analyzed in terms of molecular orbital interactions, and the effects produced by complex formation have been rationalized.

Introduction

Complexation of carbonyl compounds by Lewis acids plays an important role in many catalytic processes in organic chemistry. These include catalyzed Diels–Alder reactions,[1] aldol condensations,[2] and several photochemical reactions.[3]

The drastic effects that the activation by Lewis acids produces in the mechanism of these reactions make the knowledge of the structure and properties of such complexes necessary. In the last years, several experimental studies have shown that complexation by Lewis acids produces important modifications on UV,[3c,4] IR,[4,5] and NMR[3c,d,6,7] spectra of carbonyl compounds.

Crystal structures have also been determined for several complexes, showing a bent coordination mode of the carbonyl compound.[8] Boron and aluminum trihalides only form 1:1 complexes with carbonyl compounds. However, other Lewis acids such as $TiCl_4$ or $SnCl_4$ also form 2:1 complexes, through coordination of two different carbonyl compound molecules, and chelates with bidentate carbonyl compounds, so that a six-coordinate complex is obtained. This chelating ability seems to play an important role in the diastereofacial selectivity of reactions involving chiral carbonyl compounds.[9] In the case of $TiCl_4$, complexes with chelating esters and complexes of dimeric $TiCl_4$ have been reported.[10]

Scheme I

1. $H_2CO + TiCl_4 \longrightarrow H_2CO\text{-}TiCl_4$

2. $H_2CO\text{-}TiCl_4 + H_2CO \longrightarrow (H_2CO)_2\text{-}TiCl_4$

3. $2\ H_2CO\text{-}TiCl_4 \longrightarrow (H_2CO\text{-}TiCl_4)_2$

Complexes between Lewis acids and carbonyl compounds have also been the object of theoretical studies.[11-20] Complexes with boron trifluoride have been studied by means of semiempirical[11,13,14,18] as well as ab initio methods.[15-17,19,20] All these studies show a preference for a bent coordination mode of BF_3, in good agreement with the X-ray diffraction structure of the benzaldehyde–BF_3 complex.[13]

Complexes of formaldehyde with BF_3, BCl_3, and BBr_3 have been studied recently by us,[20] and the interaction scheme between the donor and acceptor moieties has been analyzed from molecular orbital considerations. This analysis has permitted us to rationalize the effects produced by complexation on the structure and properties of formaldehyde as well as the Lewis acidity scale of boron trihalides.

Transition metal complexes of formaldehyde have also been studied theoretically.[21] However, only complexes with electron-rich metals have been considered. For these kinds of complexes, the formaldehyde molecule is generally η^2 coordinated and the main interaction between the metal and formaldehyde is the π-back donation from the transition metal to the ligand.

The purpose of the present paper is to extend our study of the formaldehyde–Lewis acid complexes[20] to the early transition metal halide $TiCl_4$. We have considered both 1:1 and 2:1 complexes, the different structures of these complexes, and the interconversion between them. The formation of complexes of dimeric $TiCl_4$ has also been discussed. The nature of the interaction between formaldehyde and $TiCl_4$ and its effect in the formaldehyde molecule have been analyzed.

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Table I. Computed Energies[a] for H_2CO, $TiCl_4$, and $H_2CO–TiCl_4$

		level of calculation					
molecule	structure	HF/HW1	HF/HW2	HF/3-21G	HF/MIDI-3	HF/DZ	MP3/DZ
H_2CO		−113.221 820	−113.221 820	−113.221 820	−113.176 999	−113.830 448	−114.038 126
$TiCl_4$		−62.370 113	−62.374 256	−2673.744 386	−2674.223 295	−2686.423 342	−2686.716 994
$H_2CO–TiCl_4$							
	A1	−175.625 163	−175.628 028	−2787.008 575	−2787.440 349	−2800.283 660	−2800.776 926
	A2	−175.622 772	−175.623 550	−2787.006 309			
	A3	−175.622 348	−175.622 982	−2787.005 957			
	A4			−2787.005 839			
	E1	−175.615 356	−175.615 559	−2786.999 651	−2787.424 351	−2800.146 966	
	E2	−175.607 170	−175.606 804	−2786.991 673			
	E3	−175.612 448	−175.612 058	−2786.996 385			

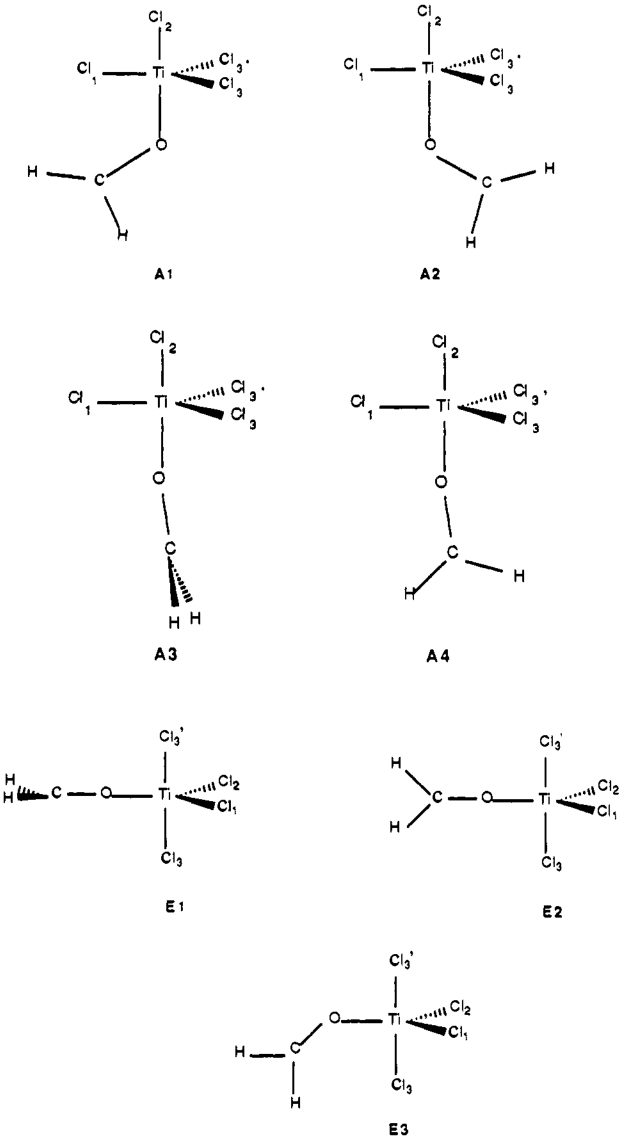
[a] In atomic units.

Table II. Relative Energies[a] and Number of Negative Force Constants[b] for the Stationary Points of the $H_2CO–TiCl_4$ System

	energy					
structure[c]	HW1	HW2	3-21G	MIDI-3	DZ	N
A1	0.0	0.0	0.0	0.0	0.0	0
A2	1.5	1.5	1.5			0
A3	1.8	1.8	1.6			1
A4			1.7			1
E1	6.2	6.5	5.6	10.0	6.0	1
E2	11.3	11.7	10.6			3
E3	8.0	8.3	7.6			2

[a] In kilocalories/mole. [b] N, computed with the 3-21G basis set. [c] See Chart I.

Chart I



A1 A2 A3 A4 E1 E2 E3

Method of Calculation

The molecular geometries of formaldehyde, titanium tetrachloride, and the studied complexes have been fully optimized through ab initio SCF-MO calculations. The computations have been carried out using the 3-21G[22] and MIDI-3[23] basis sets. The MIDI-3 basis set for Ti has been increased with a Gaussian p function of exponent 0.080.[23]

For Ti and Cl, the effective core potentials (ECP) of Hay and Wadt[24] have also been used to replace the internal electrons. For the valence shell of Ti two different contractions have been used: a 2s2p2d contraction, denoted by HW1, and a 2s2p3d contraction, denoted by HW2. In both cases a double-ζ contraction has been used for the valence shell of Cl, while 3-21G has been used for H, C, and O.

The energies of the most relevant 3-21G structures have also been calculated with a double-ζ basis set (DZ). The basis set used for Ti is that of Wachters.[25] with the addition of two Gaussian p functions of exponents 0.03 and 0.09.[23] For H, C, O, and Cl the basis sets of Dunning and Hay have been used.[26] For these calculations electron correlation has been taken into account through the third-order Møller–Plesset perturbation theory (MP3).[26]

The calculations have been carried out using the GAUSSIAN-86[28] and GAMESS[29] programs.

Results and Discussion

As we have discussed in the introduction, $TiCl_4$ and formaldehyde can form 1:1 and 2:1 complexes. X-ray diffraction structures suggest that in some cases a dimerization of the 1:1 complex has also to be considered.[10a,d] These processes are summarized in Scheme I.

We will first present the results corresponding to the $H_2CO–TiCl_4$ complex. The formation of the $(H_2CO)_2–TiCl_4$ complex and the dimerization of the 1:1 complex will be discussed in the following two sections. Finally, a comparative analysis will be done.

$H_2CO–TiCl_4$ Complex. We have considered several possible structures for the $H_2CO–TiCl_4$ complex. The geometry optimization has led to the structures represented in Chart I, all of them corresponding to stationary points in the potential energy surface of the system. Table I presents the energies of these

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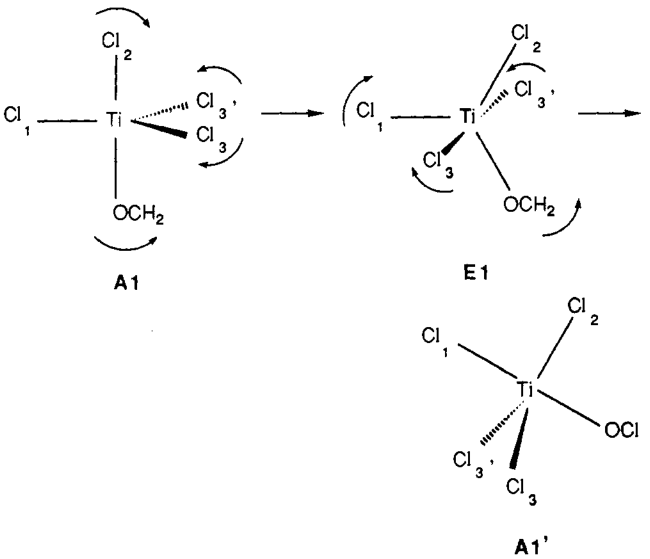
Scheme II



structures computed with different basis sets, along with those corresponding to H_2CO and $TiCl_4$. One can see that A1 is the most stable structure in all cases. Table II presents the energies of all these structures relative to A1 as well as the number of negative force constants corresponding to the 3-21G structures.

All the structures can be considered as distorted trigonal bipyramids. The formaldehyde molecule is placed in the axis of the bipyramid in A1, A2, A3, and A4 and in the equatorial plane in E1, E2, and E3. All these structures present C_s symmetry except E1 and E2, which have C_{2v} symmetry. Only A1 and A2 structures are energy minima of the potential energy surface, i.e., they have no negative force constants. In both cases formaldehyde presents a bent mode of coordination, syn with respect to the in-plane Cl atom in A1 and anti A2.

A4 corresponds to a saddle point of the potential energy surface and can be associated with the transition state linking A1 and A2. A3 is also a transition state, corresponding to the rearrangement from A1 to an analogous structure in which the formaldehyde molecule would be syn with respect to one of the out-of-plane Cl atoms of $TiCl_4$. All these processes involve very low energy barriers, thus indicating that such rearrangements are feasible. Moreover, the low energy difference between A3 and A4 indicates that rotation of the H_2CO moiety is almost free.

No energy minimum corresponding to a structure in which H_2CO is placed in an equatorial position has been found. The most stable equatorial structure, E1, is actually a saddle point of the potential energy surface. An examination of the atomic displacements corresponding to the force constant matrix eigenvector associated with the negative force constant indicates that this structure corresponds to the transition state of an A1 → A1′ rearrangement. As a matter of fact, one can envisage two successive Berry pseudorotations[30] connecting A1 with an analogous structure A1′ through the E1 structure, as indicated in Scheme II. All along the path connecting both minima, the Ti, O, and Cl_1 atoms are kept in the plane of the paper.

These results show that rearrangements from the most stable structure, A1, can take place easily, with energy barriers lower than 10 kcal/mol. This nonrigidity is normally observed in five-coordinate molecules.[31] The different basis sets lead to similar results, the only appreciable discrepancy being the MIDI-3 value corresponding to the E1 structure. The results obtained with the 3-21G basis set are very similar to those obtained with HW1 and HW2, in which ECP are used. In these cases, the use of a double-ζ or a triple-ζ contraction for the 3d orbitals of titanium does not seem to affect the results.

Table III. Computed Formation Energy of the $H_2CO–TiCl_4$ Complex

level of calcn	ΔE (kcal/mol)	level of calcn	ΔE (kcal/mol)
HF/HW1	−20.9	HF/MIDI-3	−25.1
HF/HW2	−20.1	HF/DZ	−18.4
HF/3-21G	−26.6	MP3/DZ	−13.7

Table IV. Geometry of the $TiCl_4$ Molecule

basis set	$R_{Ti–Cl}$ (Å)	basis set	$R_{Ti–Cl}$ (Å)
HW1	2.175	MIDI-3	2.183
HW2	2.167	expt[a]	2.170
3-21G	2.186		

[a] Reference 32.

Let us now focus our attention on the most stable structure, A1. Table III presents the values of the formation energy of the $H_2CO–TiCl_4$ complex from H_2CO and $TiCl_4$ computed with different basis sets. One can observe that the formation of the complex is exothermic in all cases. The 3-21G and MIDI-3 basis sets lead to an overestimation of the stability of this complex. This fact can be attributed to the basis set superposition error, which is expected to be less important when a better quality basis set, such as DZ, or a basis set with ECP is used. On the other hand, the inclusion of electron correlation leads to an additional decrease of the complexation energy.

Table IV presents the values of the Ti–Cl bond length obtained for the equilibrium geometry of $TiCl_4$. One can observe that there is good agreement between computed and experimental values.

Table V and VI present the most important geometrical parameters corresponding to the axial and equatorial structures of the $H_2CO–TiCl_4$ complex, respectively. One can observe that all the basis sets used lead to very similar results. The coordination of formaldehyde produces, in all cases, a lengthening of the Ti–Cl bond lengths.[33] This lengthening is in good agreement with that experimentally observed in other $TiCl_4$ complexes.[10] The formation of the complex also involves a distortion of the formaldehyde molecule, as seen by the increase of the C=O bond length from its equilibrium geometry value (1.207 Å with 3-21G and 1.208 Å with MIDI-3).[34]

Let us now discuss the results corresponding to the axial structures. Table V shows that the most important differences in the $TiCl_4$ moiety are the relative values of the equatorial Ti–Cl bond lengths. In A1, the Ti–Cl_1 bond, which is the bond with the Cl atom syn with respect to the H_2CO molecule, presents a greater length than the Ti–Cl_3 bonds. On the contrary, in A2, the Ti–Cl_3 bond length is greater than the Ti–Cl_1 bond length.

Regarding the Ti–O bond length, there are experimental data only for complexes of dimeric $TiCl_4$ with esters and of monomeric $TiCl_4$ with chelating esters.[10] For these complexes, the observed values of the Ti–O bond length range between 2.03 and 2.14 Å, these values being very similar to those shown in Table V. The optimized values for the ∠TiOC bond angle in the minimum structures A1 and A2 are in agreement with the observed values, which range between 132 and 169°. This wide range of values agrees with the results presented in Table II, since they show that the variation of the ∠TiOC bond angle involves a low energy cost.

If we examine the geometrical parameters corresponding to the equatorial structures (Table VI), we can see that the Ti–O bond length is smaller than that in the axial structures. One can also observe that the axial Ti–Cl bond lengths are greater than those corresponding to the equatorial Ti–Cl bonds.

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(33) The values of these bond lengths can be compared to those obtained in the 3-21G optimization of the $TiCl_5^-$ complex: 2.356 and 2.276 Å for the axial and equatorial bonds, respectively.

(34) These values are in excellent agreement with the experimental value: 1.208 Å.[35]

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Table V. Selected Geometry Parameters[a] for the Axial Structures of the $H_2CO–TiCl_4$ Complex

structure	basis	Ti–Cl$_1$	Ti–Cl$_2$	Ti–Cl$_3$	Ti–O	C–O	∠TiOC	∠Cl$_1$TiO	∠Cl$_1$TiCl$_2$	∠OTiCl$_3$
A1	HW1	2.252	2.208	2.220	2.176	1.223	146.0	82.8	96.6	83.0
	HW2	2.244	2.198	2.212	2.184	1.223	145.8	82.7	96.6	82.9
	3-21G	2.262	2.234	2.233	2.090	1.224	146.7	83.0	96.1	83.5
	MIDI-3	2.252	2.223	2.228	2.046	1.225	147.3	83.7	95.6	83.9
A2	HW1	2.209	2.205	2.239	2.189	1.222	148.0	84.6	97.7	82.4
	HW2	2.202	2.197	2.231	2.199	1.221	147.9	84.4	97.7	82.2
	3-21G	2.222	2.233	2.252	2.099	1.223	149.3	85.4	97.3	82.7
A3	HW1	2.239	2.207	2.229	2.158	1.220	176.8	81.6	96.1	84.4
	HW2	2.231	2.198	2.221	2.166	1.220	176.8	81.5	96.2	84.3
	3-21G	2.231	2.234	2.242	2.056	1.221	177.0	82.3	95.5	84.8
A4	3-21G	2.231	2.235	2.253	2.058	1.221	172.6	86.5	97.1	82.8

[a] See Chart I for numeration. Bond lengths in angstroms; bond angles in degrees.

Table VI. Selected Geometry Parameters[a] for the Equatorial Structures of the $H_2CO–TiCl_4$ Complex

structure	basis	Ti–Cl$_1$	Ti–Cl$_3$	Ti–C$_{3'}$	Ti–O	C–O	∠TiOC	∠Cl$_1$TiO	∠OTiCl$_3$
E1	HW1	2.187	2.311	2.311	2.062	1.222	180.0	125.4	78.8
	HW2	2.179	2.307	2.307	2.067	1.222	180.0	125.6	78.6
	3-21G	2.210	2.310	2.310	2.001	1.223	180.0	125.2	79.8
	MIDI-3	2.208	2.287	2.287	1.987	1.223	180.0	125.7	79.8
E2	HW1	2.185	2.322	2.322	2.078	1.223	180.0	125.7	80.2
	HW2	2.179	2.317	2.317	2.082	1.223	180.0	125.6	80.0
	3-21G	2.209	2.319	2.319	2.013	1.224	180.0	125.4	81.3
E3	HW1	2.179	2.362	2.270	2.094	1.229	145.4	125.1	79.4
	HW2	2.185	2.368	2.278	2.088	1.230	145.6	125.2	79.4
	3-21G	2.208	2.351	2.280	2.045	1.231	145.9	125.2	80.1

[a] See Chart I for numeration. Bond lengths in angstroms; bond angles in degrees.

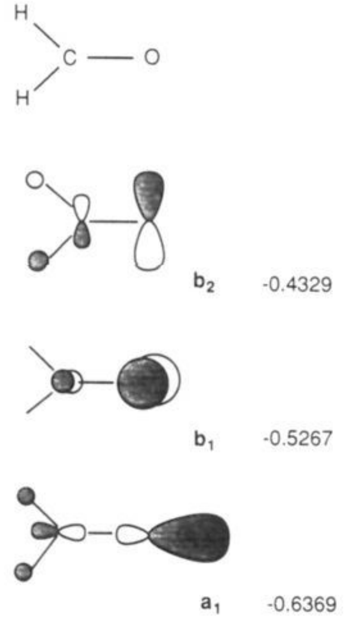

Figure 1. Occupied molecular orbitals of formaldehyde that intervene in the interaction with $TiCl_4$. Orbital energies (in a.u.) have been computed with the 3-21G basis set.

Formaldehyde and $TiCl_4$ form a typical donor–acceptor complex. The structure and properties of such complexes can be rationalized in terms of molecular orbital interactions. Figure 1 schematically represents the occupied molecular orbitals of formaldehyde that intervene in these interactions.

For $TiCl_4$, we have considered two different distortions from the equilibrium T_d geometry. The attack of a new ligand in one of the C_3 axes of the $TiCl_4$ molecule leads to an axial trigonal bipyramidal complex in which the $TiCl_4$ moiety can be considered to have a C_{3v} geometry. On the contrary, if the attack is produced in one of the C_2 axes of $TiCl_4$, the resulting complex will be an equatorial trigonal bipyramid and the $TiCl_4$ moiety will have a C_{2v} geometry. For this reason, the orbitals of $TiCl_4$ have been represented in Figure 2 for these C_{3v} and C_{2v} distorted geometries. The C_{3v} structure has been optimized, the ∠Cl$_1$TiCl$_2$ and ∠Cl$_3$TiCl$_2$ bond angles being kept equal to 90°. For the optimization of the C_{2v} structure, a ∠Cl$_1$TiCl$_2$ bond angle of 180° has been adopted. Within these constraints, the rest of the geometrical parameters have been optimized.

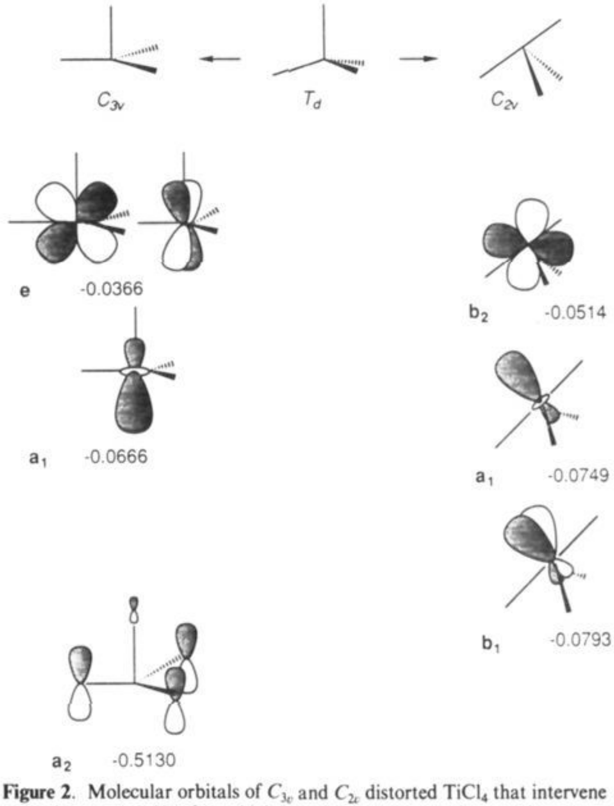

Figure 2. Molecular orbitals of C_{3v} and C_{2v} distorted $TiCl_4$ that intervene in the interaction with formaldehyde. Orbital energies (in a.u.) have been computed with the 3-21G basis set.

Let us first consider the axial complex. The a_1 and b_2 occupied orbitals of formaldehyde can interact with the a_1 orbital and the in-plane e orbital of the $TiCl_4$ moiety. These interactions can be visualized in Figure 3, where the molecular orbitals of the $H_2C–O–TiCl_4$ complex with the main contribution of the a_1 and b_2 orbitals of formaldehyde are represented. A linear Ti–O–C arrangement would involve a maximum overlap between donor and

Table VII. Total Energies[a] (and Formation Energies[b]) of the $(H_2CO)_2$–$TiCl_4$ Complex[c]

level of calcn	C	T1	T2
HF/HW1	−288.882 493 (−22.3)	−288.875 201 (−17.7)	−288.877 765 (−19.3)
HF/HW2	−288.884 430 (−21.7)	−288.876 282 (−16.6)	−288.878 988 (−18.3)
HF/3-21G	−2900.282 257 (−32.5)	−2900.277 642 (−29.6)	−2900.279 482 (−30.8)
HF/MIDI-3	−2900.662 318 (−28.8)	−2900.649 762 (−20.3)	−2900.650 539 (−20.8)
HF/DZ	−2914.146 966 (−20.6)		−2914.143 127 (−18.2)
MP3/DZ	−2914.843 148 (−17.6)		−2914.834 906 (−12.4)

[a] In atomic units. [b] In kilocalories/mole, relative to H_2CO–$TiCl_4$ and formaldehyde. [c] See Chart II.

acceptor orbitals. However, the only minimum structures present a bent Ti–O–C arrangement, since the b_2 orbital of formaldehyde is the energetically more appropriate orbital to interact with a_1 of $TiCl_4$.

The b_1 orbital of formaldehyde, which is the π_{CO} orbital, also intervenes in a stabilizing interaction with the out-of-plane e orbital of $TiCl_4$. However, this interaction is weaker than those involving the in-plane orbitals.

In addition to these stabilizing interactions, repulsive interactions have also to be taken into account. The b_2 orbital of formaldehyde can interact with occupied Cl-centered orbitals of the $TiCl_4$ moiety such as the a_2 orbital represented in Figure 2. The participation of this orbital in the interaction can also be observed in Figure 3b. The balance between stabilizing and repulsive interactions determines the value of the ∠TiOC bond angle, as it was shown for H_2CO–BX_3 complexes.[20]

In the equatorial complex, the lowest energy acceptor orbital of the $TiCl_4$ moiety is b_1. In the E1 structure, this orbital can interact with the b_2 orbital of formaldehyde, thus favoring a linear Ti–O–C arrangement, which is also favored by the interaction between a_1 of $TiCl_4$ and a_1 of formaldehyde. A π interaction involving the b_1 orbital of H_2CO and the b_2 orbital of $TiCl_4$ has also to be considered. Now, repulsive interactions do not take place due to the coordination mode of formaldehyde.

This interaction scheme helps to rationalize the relative energies of the equatorial structures of the complex. The linear E2 structure is less favorable than E1, since, in E2, the b_2 orbital of formaldehyde interacts with the b_2 orbital of $TiCl_4$, which is higher in energy than b_1 and has a less favorable overlap with the formaldehyde orbital. For this reason, the E3 structure is more stable than E2. The interactions taking place in E3 are more similar to those previously discussed for the axial structures.

The interaction between both fragments is more important in the equatorial complex, since the energies of the acceptor orbitals of $TiCl_4$ are lower in the C_{2v} geometry. However, the energy involved in the distortion from the $TiCl_4$ equilibrium geometry in the equatorial complex is greater than in the axial complex. Thus, the 3-21G computed values for the $TiCl_4$ distortion energies in the A1 and E1 structures are 11.5 and 27.8 kcal/mol, respectively. So, the acceptor ability of the metal fragment and the geometry distortion involved in the complex formation are the two factors that govern the preference toward axial or equatorial structures for H_2CO–$TiCl_4$ complexes. The greater distortion energy involved in the formation of the equatorial structures compensates the greater acceptor ability of the C_{2v} $TiCl_4$ moiety, so that axial structures become more favorable.

This greater stability of the axial structures agrees with theoretical predictions according to which in d^0-ML_5 complexes stronger ligands are preferably located at the equatorial positions.[36]

$(H_2CO)_2$–$TiCl_4$ Complex. We have considered three different structures for this complex: C, T1, and T2, which are represented in Chart II. These structures can be considered as octahedral complexes in which the H_2CO ligands are placed in cis (C) or trans (T1 and T2) positions. The C and T2 structures have C_{2v} symmetry while T1 has C_{2h} symmetry. All these structures are energy minima as shown by the computation of the force constant matrix.

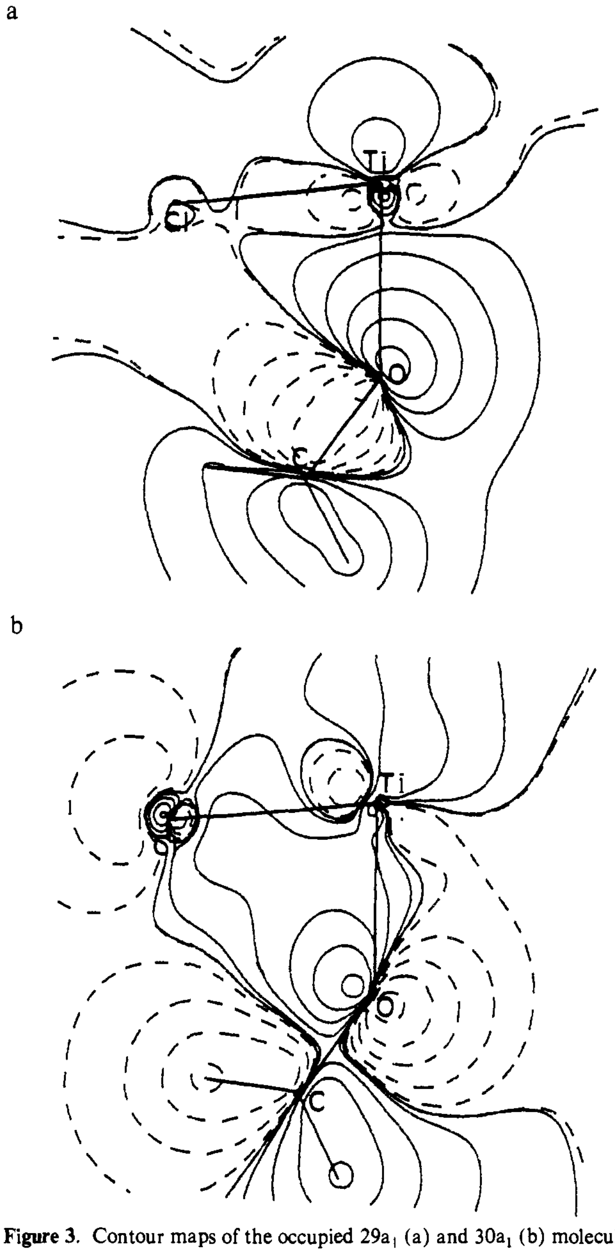

Figure 3. Contour maps of the occupied $29a_1$ (a) and $30a_1$ (b) molecular orbitals of the A1 structure of H_2CO–$TiCl_4$. The contours are ±0.0001, ±0.01, ±0.04, ±0.1, ±0.2, ±0.4, and ±1.0. Solid and dashed lines correspond to positive and negative values, respectively.

Table VII presents the computed energies for these structures as well as the values of their formation energies relative to H_2CO–$TiCl_4$ and formaldehyde. At all levels of calculation the cis isomer is found to be more stable than the trans structures. One can also observe that T2 is slightly more stable than T1. The coordination of the second formaldehyde molecule in H_2CO–$TiCl_4$ involves an extra stabilization of the system in all cases. The formation of the cis 2:1 complex is more exothermic than the formation of the 1:1 complex at all levels of calculation (see Table III). This result agrees with the recently reported experimental complexation enthalpies of the 1:1 and 2:1 complexes between

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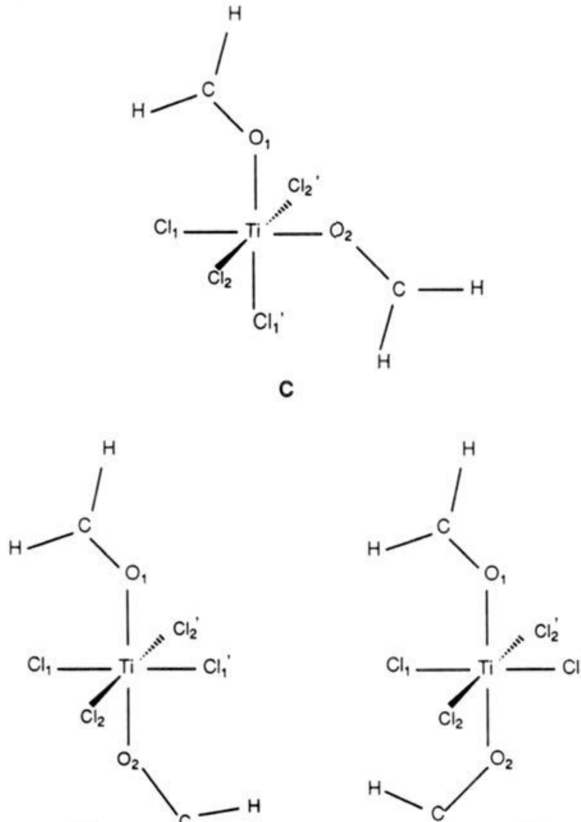
(36) (a) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374. (b) Albright, T. A. *Tetrahedron* **1978**, *38*, 1339–1388. (c) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; J. Wiley and Sons: New York, 1985.

Table VIII. Selected Geometry Parameters[a] for the $(H_2CO)_2$–$TiCl_4$ Complex

structure	basis	Ti–Cl_1	Ti–$Cl_{1'}$	Ti–Cl_2	Ti–O	C–O	∠TiOC	∠Cl_1TiO_1	∠$Cl_{1'}TiO_1$	∠O_1TiO_2	∠O_1TiCl_2	∠Cl_1TiCl_1
C	HW1	2.251	2.251	2.322	2.135	1.223	141.6	87.6	173.1	85.5	82.3	99.3
	HW2	2.244	2.244	2.319	2.140	1.223	141.4	87.6	172.9	85.3	82.2	99.5
	3-21G	2.279	2.279	2.323	2.064	1.225	141.7	87.6	174.5	86.9	83.4	97.8
	MIDI-3	2.262	2.262	2.305	2.039	1.224	141.4	88.2	174.1	85.9	83.4	97.8
T1	HW1	2.353	2.353	2.327	2.027	1.229	142.5	87.1	92.9	180.0	90.0	180.0
	HW2	2.353	2.353	2.326	2.028	1.229	142.5	87.1	92.9	180.0	90.0	180.0
	3-21G	2.350	2.350	2.320	2.002	1.229	143.2	87.1	92.9	180.0	90.0	180.0
	MIDI-3	2.325	2.325	2.298	2.006	1.229	140.2	88.0	92.0	180.0	90.0	180.0
T2	HW1	2.502	2.252	2.324	2.014	1.230	142.7	84.0	96.0	168.0	89.7	180.0
	HW2	2.506	2.248	2.322	2.016	1.229	143.0	84.2	95.8	168.4	89.7	180.0
	3-21G	2.463	2.272	2.316	1.992	1.230	143.5	84.5	95.5	169.0	89.8	180.0
	MIDI-3	2.414	2.257	2.298	2.001	1.229	140.9	86.0	94.0	171.9	89.8	180.0

[a] See Chart II for numeration. Bond lengths in angstroms; bond angles in degrees.

Chart II



monodentate ketones and $VOCl_3$.[37]

Table VIII presents the main geometrical parameters obtained for these structures. Again, the different basis sets lead to very similar results for each structure. One can observe that the coordination of the second formaldehyde molecule leads to an additional lengthening of the Ti–Cl bond lengths with respect to the values corresponding to the H_2CO–$TiCl_4$ complex (see Table V).[38] In the cis isomer, the Ti–Cl_1 bond length is slightly smaller than the Ti–Cl_2 bond length. On the contrary, in the trans structures, the out-of-plane Ti–Cl bonds are longer. These facts indicate that H_2CO produces a smaller trans effect than Cl. In T2, the Ti–Cl_1 and Ti–$Cl_{1'}$ bonds have different lengths, the Ti–Cl_1 bond being noticeably longer. This effect of the formaldehyde ligand on the syn Ti–Cl bond has already been discussed for the H_2CO–$TiCl_4$ complex.

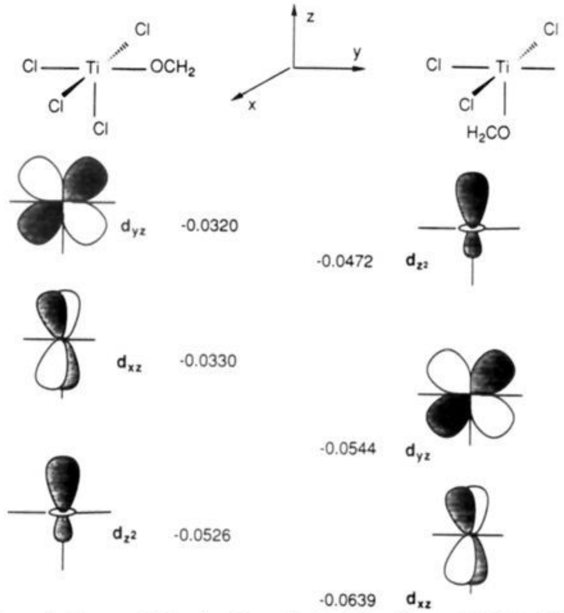


Figure 4. Unoccupied molecular orbitals of the distorted H_2CO–$TiCl_4$ fragment that intervene in the interaction with the second formaldehyde molecule in C and T2. Orbital energies (in a.u.) have been computed with the 3-21G basis set.

The computed average values of the Ti–Cl bond lengths range between 2.28 Å for the HW2 calculations and 2.30 Å for the 3-21G results, in excellent agreement with the experimental values of 2.26 Å[10b,c] and 2.27 Å[10d] corresponding to $TiCl_4$ complexes of chelating esters.

Regarding the coordinated formaldehyde molecules, one can observe that the Ti–O bond length is smaller in the trans structures than in the cis isomer. In all cases, the Ti–O bond is shorter than the same bond in the 1:1 complex (see Table V). The smaller the Ti–O bond length, the greater the distortion of the H_2CO fragments, as shown by the values of the C=O bond lengths. Finally, the ∠TiOC bond angle has very similar values in all structures, being smaller than the value corresponding to the H_2CO–$TiCl_4$ complex (see Table V).

Let us now consider the formation of the $(H_2CO)_2$–$TiCl_4$ complex from H_2CO–$TiCl_4$ and H_2CO. The cis isomer can be formed from the A1 structure through the opening of the ∠$Cl_3TiCl_{3'}$ bond angle (see Chart I). The formation of the trans isomer involves a major rearrangement. One possible path consists of a A1 → E1 rearrangement (see Scheme I) along with the opening of the ∠Cl_1TiCl_2 bond angle. The distortion energy of the H_2CO–$TiCl_4$ moiety computed with the 3-21G basis set is 11.4 kcal/mol for the cis isomer and 27.4 kcal/mol for the T2 structure. Similar values are obtained with the DZ basis set (11.3 and 25.2 kcal/mol, respectively). These results seem to indicate that the formation of the trans isomer from the H_2CO–$TiCl_4$ complex will involve a greater energy barrier than the formation of the cis isomer.

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(37) These values can be compared to that obtained in the 3-21G optimization of the $TiCl_6^{2-}$ complex: 2.401 Å.

(38) Viet, M. T. P.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026–3032.

Chart III

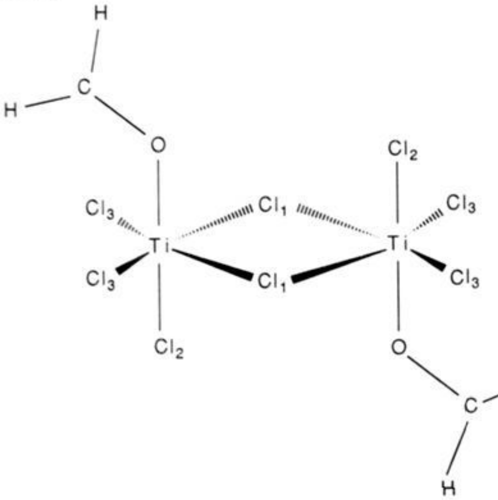

Figure 4 schematically represents the most important acceptor orbitals of the $H_2CO–TiCl_4$ fragment in the C and T2 structures of the $(H_2CO)_2–TiCl_4$ complex. The $H_2CO–TiCl_4$ moiety can be considered a square pyramidal ML_5 fragment in which H_2CO is placed in a basal position in the cis structure and in the the apical position in the trans structures. In both cases, the d_{z^2} and d_{yz} orbitals of this moiety can interact with the a_1 and b_2 orbitals of formaldehyde. The d_{z^2} orbital has lower energy in the H_2CO basal fragment, while d_{xz} and d_{yz} have lower energies in the H_2CO apical fragment. This difference is more important in the d_{xz} orbital, which becomes the LUMO in the apical fragment. This fact is a consequence of the better π-donor ability of Cl^- in front of H_2CO. In spite of the presence of this low-energy d_{xz} orbital, d_{z^2} leads to a better overlap with the occupied orbitals of H_2CO and the *trans*-$(H_2CO)_2–TiCl_4$ complex also presents a bent coordination mode for the second formaldehyde molecule.

Interactions involving the π_{CO} orbital of formaldehyde also take place. This kind of interaction will be more important in the trans structures since the d_{xz} orbital has a lower energy.

In addition to these stabilizing interactions, repulsive interactions involving occupied Cl-centered orbitals of the $H_2CO–TiCl_4$ fragment also exist. In both the cis and trans isomers, the $\angle O_1TiCl_1$ bond angles are greater than in $H_2CO–TiCl_4$ (see Tables V and VIII). So, these repulsive interactions are less important in the 2:1 complex.

$(H_2CO–TiCl_4)_2$ Complex. As we have mentioned in the Introduction, several complexes between carbonyl compounds and dimeric $TiCl_4$ have been characterized through X-ray diffraction.[10a,d] For this reason, we have considered the dimerization of $H_2CO–TiCl_4$ leading to the formation of a $(H_2CO–TiCl_4)_2$ complex (step 3 in Scheme I). Among the several possible structures for this complex, we have only considered that schematically represented in Chart III. This structure, which has C_{2h} symmetry, consists of two Ti-centered octahedral units linked through two bridged Cl atoms, forming a four-center cycle. The H_2CO ligands are placed in anti positions in the plane perpendicular to the cycle. This structure is similar to that experimentally observed for this kind of complex.

The energy of the $(H_2CO–TiCl_4)_2$ complex has been computed with the HW1 and 3-21G basis sets. The geometry of the complex has been taken from experimental data and from the optimized geometries corresponding to the $(H_2CO)_2–TiCl_4$ complex.[39] The results obtained show that the energy involved in the dimerization of $H_2CO–TiCl_4$ is 20.5 kcal/mol with HW1 and −2.0 kcal/mol with 3-21G. It is to be remarked that these values correspond to a nonoptimized geometry of the $(H_2CO–TiCl_4)_2$ complex, so that the stability of this complex with respect to the $H_2CO–TiCl_4$ complex is underestimated. The great difference between the results obtained with both basis sets can be attributed to a greater basis set superposition error in the 3-21G calculation. The dimerization of $H_2CO–TiCl_4$ involves the same kind of geometry distortion as the formation of *cis*-$(H_2CO)_2–TiCl_4$ from $H_2CO–TiCl_4$, i.e., the opening of an equatorial ∠ClTiCl bond angle. So, the energy barrier of the dimerization is expected to be similar to that corresponding to the formation of $(H_2CO)_2–TiCl_4$ from $H_2CO–TiCl_4$.

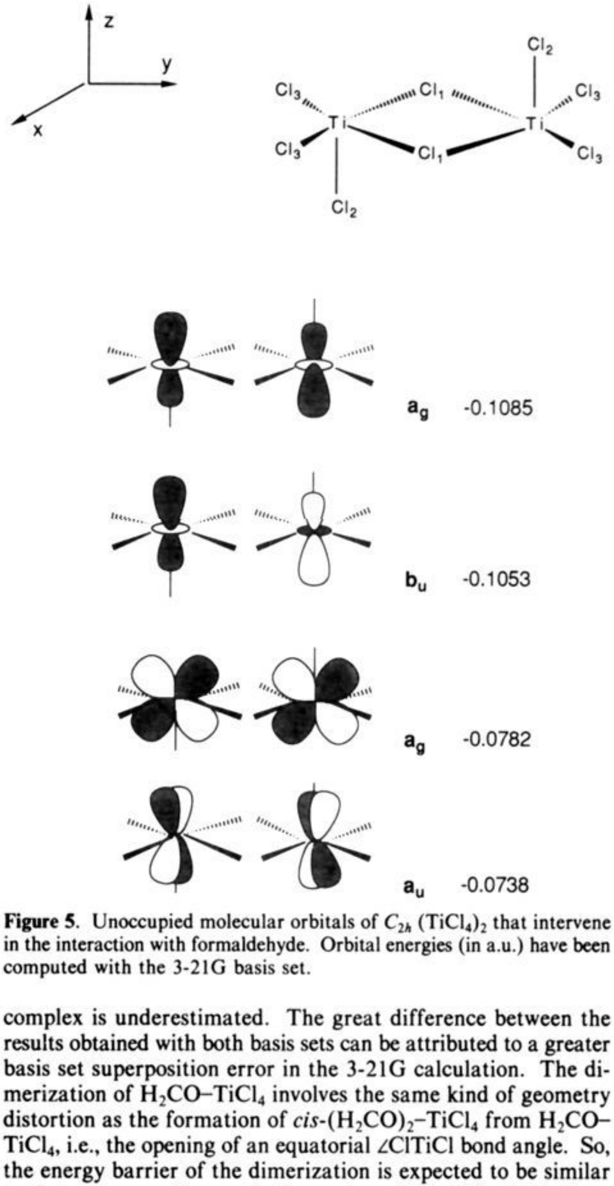

Figure 5. Unoccupied molecular orbitals of C_{2h} $(TiCl_4)_2$ that intervene in the interaction with formaldehyde. Orbital energies (in a.u.) have been computed with the 3-21G basis set.

Figure 5 schematically represents the most important acceptor orbitals of the $(TiCl_4)_2$ moiety in the $(H_2CO–TiCl_4)_2$ complex. The d_{z^2} and d_{yz} orbitals of both Ti atoms can interact with the a_1 and b_2 orbitals of formaldehyde, while the d_{xz} orbitals can interact with π_{CO} of formaldehyde. The energies of the acceptor orbitals are lower in the $(TiCl_4)_2$ moiety than in the $TiCl_4$ and $H_2CO–TiCl_4$ moieties of the 1:1 and 2:1 complexes (see Figures 2 and 4). So, the interaction between formaldehyde and $TiCl_4$ seems to be stronger in a $(H_2CO–TiCl_4)_2$ complex.

Comparative Discussion. The above results presented show that H_2CO and $TiCl_4$ can form three kinds of complexes: the 1:1 $H_2CO–TiCl_4$ complex, two isomers of the 2:1 $(H_2CO)_2–TiCl_4$ complex, and a $(H_2CO–TiCl_4)_2$ complex. The only known X-ray diffraction structures between $TiCl_4$ and carbonyl compounds correspond to complexes with chelating esters, in which the two carbonyl groups are cis-coordinated, and complexes of dimeric $TiCl_4$. No monodentate 1:1 or trans 2:1 structures have been characterized. These facts support our results, which show that the coordination of a second H_2CO molecule in the $H_2CO–TiCl_4$ complex involves a greater stabilization of the system than the one corresponding to the coordination of the first H_2CO molecule (see Tables III and VII). The computed energies also show a preference for the cis isomer of the $(H_2CO)_2–TiCl_4$ complex at all levels of calculation. The formation of the trans isomer from

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(39) Ti–Cl_1 = 2.50 Å, Ti–Ti = 3.85 Å, and $\angle Cl_1TiCl_1$ = 79.1°.[10a,d] Ti–Cl_2 = 2.322 Å, Ti–Cl_3 = 2.251 Å, Ti–O = 2.135 Å, C=O = 1.223 Å, $\angle Cl_3TiCl_3$ = 90°, and ∠TiOC = 141.6°. See Chart III for numeration.

Table IX. Charge[a] over the Formaldehyde Fragment in Formaldehyde–$TiCl_4$ Complexes

complex	structure	q
$H_2CO–TiCl_4$	A1	0.170
$(H_2CO)_2–TiCl_4$[b]	C	0.182
	T2	0.213
$(H_2CO–TiCl_4)_2$[b]		0.212

[a] q, in atomic units, computed from the Mulliken population analysis of the 3-21G structures. [b] The charge has the same value in both formaldehyde ligands.

$H_2CO–TiCl_4$ and H_2CO seems to involve an important energy barrier due to the geometry distortion of the $H_2CO–TiCl_4$ moiety.

The trans isomer could also be formed from the cis isomer through a cis–trans interconversion process. Recently, Hansen and Marynick have suggested that cis–trans isomerization in octahedral ML_6 complexes takes place through a trigonal prism transition state.[40] The investigation of the isomerization in the $(H_2CO)_2–TiCl_4$ complex involves a huge computational effort. However, significative information can be obtained if the model complex $TiCl_6^{2-}$ is studied. For this system, a D_{3h} trigonal prism transition state has been located with the 3-21G basis set, the energy barrier being 32.3 kcal/mol. For $(H_2CO)_2–TiCl_4$, this barrier is expected to be greater, given the steric repulsion between both H_2CO ligands in the transition state. So, any cis–trans interconversion should take place through a dissociative mechanism, involving $H_2CO–TiCl_4$ as an intermediate.

Our pilot calculations have shown that the formation of the $(H_2CO–TiCl_4)_2$ complex from $H_2CO–TiCl_4$ (step 3 in Scheme I) can be a competitive process with the formation of $(H_2CO)_2–TiCl_4$ (step 2 in Scheme I). The experimental structures suggest that this dimerization is the most favorable process in the case of monodentate carbonyl compounds, while the formation of chelates (similar to cis 2:1 complexes) is favored for bidentate carbonylic compounds.

The interaction scheme discussed above shows that the interaction of formaldehyde with $TiCl_4$ increases in the order $H_2CO–TiCl_4 < (H_2CO)_2–TiCl_4 < (H_2CO–TiCl_4)_2$. In the cases in which geometry optimization has been carried out, this ordering can be related to the values of the Ti–O bond lengths and to the degree of distortion of the H_2CO molecules in the complexes (see Tables V and VIII). The same trends can be observed from the values of the charge over the H_2CO fragment in the complexes presented in Table IX. These results show that $TiCl_4$ is a stronger Lewis acid when it forms dimeric complexes with carbonyl compounds.

Concluding Remarks

The results obtained in this work show that formaldehyde forms 1:1 and 2:1 complexes with $TiCl_4$. In the first case, the complex has a trigonal bipyramidal structure with the H_2CO molecule in an axial position. The formation of 2:1 complexes is predicted to be energetically favorable. In this case, two different cis–trans isomers can be considered. However, the formation of the trans isomer seems to involve a greater energy barrier. The formation of a $(H_2CO–TiCl_4)_2$ complex through dimerization of $H_2CO–TiCl_4$ has also been discussed, and it has been shown that in such a complex the interaction between $TiCl_4$ and formaldehyde is stronger. These results agree with the experimental results, according to which monodentate carbonyl compounds form complexes with dimeric $TiCl_4$, while chelating esters or ketones can form octahedral 1:1 complexes in which two carbonyl groups are cis coordinated to the Ti atom of $TiCl_4$.

Acknowledgment. Parts of the calculations presented in this paper have been carried out in the CRAY XMP/14se supercomputer of Construcciones Aeronáuticas S.A. with a grant of computer time from the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT).

Registry No. H_2CO-$TiCl_4$ (A1), 140411-13-8; $(H_2CO)_2$-$TiCl_4$ (C), 140411-14-9; $(H_2CO)_2$-$TiCl_4$ (T1), 140629-70-5; $(H_2CO$-$TiCl_4)_2$, 140411-15-0; H_2CO, 50-00-0; $TiCl_4$, 7550-45-0.

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[40] Hansen, L. M.; Marinyck, D. S. *Inorg. Chem.* **1990**, *29*, 2482–2486.

Charge Oscillation in the Homolysis of MeX Derivatives

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Abstract: Ab initio electronic structure methods are used to show that, in the (barrierless) homolytic dissociation of the CH_3X system (X = an atom or group more electronegative than CH_3) going from equilibrium geometry to products ($CH_3^{\bullet} + X^{\bullet}$), the charge on CH_3 first increases and then decreases to zero. This result, which can be rationalized on the basis of simple models, violates the common assumption that the character of intermediates along a reaction path is bound by the properties of reactants and products. The implications of this new conclusion to kinetic/thermodynamic data relationships in chemical reactions are discussed.

A basic assumption in the field of reaction mechanisms is that the electronic structure description of the system anywhere along the reaction coordinate varies monotonically from reactants to products and is bound by their property values. Therefore, the transition state (TS), regardless of its location (early or late), has a structure intermediate between that of reactants and products. This assumption also provides the foundation for the mechanistic significance of linear free energy relationships (LFER).[1]

In this work, changes in ionicity which occur during the homolysis of MeX (Me = CH_3, X = an atom or a group which is more electronegative than Me) from equilibrium geometry to radical fragments were investigated. Since MeX in its ground-state (GS) equilibrium geometry is polarized $Me^{\delta+} + X^{\delta-}$, it is expected on the basis of the above binding assumption that, upon dissociation, the charge on X (= −charge on the Me group) will be gradually reduced from $\delta-$ to zero as the system approaches the neutral dissociation products $Me^{\bullet} + X^{\bullet}$.

The dissociation energy curve of MeX as a function of the C–X distance for a series of nine methyl derivatives was calculated using the ab initio multiconfiguration self-consistent field (MCSCF)

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[‡] Ministry of Defense.

[1] Leffler, J. E.; Grunwald, E. *Rates and Equilibrium of Organic Reactions*; Wiley: New York, 1963; p 157.

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