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Investigation of Dienophile−$TiCl_4$ Complexation by Means of X-ray Absorption and ^{13}C-NMR Spectroscopies[§]

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Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) techniques, in combination with ^{13}C−NMR spectroscopy, have been used to study the complexation of methyl acrylate (**1**), *N*-acryloylbenzylamine (**2**), *O*-acryloyl-(*R*)-pantolactone (**3**), methyl *N*-acryloyl-(*S*)-prolinate (**4**), and methyl *N*-acryloyl-(*S*)-phenylalaninate (**5**) with excess $TiCl_4$ in solution. The results obtained show that $TiCl_4$ has a great tendency to coordinate with two ester ligands, but this tendency is not so marked with amides, which is related to the greater basicity of the latter. Complexation increases the Ti−Cl bond distance, in comparison with $TiCl_4$, which is clearly shown by the EXAFS spectra. Chelate complexes are formed with bidentate ligands, but comparison between the EXAFS spectra, obtained with different $TiCl_4$/dienophile ratios, shows that chelation is more difficult with methyl *N*-acryloyl-(*S*)-phenylalaninate (**5**).

Introduction

Complexes formed between Lewis acids and carbonyl compounds are reactive intermediates in a large number of organic reactions. In the context of asymmetric synthesis, many of the Lewis acid-mediated reactions are known to proceed with improved stereoselectivities in comparison with their noncatalyzed counterparts. Consequently, knowledge of the structure of these complexes is of vital importance for the future development of these reactions, and a great deal of theoretical[1] and experimental[2] work has been performed on this subject.

The Diels−Alder reaction is one of the most important among the Lewis acid-catalyzed reactions and excellent diastereofacial selectivities have been achieved in asymmetric Diels−Alder reactions of chiral α,β-unsaturated acid derivatives and prochiral 1,3-dienes.[3−8] In particular, the formation of chelate complexes between dicarbonyl dienophiles and suitable Lewis acids has allowed high levels of asymmetric induction to be obtained, such as in the case of *N*-acyloxazolidinones,[4] enoates of (*S*)-*N*-methyl-2-hydroxysuccinimide,[5] (*S*)-ethyl lactate,[6] (*R*)-pantolactone,[7] and *N*-acryloyl-α-amino esters.[8] In most cases, the formation or lack of formation of the chelate complexes has been deduced from the stereochemical results of the reactions. However, Helmchen *et al.*[9] have published the X-ray structure of the acrylate of the (*S*)-ethyl lactate−$TiCl_4$ complex and Castellino has characterized[10] by ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopies an *N*-acyloxazolidinone−$SnCl_4$ chelate complex.

X-ray crystallographic studies provide detailed structural information on these complexes, but it is difficult to obtain good crystals of these often unstable species. Frequently, scientists assume these data referred to the crystalline structure as the structure of the complex in solution. NMR studies of solutions provide information on whether or not chelate complexes are formed, and on the structure of their organic part. However, structural information on the environment of the metal in these complexes in solution is still absent.

X-ray absorption spectroscopy provides information on the local structure around the absorbing atom.[11,12] EXAFS enables interatomic distances, coordination numbers, and Debye−Waller factors of the first coordination

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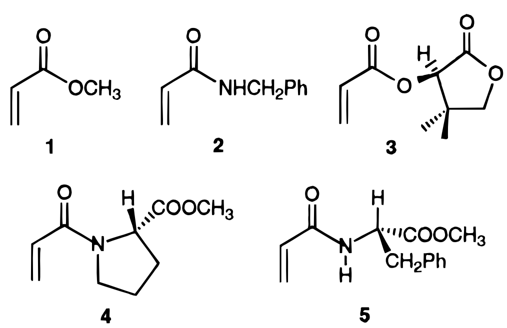
Scheme 1



shells to be determined,[11] while XANES gives direct information on the coordination geometry located at the absorbing atom.[12] This kind of spectroscopy can be employed for a wide range of materials be they liquid, solid, or gaseous, and it is therefore suitable to determine the structural properties of the solutions of the compounds under investigation.

Recently we have studied, by means of X-ray absorption spectroscopy, the structure of methyl acrylate–$TiCl_4$ complexes in solution,[13] demonstrating the suitability of EXAFS and XANES for the study of dienophile–$TiCl_4$ intermediates. We therefore decided to extend our study to the formation of chelate complexes between bidentate acrylic acid derivatives and $TiCl_4$ and to investigate the structure of such complexes. We have chosen two bidentate dienophiles which, in view of the results of their Diels–Alder reactions, seem to form chelate complexes with $TiCl_4$, an ester-ester and an ester-amide, namely *O*-acryloyl-(*R*)-pantolactone (**3**)[7] and methyl *N*-acryloyl-(*S*)-prolinate (**4**).[8] We have also studied a compound, methyl *N*-acryloyl-(*S*)-phenylalaninate (**5**), which does not seem to form these kinds of complexes easily.[8] Methyl acrylate (**1**) and *N*-acryloylbenzylamine (**2**), both with $TiCl_4$, have also been studied as model compounds (Scheme 1). The results obtained from X-ray absorption spectroscopy are complemented by ^{13}C-NMR spectroscopy.

Results

Most of the $TiCl_4$-catalyzed Diels–Alder reactions are carried out in methylene chloride or hydrocarbons. Unfortunately the X-ray absorption measurements cannot be carried out using the same solvents since chlorinated solvents present too large an absorption at the titanium K edge energy (5 keV), while the solubility of the dienophile–$TiCl_4$ complexes in aliphatic or aromatic hydrocarbons is very low. Clearly solvents that are Lewis bases cannot be used either. Therefore, we decided to use nitrobenzene, a low X-ray absorbing solvent with a weak coordinating ability, in which the complexes are soluble enough to carry out the experiments. The possibility of the presence of nitrobenzene–$TiCl_4$ complexes was eliminated by ^{13}C-NMR, given that the four signals of nitrobenzene remain unchanged after the addition of either a small amount or an equimolecular proportion of $TiCl_4$.

When solutions of $TiCl_4$ in nitrobenzene are left to stand, the appearance of a precipitate is observed, which prevents X-ray absorption experiments being carried out. However, the presence of a dienophile makes this process slower, and a precipitate was not observed after any of the X-ray experiments described in this work.

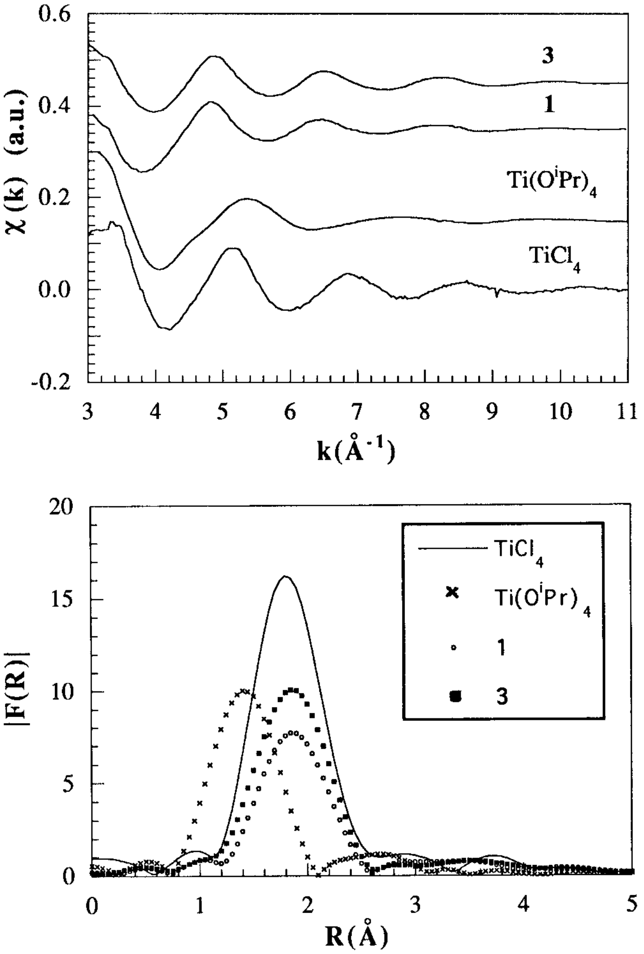


Figure 1. EXAFS spectra (top) and Fourier transforms (bottom) of $TiCl_4$, $Ti(O^iPr)_4$, and methyl acrylate (**1**), and *O*-acryloyl-(*R*)-pantolactone (**3**)–$TiCl_4$ complexes.

EXAFS. The experimental EXAFS signal has been extracted from the raw spectra following standard methods.[11] Background removal was performed, and the atomic absorption coefficient was determined by a low order polynomial fit of the spectra. As a matter of illustration, the EXAFS spectra and the Fourier transform (FT) of $TiCl_4$, $Ti(O^iPr)_4$, and methyl acrylate–$TiCl_4$, and *O*-acryloyl-(*R*)-pantolactone–$TiCl_4$ complexes are shown in Figure 1. The modulus of the FT shows a main peak ascribed to the first coordination shell contribution; the smaller peaks at higher distances have not been considered here. For the whole series of complexes, the amplitude of the EXAFS spectra, *i.e.* the FT height, is lower than that for $TiCl_4$ and similar to that for $Ti(O^iPr)_4$, and the corresponding frequency is lower for $Ti(O^iPr)_4$. As we will show later, this effect comes from the destructive interference between the oxygen and chlorine signals. The EXAFS spectra have been analyzed by curve fitting of the filtered first shell contribution to the EXAFS formula[11]

$$\chi(k) = \sum_i 1/k(N_i/R_i^2)A_i(k)\sin[2kR_i + \Phi_i(k)]$$

where, according to the small-atom (plane wave) approximation

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Table 1. Results Obtained from the Analysis of the EXAFS Spectra of the Dienophile–TiCl$_4$ Complexes[a]

		Ti–Cl			Ti–O		
organic compound	equiv of TiCl$_4$	N	R (Å)	$\Delta\sigma^2$ (10^3 Å^2)	N	R (Å)	$\Delta\sigma^2$ (10^3 Å^2)
1	0.25	4	2.27	4.3	2	2.12	2.4
	0.50	4	2.26	4.8	2	2.14	1.9
	0.75	4	2.28	6.2	2	2.13	5.2
	1.00	4	2.27	3.9	2	2.15	1.4
2	0.25	4	2.32	4.1	–	–	–
	0.50	4	2.30	4.7	–	–	–
	0.75	4	2.28	4.8	1	2.16	5.7
	1.00	4	2.26	4.9	1	2.19	10.7
3	0.25	4	2.28	3.2	2	2.22	4.4
	0.50	4	2.28	3.2	2	2.22	4.4
	0.75	4	2.28	3.2	2	2.22	4.4
	1.00	4	2.28	3.2	2	2.22	4.4
4	0.25	4	2.29	4.8	2	2.15, 2.49	2.2, 3.1
	0.50	4	2.29	4.8	2	2.15, 2.49	2.2, 3.1
	0.75	4	2.29	4.8	2	2.15, 2.49	2.2, 3.1
	1.00	4	2.29	4.8	2	2.15, 2.49	2.2, 3.1
5	0.25	4	2.31	5.6	–	–	–
	0.50	4	2.30	2.9	–	–	–
	0.75	4	2.31	4.2	2	2.39, 2.39	5.2
	1.00	4	2.29	5.1	2	2.17, 2.46	2.4, 2.9

[a] 0.4 mL of TiCl$_4$ 1 M in toluene is added to the corresponding amount of the organic compound (**1**–**5**) in 2 mL of nitrobenzene.

$$A_i(k) = e^{-2R_i/\lambda(k)} e^{-2\sigma_i^2 k^2} F_i(k)$$

The amplitudes, $A(k)$, and phase shifts, $\Phi(k)$, for the first shell contribution were extracted from the experimental spectra of TiCl$_4$ and Ti(O^{i}Pr)$_4$, whose interatomic distances for the Ti–Cl and Ti–O pairs are known from literature and are 2.19 and 1.78 Å, respectively. Corrections due to the spherical nature of the outgoing photoelectron wave are related to some dependence of $F_i(k)$ from the interatomic distance R_i. They can be considered negligible in this case because of the quite small differences in the interatomic distances between model compounds and analyzed spectra. We have analyzed the data by fixing different integer coordination numbers N for the oxygen and chlorine atoms and by using different coordination shells (all combinations of one and two Ti–Cl and one and two Ti–O distances have been considered). The results were analyzed by means of a best fit procedure in which the goodness of fit was evaluated by comparing the residual values at the minimum in the different cases, according to standard statistical criteria for data analysis. Table 1 shows the best fit structural parameters, *i.e.* interatomic distances, Debye–Waller factor differences and coordination numbers. The error in the interatomic distances is about 0.02 Å, while a 20% relative error must be given in Debye–Waller factors and coordination numbers. They have been estimated, according to ref 11d, by changing each variable, while refining the others, until the residual at minimum was doubled. The comparisons between the experimental and fitted spectra for some selected samples are shown in Figure 2.

In TiCl$_4$ complexes with methyl acrylate (**1**), titanium atoms are coordinated to four chlorine atoms (at an average distance of 2.27 Å) and two oxygen atoms (at a distance of 2.13 Å) within the range of TiCl$_4$–**1** ratios studied. Coordination increases the Ti–Cl distance from 2.19 to 2.27 Å.

The data from *N*-acryloylbenzylamine (**2**) show the influence of the relative proportions of the reagents on the titanium coordination sphere. For TiCl$_4$/**2** ratios higher than 0.5, four chlorine atoms and one oxygen atom lead to the best fit. In fact, the use of two oxygen atoms increases the residual values. However, for TiCl$_4$/**2** ratios equal or lower than 0.5, the best fit is obtained only with four chlorine atoms. Nevertheless, the long Ti–Cl distance (2.32 Å) indicates that TiCl$_4$ is coordinated to the amide (see below).

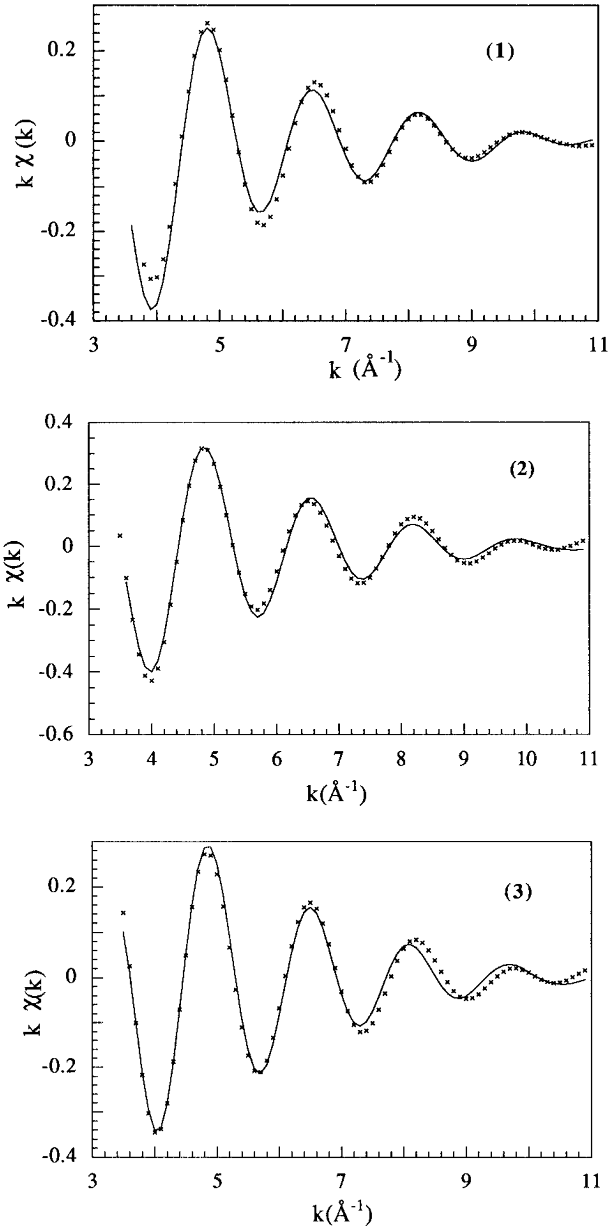

Figure 2. Theoretical and experimental Fourier-filtered EXAFS spectra of the complexes of methyl acrylate (**1**), *N*-acryloylbenzylamine (**2**), and *O*-acryloyl-(*R*)-pantolactone (**3**) with 0.75 equiv of TiCl$_4$.

The EXAFS spectra of *O*-acryloyl-(*R*)-pantolactone (**3**)–TiCl$_4$ complexes do not change within the range of reagent ratios studied. The best fit is obtained with titanium coordinated to four chlorine atoms (at a distance of 2.28 Å) and two oxygen atoms (at a distance of 2.22 Å). These distances are similar to those obtained from the X-ray diffraction analysis of the closely-related complex of *O*-acryloyl-(*S*)-ethyl lactate with TiCl$_4$.[9]

The best fit results for the methyl *N*-acryloyl-(*S*)-prolinate (**4**)–TiCl$_4$ complexes show that titanium is coordinated to four chlorine atoms at 2.29 Å and two oxygen atoms at different distances (2.15 and 2.49 Å), which seems logical due to the different nature of the

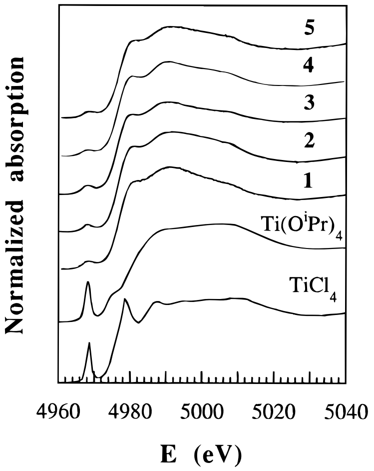

Figure 3. Experimental XANES spectra of TiCl$_4$, Ti(O^{i}Pr)$_4$, and the complexes of all the organic ligands (**1**−**5**) with 0.75 equiv of TiCl$_4$.

two carbonyl groups (ester and amide). The spectra do not change within the range of TiCl$_4$/**4** ratios studied.

Comparison of the residual values indicates that the presence of the second Ti−O shell at longer distance should be considered significant from a statistical point of view. For instance, the residual value, scaled by ν (*i.e.*, the difference between the number of independent parameters and the number of fit parameters, which changes from 2 to 4 when suppressing the two Ti−O shells), was increased by factors of 1.5 and 2.0 when suppressing the Ti−O shell at the long distance and fixing the Ti−O coordination equal to 1 and 2, respectively. The other parameters were allowed to change freely, and it is worth mentioning that the minimum was found for R values of 2.34 and 2.37, which indicates the need for a long distance to reach the best fit and increases our confidence of the presence of a second, longer distance.

The complexation of methyl *N*-acryloyl-(*S*)-phenylalaninate (**5**) with TiCl$_4$ is somewhat more complicated. The EXAFS spectra show that for 0.25 and 0.50 TiCl$_4$/**5** ratios this compound behaves like *N*-acryloylbenzylamine (**2**). When this ratio reaches 0.75, two oxygen atoms at the same distance and four chlorine atoms are needed to fit the spectrum. Finally, when the reagents are in an equimolar ratio, the two Ti−O distances are different, as is observed for the complexes of methyl *N*-acryloyl-(*S*)-prolinate (**4**).

XANES. After background subtraction from the raw spectra, the XANES spectra were normalized taking unity as atomic absorption. Normalized XANES spectra at the titanium K edge of the dienophile−TiCl$_4$ complexes, TiCl$_4$, and Ti(O^{i}Pr)$_4$ are shown in Figure 3.

The XANES spectra of the complexes under study are very similar, but they are different from those of the reference compounds. In particular, the prepeak structure, typical of TiCl$_4$ and Ti(O^{i}Pr)$_4$, is very small for all samples.

Spectra of transition metal compounds and complexes with 3d vacancy show a preedge structure which corresponds to a 1s−3d transition. For free atoms and environments with free inversion symmetry, this transition is dipole forbidden, and only an insignificant feature, due to a quadrupolar transition, is observed. For local geometries without inversion symmetry this transition is dipole allowed, due to 3d−4p orbital mixing. In particular, for tetrahedral complexes, a prominent prepeak is observed in the k edge absorption spectra. The features of XANES spectra reflect the coordination geometry around the absorbing atom.[14]

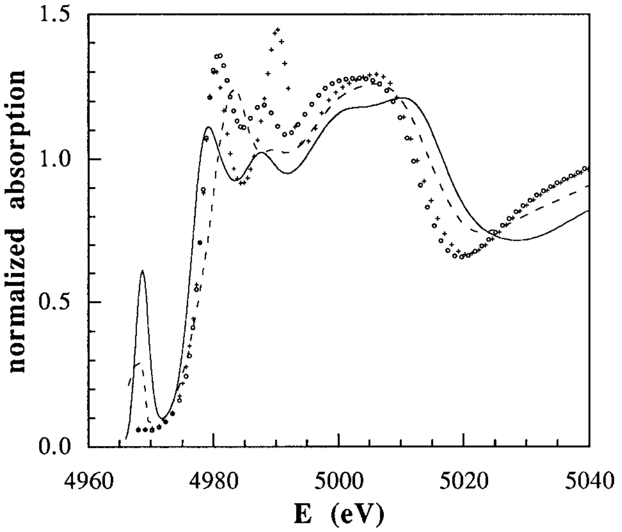

Figure 4. Calculated XANES spectra of TiCl$_4$ (—) and of the complexes with different geometries: pentacoordinated (- - -), octahedral with two apical oxygen atoms (+), and octahedral with two adjacent oxygen atoms (○).

In order to test this influence in our case we carried out theoretical XANES calculations for TiCl$_4$ (Ti−Cl distance = 2.19 Å) and three different models of the complexes: the pentacoordinated cluster TiCl$_4$O, and two TiCl$_4$O$_2$ octahedral clusters, one with the two oxygen atoms in adjacent positions and another with the two oxygen atoms in apical position (in all cases the Ti−Cl distace was taken equal to 2.28 Å, and the Ti−O distance equal to 2.12 Å). The theoretical calculations are rather approximate because of the use of a muffin-tin potential and the neglect of manybody effects. Furthermore, we have limited our computations to atoms in the first coordination shell. These limitations have a great influence on the peak intensities. Although the XANES calculations can be improved, the computational cost would be too high, which is not justified in the present study; however, some qualitative trends can be stressed (Figure 4). Three main resonances above the edge are obtained for octahedral clusters, while only two are found for the simulation of the pentacoordinated cluster. Moreover, for the latter geometry, as well as for TiCl$_4$, a large prepeak appears. Thus, on the basis of the XANES results it can be concluded that, in most cases, the major species in solution are complexes formed by four chlorine atoms and two oxygen atoms in an octahedral symmetry. The behavior of the **2**−TiCl$_4$ complexes deserves particular comment, given that in this case the intensity of the prepeak increases with the TiCl$_4$/**2** ratio (Figure 5).

^{13}C NMR. The chemical shifts of the carbonyl carbon signals of the methyl acrylate (**1**), *N*-acryloylbenzylamine (**2**), and of the bidentate compounds **3**−**5** in the absence and in the presence of TiCl$_4$ are given in Table 2. As expected, coordination occurs *via* the carbonyl group, so that the carbonyl carbon signal of **1** and **2** are shifted downfield by the addition of TiCl$_4$.

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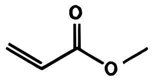
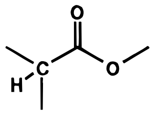
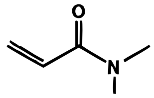
Table 2. Chemical Shifts (in ppm) of the Carbonyl Carbons of the Dienophiles in Nitrobenzene at Room Temperature, Alone and in the Presence of $TiCl_4$

Dienophile	eq. of $TiCl_4$				
1	–	166.1[a]	–		–
	0.75	172.8[b]	–		–
2	–	–	–		164.4
	0.20	–	–		167.6
3	–	164.7	172.4		–
	0.20	165.4	173.2		–
	0.50	168.2	175.8		–
	0.70	174.6	179.6		–
4	–	–	171.3		163.3
	0.30	–	170.4		169.9
	0.75			170.6[c]	
5	–	–	171.6		164.5
	0.20	–	171.8		166.2
	0.30	–	171.2		168.7
	0.50			171.9[c]	
	0.75			173.5[c]	

[a] Other signals: CH_3 (51.1), C_α (129.6), C_β (130.3). [b] Other signals: CH_3 (55.7), C_α (137.2), C_β (137.7). [c] Only a broad signal is observed.

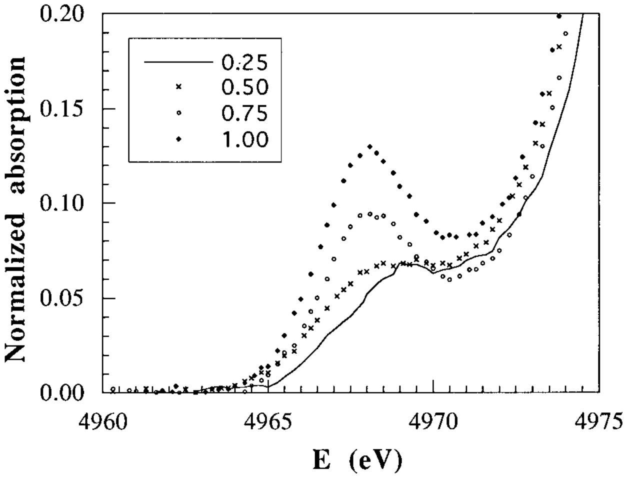


Figure 5. Detail of the preedge structure of the XANES spectra of the *N*-acryloyl benzylamine (**2**)–$TiCl_4$ complexes for several $TiCl_4$/**2** ratios.

The ^{13}C-NMR spectra of *O*-acryloyl-(*R*)-pantolactone (**3**) shows the simultaneous shift of both carbonyl signals when increasing amounts of $TiCl_4$ are added. However, in the spectra of both *N*-acryloyl-α-amino esters **4** and **5** large shifts of the carbonyl amide carbon signal are observed, whereas the position of the carbonyl ester carbon signal is relatively unaffected.

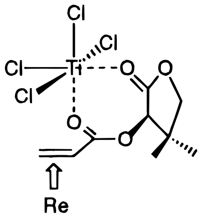
Although signals other than that of the carbonyl carbon are difficult to follow, due to the interference of nitrobenzene, this has been accomplished in the case of methyl acrylate (**1**). All the signals show strong shifts (>4 ppm) upon coordination (Table 2).

Discussion

The EXAFS and XANES results for methyl acrylate (**1**) complexes with different proportions of $TiCl_4$ show that, for the major species present in solution, titanium is coordinated by two oxygen atoms and four chlorine atoms in an octahedral symmetry for all the dienophile/$TiCl_4$ ratios studied in this work. Furthermore, the lack of a significant prepeak indicates that free $TiCl_4$ or pentacoordinated clusters are not present to a significant extent. As a consequence, for $TiCl_4$/**1** ratios greater than 0.5 we must assume the existence of complexes with a 1:1 stoichiometry in which each titanium atom is coordinated by two oxygen ligands, but that each oxygen atom is in turn coordinated to two titanium atoms. Further confirmation of this fact is obtained from IR spectroscopy experiments carried out in CH_2Cl_2 (the absorption band of nitrobenzene prevents its use as a solvent for this study). The carbonyl stretching band of methyl acrylate (**1**) in solution appears at 1725 cm^{-1}. The addition of $TiCl_4$ gives rise to the appeareance of two new bands (at *ca.* 1650 and 1588 cm^{-1}) which can be ascribed to the carbonyl group coordinated to one or two molecules of $TiCl_4$.[13]

The EXAFS spectra for *N*-acryloylbenzylamine (**2**)–$TiCl_4$ complexes are strongly dependent on the relative amounts of both compounds. For $TiCl_4$/**2** ratios equal to or less than 0.5 the best fit is obtained with only four chlorine atoms, with a Ti–Cl distance of 2.32 Å (Table 1). This Ti–Cl distance does not correspond to that found for free $TiCl_4$. In addition, a large prepeak corresponding to free $TiCl_4$ does not appear in the XANES spectrum. Furthermore, the ^{13}C-NMR spectra (Table 2) show that the carbonyl peak is shifted from its original position. Thus, in spite of the absence of a Ti–O signal in the EXAFS spectra, these data suggest that coordination with oxygen exists. Due to the low scattering power of the oxygen atom, its contribution to the EXAFS spectra can be smeared out when large thermal or structural disorder exists. A possible explanation for such a large disorder can be given by assuming rapid equilibrium between **2**–$TiCl_4$ complexes with 1:1 and 2:1 stoichiometries. It could be argued that this equilibrium is the reason why the Ti–O bond is not detected. The EXAFS spectra obtained for higher proportions of $TiCl_4$ are best fitted by four chlorine atoms and one oxygen atom (Table

Scheme 2



1). As expected for a noninversion symmetry, XANES calculations have shown that the presence of pentacoordinated structures would give rise to the appearance of a 1s−3d prepeak. Indeed, the presence of this prepeak, which increases slightly with the TiCl$_4$/**2** ratio, is observed in the XANES spectra. These results indicate that the equilibrium between 1:1 and 2:1 complexes of TiCl$_4$ and the amide is shifted toward the former when the amount of TiCl$_4$ increases. It can be concluded that the tendency of TiCl$_4$ to coordinate to two carbonyl groups is higher with esters than with amides, which is not surprising, given the higher electron donor ability of amides.

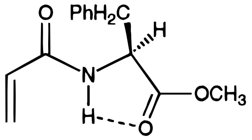
Helmchen *et al.*[7] have reported that *O*-acryloyl-(*R*)-pantolactone (**3**) is an excellent chiral dienophile, leading to almost complete asymmetric induction in TiCl$_4$-catalyzed reactions. This behavior has been explained by the formation of a seven-membered chelate complex, where a chlorine atom shields the Si face of the double bond of the enoate in the *s-cis* conformation (Scheme 2). In agreement with this hypothesis, the EXAFS spectra of **3**−TiCl$_4$ complexes do not change with the TiCl$_4$/**3** ratio and, for all the proportions tested, the experimental spectra are well fitted by a titanium center coordinated to four chlorine atoms and two oxygen atoms at the same distance (Table 1). Moreover, the simultaneous downfield shift of the ^{13}C-NMR signals of both carbonyl carbons, on addition of TiCl$_4$, confirms chelate formation (Table 2).

The behavior of *N*-acryloyl-α-amino esters as dienophiles depends on the nature of the amino acid.[8] The results obtained in the TiCl$_4$-catalyzed reactions of *N*-acryloyl-(*S*)-prolinates with prochiral 1,3-dienes are accounted for by the formation of dienophile−TiCl$_4$ chelate complexes. However, when methyl *N*-acryloyl-(*S*)-phenylalaninate is used as a dienophile, the asymmetric inductions obtained are better accounted for by a nonchelate dienophile−Lewis acid intermediate, even in the TiCl$_4$-catalyzed reaction.

The best fit results obtained from the Ti K-edge EXAFS spectra of methyl *N*-acryloyl-(*S*)-prolinate (**4**)−TiCl$_4$ complexes indicate the presence of four chlorine atoms at a distance of 2.29 Å and two oxygen atoms at distances of 2.15 and 2.49 Å (Table 1). The presence of two different Ti−O distances is in agreement with the different chemical nature (amide and ester) of the dienophile coordination groups. The large downfield shift of the ^{13}C-NMR signal of the amide carbonyl carbon by addition of TiCl$_4$ seems to indicate that the shorter Ti−O distance corresponds to coordination with the more basic amide group. The EXAFS spectra do not change with the TiCl$_4$/**4** ratio which, considering the behavior of the *O*-acryloyl-(*R*)-pantolactone (**3**)−TiCl$_4$ complexes, agrees with the formation of the dienophile−TiCl$_4$ chelate complexes.

The complexation of methyl *N*-acryloyl-(*S*)-phenylalaninate (**5**) with TiCl$_4$ presents some special features. At low TiCl$_4$ proportions this compound behaves like *N*-acryloylbenzylamine (**2**). When the TiCl$_4$/**5** ratio reaches 0.75, two oxygen atoms (Ti−O distance = 2.39 Å) and four chlorine atoms (Ti−Cl distance = 2.31 Å) are needed to fit the EXAFS spectrum (Table 1). The two oxygen atoms are at the same distance from the titanium atom, which may be due to the fact that they belong to functional groups of the same type. Moreover, the Ti−O distance is much longer than that observed when two ester groups are coordinated to titanium, which seems to indicate the coordination of two amides to the titanium atom. Analysis by ^{13}C-NMR spectroscopy, where only the amide carbonyl signal is shifted from its original position (Table 2), agrees with this hypothesis. Finally, when equimolar amounts of **5** and TiCl$_4$ are used, the EXAFS spectrum can be accounted for by a chelate complex, which is very similar to that formed between TiCl$_4$ and methyl *N*-acryloyl-(*S*)-prolinate (**4**). The results obtained indicate that methyl acryloyl-(*S*)-phenylalaninate (**5**) has a lower tendency to form chelate complexes than methyl *N*-acryloyl-(*S*)-prolinate (**4**), which agrees with the results obtained from their TiCl$_4$-catalyzed Diels−Alder reactions and has been explained by the formation, for the latter dienophile, of an intramolecular hydrogen bond (Scheme 3).[8,15]

Scheme 3



Conclusions

EXAFS and XANES can provide valuable information on the environment of certain atoms, such as titanium in reagent−catalyst complexes in solution. These spectroscopic methods have shown that TiCl$_4$ has a great tendency to be coordinated by two ester ligands, but this tendency is not so marked for amides, which can be accounted for by their higher electron donor ability. The formation of chelate intermediates is detected in the case of bidentate ligands by the fact that no variations in the EXAFS spectra are observed on changing the TiCl$_4$/dienophile ratio. This behavior is observed with ester−ester [*O*-acryloyl-(*R*)-pantolactone (**3**)] and ester−amide [methyl *N*-acryloyl-(*S*)-prolinate (**4**)] ligands. However, the EXAFS results indicate that chelation is more difficult with open chain *N*-acryloyl-α-amino esters, such as methyl *N*-acryloyl-(*S*)-phenylalaninate (**5**). These results are in agreement with the results obtained from the TiCl$_4$-catalyzed Diels−Alder reactions of these chiral dienophiles and confirm the previous hypothesis which explains these results.

Experimental Section

Solutions were prepared by adding, under argon, 0.4 mL of TiCl$_4$ (1 M in toluene) to a solution of the corresponding amount of organic ligand (**1**−**5**) in 2 mL of nitrobenzene.

EXAFS and XANES spectra at the titanium K edge were measured at the beam line XAFS4 of the "Laboratoire pour L'Utilization de la Radiation Electromagnetique" of Orsay (France). The storage ring worked at 1.8 GeV with an average current of 200 mA. Monochromatization was performed with a double Si(111) crystal, and controlled misalignments of the

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(15) Torrens, F.; Ruiz-López, M. F.; Cativiela, C.; García, J. I.; Mayoral, J. A. *Tetrahedron* **1992**, *48*, 5209.

two crystals were used in order to avoid higher harmonic contamination of the monochromatized beam. X-ray absorption spectra were recorded in the transmission mode using special cells with thickness ranging from 0.2 to 1 mm and Mylar windows. Special care was taken to avoid air contamination. The spectra of $TiCl_4$ (1 M in toluene) and $Ti(O^iPr)_4$ in nitrobenzene solution were measured as reference samples.

^{13}C-NMR spectra in nitrobenzene were obtained using a Varian Unity 300 spectrometer at 75 MHz. *O*-Acryloyl-(*R*)-pantolactone (**3**)[7] and *N*-acryloyl-α-amino esters[8] **4** and **5** were prepared and characterized as previously described.

Theoretical Calculations. XANES calculations were carried out using a Multiple-Scattering approach previously described[16] and the MSXAS program.[17] The Hedin−Lundqvist density functional[18] was employed as well as the muffin−tin approximation with 10% of atomic sphere overlap. The interstitial potential was computed with the help of an outer sphere. The outer sphere, however, is not included in the computation of the absorption coefficient, which was performed by direct scattering-matrix inversion.

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