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Articles

Zirconium Tetrachloride−Formaldehyde σ-Complexes: A Computational and Spectroscopic Investigation

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We have carried out a combined theoretical−experimental study of the structures and energies of $ZrCl_4$−aldehyde complexes using ^{13}C NMR spectroscopy and a DFT (B3LYP) computational approach. The computational investigation has demonstrated the existence of different types of complexes: a 1:1 complex ($H_2CO-ZrCl_4$), various 2:1 complexes ($(H_2CO)_2-ZrCl_4$), and several dimeric species. The analysis of the energies involved in the formation of the various complexes has indicated that the dimeric species should correspond to the only adduct observed in the ^{13}C NMR spectra (carbonyl resonance at 226.96 ppm) when a 1:1 $ZrCl_4$/aldehyde molar ratio is used, while the 2:1 complex should be responsible for the signal at 224.30 ppm that is recorded when this molar ratio is 1:2.

Introduction

Thanks to its easy availability, low cost, and excellent acidic properties, zirconium tetrachloride is widely used as a Lewis acid in organic synthesis. A survey of the literature reveals that $ZrCl_4$ has been employed to activate carbonyl compounds toward the addition of a variety of reagents: allyl stannanes and silanes (Sakurai reaction);[1] alcohols[2a] and thiols[2b] for the synthesis of acetals and thioacetals or for their hydrolysis; diazoketones or diazoesters;[3] enolates or enolate-type reagents (aldol or Mukaiyama reactions);[4] and hydride reducing agents.[5] The analogous addition of allylstannanes to imines[6] and of diazoketones to nitriles[7] can also be promoted. Olefins conjugated with electron-withdrawing groups can be effectively activated by $ZrCl_4$ either toward conjugate addition[8] or cycloadditions (Diels−Alder[9a,b] or [2 + 2][9c]). Furthermore, a unique hydrostannylation of

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alkynes has been achieved by means of this Lewis acid.[10] Finally, electrophilic aromatic substitutions have also been performed with the aid of $ZrCl_4$.[11] Our interest in Lewis acid promoted additions of carbon nucleophiles to carbonyl compounds relies on the catalytic asymmetric allylations of aldehydes with titanium[12a] and zirconium[12b] chiral Lewis acids. For instance, we have recently reported that the combination $ZrCl_4$−binaphthol, either in the absence or in the presence of 4-*tert*-butylcalixarene, is a very effective catalyst for the asymmetric addition of allyltributyltin to aldehydes.[13]

The previous short introduction points out that the basic role played by Lewis acids in the activation of carbonyl compounds and in the mechanism of many related reactions makes it very important to achieve a deeper knowledge of the structures and properties of these species. Adducts of zirconium tetrachloride with acetone, pinacolone, 3-pentanone, and tetrahydrofuran have been investigated by infrared spectroscopy in solution and in solid state and by low-temperature ^1H NMR spectroscopy in solution.[14] These studies have suggested that all four Lewis bases form octahedral 1:2 complexes. This conclusion has been supported by an X-ray crystallographic study of the $ZrCl_4$−pinacolone adduct,[14] where it has been demonstrated that the two ketone ligands are *cis* in the octahedral complex. To our knowledge no additional experimental studies on the structure of these complexes have been carried out. Furthermore, as far as we know, in the literature no theoretical investigations exist on these complexes, while a number of computational studies have already been published on adducts involving aldehydes and other Lewis acids such as $TiCl_4$[15] and boron trihalides.[16] For this reason in the present paper we have carried out a combined computational and spectroscopic study of $ZrCl_4$−aldehyde complexes. Aliphatic straight-chain aldehydes−$ZrCl_4$ complexes have been investigated with ^{13}C NMR spectroscopy, and DFT[17] and MP2 computations have been used to investigate the simpler model-system formed by $ZrCl_4$ and one or two formaldehyde molecules.

Computational Methods

All ab initio and DFT molecular computations reported here have been performed with the Gaussian 94[18] series of programs using a local spin density (LSD) optimized basis set of double-ξ quality in the valence shell plus polarization function (DZVP)[19] and an effective core potential (ECP) basis set (LANL2DZ).[20] The DFT computations have been carried out with the hybrid Becke's three-parameter exchange functional (denoted as B3LYP)[21] as implemented in Gaussian 94.

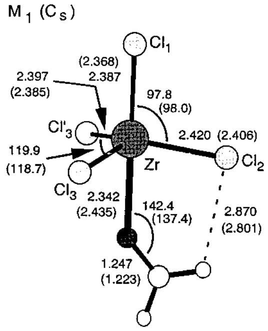

Figure 1. Schematic representation of the 1:1 complex (H_2CO−$ZrCl_4$) M_1 with the values of the most relevant geometrical parameters obtained with the LANL2DZ and the DZVP (in parentheses) basis sets (bond lengths are in Ångstroms and angles are in degrees).

In all cases the geometrical parameters of the various critical points have been fully optimized with the gradient method available in Gaussian 94. The nature of each critical point has been characterized by computing the harmonic vibrational frequencies.

Computational Results

In this section we discuss the singlet potential energy surface obtained for the 1:1 and 2:1 complexes between zirconium tetrachloride and formaldehyde (H_2CO−$ZrCl_4$ and $(H_2CO)_2$−$ZrCl_4$, respectively) and for the dimerization of the 1:1 complex. All of the results are collected in Tables 1 and 2 and Figures 1−7.

A. 1:1 and 2:1 Complexes. We have considered several possible structures for the H_2CO−$ZrCl_4$ complex. The geometry optimization has led to only one structure (M_1) corresponding to a minimum of the potential surface. This complex, which is represented in Figure 1 with the values of the most relevant geometrical parameters, corresponds to a distorted trigonal bipyramid with C_s symmetry where the formaldehyde molecule is placed in the axial position. No energy minimum with H_2CO in an equatorial position has been found. It is interesting to point out that the formaldehyde molecule is oriented in such a way as to form a hydrogen bond between one hydrogen atom of the CH_2 group and one equatorial chlorine atom (Cl_2). The $Cl_2 \cdots H$ distance is 2.870 and 2.801 Å at the LANL2DZ and DZVP levels, respectively. The existence of C−H···Cl interactions has been experimentally demonstrated in a neutron diffraction study[22]

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on platinum complexes where the Cl···H distances have been found to be in the range 2.75−2.95 Å, in good agreement with our theoretical finding. As pointed out in ref 22 the C−H···Cl hydrogen bonds should be considered relatively weak interactions in comparison with O−H···O bonds as a consequence of the fact that carbon is significantly less electronegative than oxygen.

The coordination of the formaldehyde ligand to form the M_1 complex causes only a slight lengthening of the Zr−Cl bonds with respect to the isolated $ZrCl_4$ molecule where these bonds are 2.370 Å at the DZVP level (2.359 Å with the LANL2DZ basis). In the complex the axial Zr−Cl_1 bond is 2.368 Å and the two equivalent equatorial Zr−Cl_3 and Zr−Cl_3' bonds are 2.385 Å with the DZVP basis set. Similar values have been obtained with the ECP basis, i.e., 2.387 and 2.397 Å respectively. The two basis sets provide similar values also for the Zr−Cl bond involved in the Cl_2···H−C interaction: 2.406 (LANL2DZ basis) and 2.420 Å (DZVP basis). Also the C═O bond in formaldehyde does not change significantly after coordination; with the all-electron basis this bond is 1.223 Å in the complex and 1.212 Å in the noninteracting formaldehyde, whereas with the ECP basis these values are 1.247 and 1.241 Å, respectively.

The formation of the complex M_1 is exothermic with respect to the noninteracting molecules $ZrCl_4$ and H_2C═O and occurs without any barrier. This exothermicity is 19.51 kcal mol^{-1} at the LANL2DZ level and becomes 13.46 kcal mol^{-1} with the more accurate DZVP basis set. It is worth noting that, since the two sets of geometrical parameters obtained with the two basis sets are in fairly good agreement, it is reasonable to carry out single-point DZVP computations on the LANL2DZ optimized structures. In this way we obtain an exothermicity of 14.01 kcal mol^{-1}, which agrees very well with that obtained using the DZVP optimized geometries.

For the 2:1 complex we have located five different structures at both levels of accuracy (see Figures 2 and 3). All five structures are real minima of the potential surface as shown by the frequency computations and correspond to distorted octahedral complexes characterized by different symmetries, where the H_2CO ligands are placed in *cis* (M_3 and M_5) or *trans* positions (M_2, M_4 and M_6). As found in M_1 each formaldehyde molecule forms a weak hydrogen bond with a chlorine atom in all 2:1 complexes. Since the two basis sets lead again to very similar results, as pointed out for the 1:1 complex, we discuss in detail only the geometrical data obtained at the DZVP level. The lowest energy structure is the M_3 complex (Figure 2), which is characterized by a C_{2v} symmetry. In this complex the two formaldehyde molecules lie on the same plane (Cl_1−Zr−Cl_1' plane) and form two weak hydrogen bonds with the two chlorine atoms Cl_1 and Cl_1'. This interaction is characterized by a Cl···H distance of 2.867 Å. The analysis of the values of the geometrical parameters shows that the coordination of an additional formaldehyde molecule leads to a further lengthening of the Zr−Cl bonds with respect to the 1:1 complex (the in-plane Zr−Cl_1 and Zr−Cl_1' bonds become 2.403 Å, while the two out-of-plane Zr−Cl_2 and Zr−Cl_2' bonds become 2.437 Å). On the contrary one can observe a shortening of the Zr−O bond (2.403 Å) as a consequence of the coordination of the second H_2CO ligand. The geometrical features of the M_3 complex are in quite good agreement with the crystal structure obtained in the X-ray study of the 1:2 adduct of $ZrCl_4$ with pinacolone.[14] In this study it was demonstrated that the coordination is nearly octahedral and the bound pinacolones are *cis* as found in our computations. While the experimental average values of the Zr−Cl bonds (2.383 Å) are in reasonable agreement with the computed values, the average Zr−O−C angle (151°) is significantly larger than that determined in our computations (134.4°); this is probably due to the steric effect associated with the more cumbersome substituents in the pinacolone ligands.

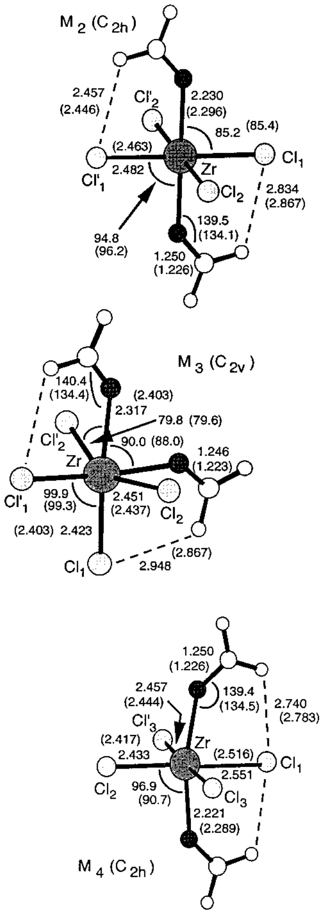

Figure 2. Schematic representation of the 2:1 complexes ($(H_2CO)_2$−$ZrCl_4$) M_2, M_3, and M_4 with the values of the most relevant geometrical parameters obtained with the LANL2DZ and the DZVP (in parentheses) basis sets (bond lengths are in Ångstroms and angles are in degrees).

The second lowest energy structure is M_5 where the two H_2CO ligands are again *cis*. M_5 is only 1.11 kcal mol^{-1} higher in energy than M_3 at the DZVP level and is characterized by a C_1 symmetry. In this case the two H_2CO ligands lie in two planes that are approximately orthogonal. The Zr−Cl bonds range between 2.464 and 2.402 Å, while the H···Cl distances involved in the hydrogen bonding are 2.713 and 2.853 Å.

The three remaining structures M_2, M_4, and M_6 have a C_{2h}, C_{2v}, and C_2 symmetry, respectively, and are all characterized by a *trans* arrangement of the two aldehyde ligands. As already pointed out by Branchadell and Oliva for the analogous titanium complexes,[15a] the Zr−O bond is shorter in the *trans* structures with respect to the *cis* structures (2.296, 2.289, and 2.301 Å in M_2, M_4, and M_6, respectively) while the Zr−O−C angle remains approximately the same (about 134°). Also the Zr−Cl bonds do not change significantly in the comparison between the *cis* and *trans* structures.

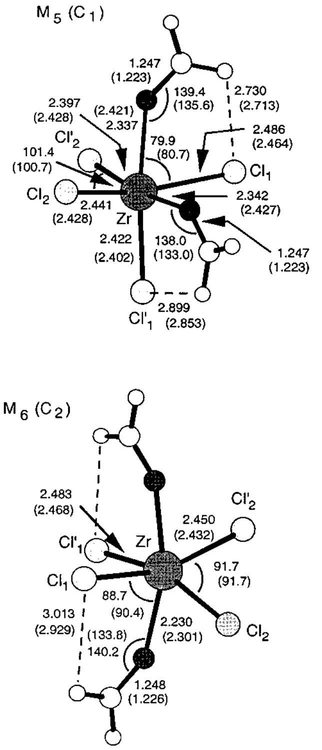

Figure 3. Schematic representation of the 2:1 complexes ($(H_2CO)_2-ZrCl_4$) M_5 and M_6 with the values of the most relevant geometrical parameters obtained with the LANL2DZ and the DZVP (in parentheses) basis sets (bond lengths are in Ångstroms and angles are in degrees).

The formation of the 2:1 complexes is exothermic by 13.05 kcal mol^{-1} at the DZVP level (M_3 complex) if we assume the 1:1 complex and a noninteracting H_2CO molecule as asymptotic limit. This exothermiciy is significantly larger with the ECP basis, being 19.21 kcal mol^{-1}. It is again important to point out that single-point computations with the DZVP basis on the LANL2DZ optimized structures provide energy values that agree very well with those obtained using the DZVP optimized structures (−11.83 kcal mol^{-1}). This evidence suggests that we can use this type of computational strategy, i.e., geometry optimization using the cheaper LANL2DZ basis and single-point computations with the all-electron DZVP basis, to investigate larger systems such as the dimers discussed in the following section.

To check the reliability of the B3LYP functional we have also carried out single-point MP2 computations on the B3LYP optimized structures using the DZVP basis. These results are also reported in Table 1 and do not differ significantly from those obtained at the DFT level: the energy order of the various complexes does not change and M_3 and M_5, which are again almost degenerate (the energy difference is 0.71 kcal mol^{-1}), correspond to the most stable 2:1 complexes.

Table 1. Energies (kcal mol^{-1})^a of the 1:1 and 2:1 Complexes Computed at the DFT (B3LYP) and MP2 Levels with the LANL2DZ and DZVP Basis Sets

	LANL2DZ/ B3LYP	DZVP/ B3LYP^b	DZVP/ MP2
1:1 complex (M_1)	−19.51	−13.46 (−14.01)	−16.50
2:1 complexes			
M_2	−10.99	−3.79 (−2.67)	−5.58
M_3	−19.21	−13.05 (−11.83)	−17.11
M_4	−11.86	−4.28 (−3.01)	−6.06
M_5	−17.60	−11.94 (−10.84)	−16.40
M_6	−13.32	−5.22 (−4.12)	−6.84

[a] The energy values are relative to the noninteracting $ZrCl_4$ and H_2CO molecules for the 1:1 complex and to the noninteracting M_1 complex and H_2CO molecule for the 2:1 complexes. The absolute energy (hartree) for $ZrCl_4 + H_2CO$ is −221.15344 (LANL2DZ), −5496.13068 (DZVP), −5496.13063 (DZVP single point), −5491.32456 (MP2). The absolute energy (hartree) for $M_1 + H_2CO$ is −335.66814 (LANL2DZ), −5610.67428 (DZVP), −5610.67388 (DZVP single point), −5605.51715 (MP2). [b] The values in parentheses correspond to single-point computations with the DZVP basis on the LANL2DZ optimized structures.

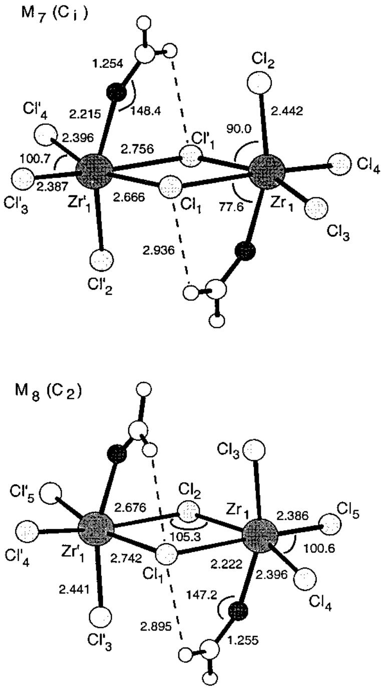

Figure 4. Schematic representation of the dimer complexes M_7 and M_8 with the values of the most relevant geometrical parameters obtained with the LANL2DZ basis set (bond lengths are in Ångstroms and angles are in degrees).

B. ($H_2CO-ZrCl_4$)$_2$ Dimers. We have determined six different dimeric structures, which are depicted in Figures 4−6. All of these structures, which are very similar to the ($H_2CO-TiCl_4$)$_2$ complexes investigated by Branchadell and Oliva at the Hartree−Fock level,[15a] consist of two Zr-centered octahedral units, which form a four-member cycle through two bridged Cl atoms. The two lowest energy structures (M_7 and M_8 in Figure 4) are characterized by a C_i and a C_2 symmetry, respectively. In both cases the two formaldehyde molecules are axial and are placed on the opposite sides of the plane formed by the two Zr atoms and the two Cl-bridged atoms. In M_7 these two in-planes Cl atoms (Cl_1 and Cl_1') are both involved in a C−H···Cl interaction similar to those previously pointed out in the 1:1 and 2:1 complexes, whereas in M_8 the two H_2CO molecules form a weak hydrogen bond with the same in-plane chlorine atom Cl_1. Furthermore, while the values of the H···Cl distance in both M_7 and M_8 (2.936 and 2.895 Å, respectively) show a negligible change with respect to the 1:1 and 2:1 complexes, the C−H···Cl angle increases significantly, its average value being 147.6°. One can also observe that the Zr−Cl bonds of the cycle (average value of 2.71 Å) are significantly longer than the Zr−Cl bonds not involved in the bridged structure, the average value being in this case 2.39 Å for the chlorine atoms in equatorial

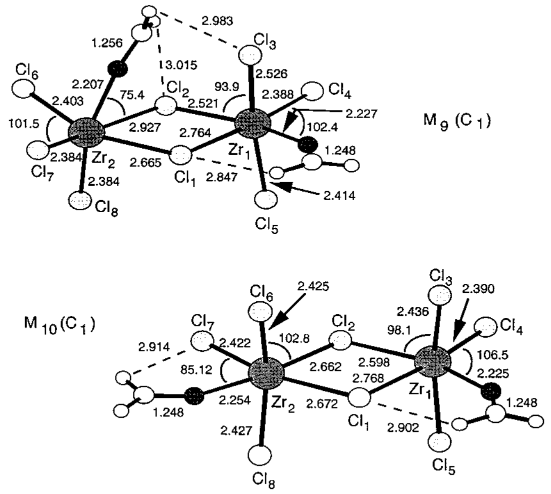

Figure 5. Schematic representation of the dimer complexes M_9 and M_{10} with the values of the most relevant geometrical parameters obtained with the LANL2DZ basis set (bond lengths are in Ångstroms and angles are in degrees).

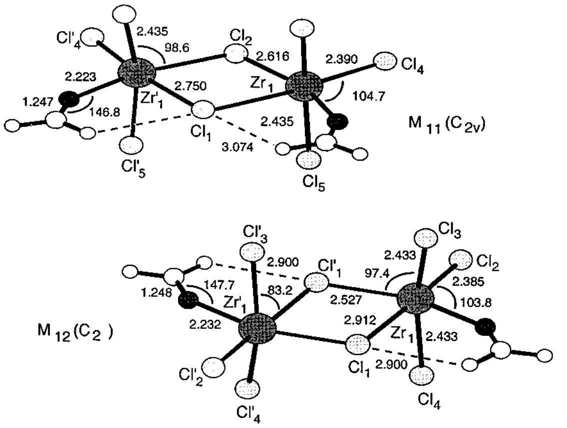

Figure 6. Schematic representation of the dimer complexes M_{11} and M_{12} with the values of the most relevant geometrical parameters obtained with the LANL2DZ basis set (bond lengths are in Ångstroms and angles are in degrees).

position and 2.44 Å for those in axial position. The third lowest energy dimer (M_9 with C_1 symmetry) has only one formaldehyde ligand that is axial and forms simultaneously two hydrogen bonds with two chlorine atoms. The second formaldehyde molecule is equatorial (it lies on the same plane of the four-member cycle) and forms an additional hydrogen bond with one of the Cl-bridged atoms (Cl_1); the three remaining dimers (M_{10}, M_{11}, and M_{12} with C_1, C_{2v} and C_2 symmetry, respectively) are significantly higher in energy and are all characterized by having both formaldehyde ligands in equatorial position.

The energy values obtained with the two basis sets are reported in Table 2. We discuss here in detail the values obtained with the DZVP basis (single-point computations on the LANL2DZ optimized structures), which show that the formation of the dimer from two isolated H_2CO−$ZrCl_4$ (M_1) complexes is significantly exothermic for M_7 (11.19 kcal mol^{-1}), M_8 (12.11 kcal mol^{-1}), and M_9 (5.55 kcal mol^{-1}), while the formation of M_{10}, M_{11} and M_{12} becomes slightly endothermic.

In addition to the previously discussed dimers, we have also considered the formation of a dimer involving only one bridged Cl atom. We have found that, using the same stoichiometric ratio of the other dimers (i.e., two $ZrCl_4$ units and two H_2CO units), this structure does not exist; the structure with only one bridged Cl atom, which has been used as a starting point in the search on the potential surface, evolves to reach lower-energy coordinatively saturated compounds with two bridged Cl atoms such as M_7 or M_8. However, in the presence of an additional formaldehyde molecule, which can saturate the free coordination site on one zirconium atom, we have located a new dimeric structure where only one Cl atom links an H_2CO−$ZrCl_4$ unit and a $(H_2CO)_2$−$ZrCl_3$ unit. The additional H_2CO molecule can be thought to mimic a situation where an excess of formaldehyde with respect to $ZrCl_4$ is used. This new structure (M_{13}) is shown in Figure 7. Inspection of this figure shows that this dimer is highly distorted when compared to the M_7−M_{12} complexes. The bridged Cl atom forms two Zr−Cl bonds that are 2.631 and 2.502 Å. Two of the three formaldehyde molecules are in axial position, and only one of these two molecules forms a weak hydrogen bond with an equatorial chlorine atom (the H···Cl distance is 2.847 Å, in agreement with the values found in the previously discussed complexes).

The new dimeric species M_{13} can be thought to originate from the interaction between one of the two lowest energy dimers (M_7 or M_8) and one formaldehyde molecule. This process, which implies the breaking of one bridging Zr−Cl bond and the formation of a new Zr−O bond, is thermodynamically favored since it is exothermic by 3.95 kcal mol^{-1} at the DZVP level.

Table 2. Energies (kcal mol^{-1})^a of the (H_2CO−$ZrCl_4$) Dimer Complexes Computed at the DFT (B3LYP) Level with the LANL2DZ and DZVP Basis Sets

	LANL2DZ/B3LYP	DZVP/B3LYP^b
M_7	−17.81	−11.19
M_8	−18.07	−12.11
M_9	−11.77	−5.55
M_{10}	−1.51	+3.92
M_{11}	−0.53	+4.53
M_{12}	−4.91	+1.20

^{a} The energy values are relative to two noninteracting $ZrCl_4$−H_2CO (M_1) complexes. The absolute energy (hartree) for M_1 + M_1 is −442.36906 (LANL2DZ), −10992.30590 (DZVP single point). ^{b} The DZVP values have been obtained by means of single-point computations on the LANL2DZ optimized structures.

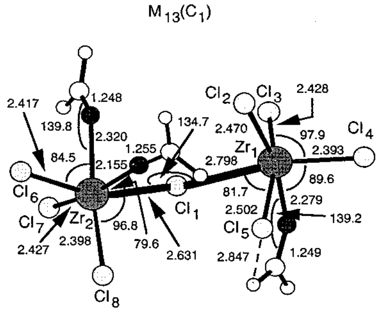

Figure 7. Schematic representation of the dimer complex M_{13} with the values of the most relevant geometrical parameters obtained with the LANL2DZ basis set (bond lengths are in Ångstroms and angles are in degrees).

Spectroscopic Results

We discuss here the ^{13}C NMR spectra that have been used to characterize $ZrCl_4$−aldehyde complexes of dif-

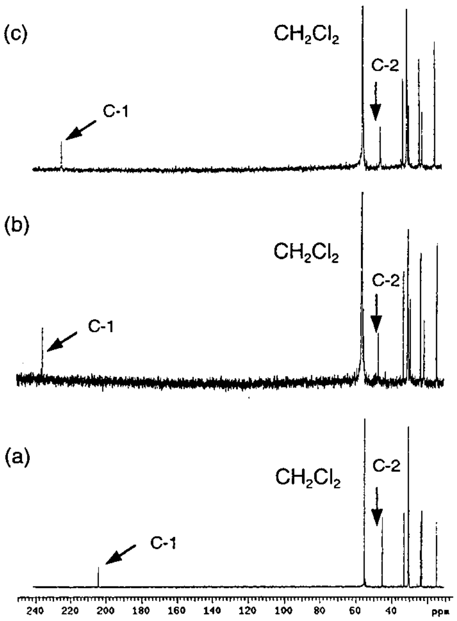

Figure 8. ^{13}C NMR spectra at −80 °C in CH_2Cl_2 of (a) dodecanal; (b) a 1:1 $ZrCl_4$/dodecanal mixture; (c) a 1:2 $ZrCl_4$/dodecanal mixture.

ferent stoichiometries. These complexes have been prepared by stirring the insoluble $ZrCl_4$ with a solution of the aldehyde in CH_2Cl_2 at 0 °C for 1 h, filtering off the insoluble material, and adding 10% CD_2Cl_2. Both aromatic (benzaldehyde) and aliphatic substrates have been tested. We have found that the solubility of the $ZrCl_4$−benzaldehyde complexes is exceedingly poor to obtain acceptable spectra, while meaningful results have been obtained for long straight-chain aldehydes such as dodecanal. In the case of the dodecanal complexes, the soluble fraction represents at least 90% of the total material, as found by weighting the filtered solution after evaporation of the solvent. In some cases, a clear solution is directly achieved, and filtration is avoided. The insoluble fraction, when present, has been found to contain dodecanal as the only organic component after quenching with H_2O. For a 1:1 (or higher) $ZrCl_4$/$C_{11}H_{23}CHO$ molar ratio (Figure 8b) only one sharp carbonyl peak at 226.96 ppm has been detected at −80 °C. This signal is strongly deshielded with respect to the noncomplexed aldehyde (203.40 ppm in Figure 8a), while only minor changes have been recorded for the resonances of C-2 and of the other carbons (the changes observed for these resonances are all less than 2 ppm; for instance, C-2 varies from 44.21 to 45.75 ppm, C-3 from 22.48 to 21.42 ppm, etc.). These peaks remained essentially unchanged in the −80 to 0 °C temperature range, while further heating caused the partial decomposition of the aldehyde essentially through aldol reactions. We attribute the signal at 226.96 ppm to a $ZrCl_4$−aldehyde complex, which we indicate temporarily as complex A. When a 1:1.5 $ZrCl_4$/$C_{11}H_{23}CHO$ molar ratio has been used, two sets of sharp signals have been detected for C-1, C-2, C-3, and C-4 carbons at −80 °C (Figure 9a). One of these sets corresponds to that previously observed for complex A and includes the 226.96 ppm carbonyl peak. The other set contains a more shielded carbonyl peak at 224.30 ppm, while the other resonances are intermediate between those of complex A and those of the free aldehyde. We believe that this new set comes from a different $ZrCl_4$−aldehyde complex, which we indicate at the moment as complex B. Heating the mixture results in a broadening of the C-4, C-3, C-2, C-1 pairs that undergo a fast exchange regime at different temperatures. The C-3 and C-4 pairs (with a separation of only 20 Hz) give single peaks at −40 °C (Figure 9b). The C-2 pair (with a separation of 57 Hz) remains unchanged at −40 °C, broadens at −20 °C (Figure 9c), and gives a single peak at 0 °C (Figure 9d). Finally, the C-1 pair (with a separation of 209 Hz) is not affected until a temperature of 0 °C is reached; at this temperature coalescence is observed (Figure 9d). This dynamic situation is reversible, and freezing again to −80 °C restores the slow exchange regime. The ^{1}H NMR spectrum of this mixture was also recorded. This spectrum shows only minor chemical shift changes with respect to the free dodecanal. Two peaks could be detected for H-1 (9.89 and 9.85 ppm) and for H-2 (3.13 and 3.03 ppm), while a single peak was present for H-3 (1.56 ppm), for the hydrogens from H-4 to H-11 (1.12 ppm) and for H-12 (0.76 ppm). This finding is in agreement with the presence in the mixture of the two different complexes A and B, as previously suggested. To unambiguously assign the NMR resonances, a bidimensional C−H HETCOR spectrum has also been acquired. It contains evident correlation peaks at the following chemical shift pairs: (226.96, 9.84 ppm C-1, H-1), (45.75, 3.13 ppm C-2, H-2), and (21.35, 1.56 ppm C-3, H-3), which belong to complex A, and (224.30, 9.89 ppm C-1, H-1), (44.98, 3.03 ppm C-2, H-2), and (21.78, 1.55 ppm C-3, H-3), which belong to complex B. The other cross-peaks for the carbons from C-4 to C-12 and the hydrogen atoms from H-4 to H-12 are common to both complexes as expected. For a 1:2 $ZrCl_4$/$C_{11}H_{23}CHO$ stoichiometry (Figure 8c), only the set corresponding to complex B, with the C-1 peak at 224.30 ppm, can be detected in the temperature range −80 to −40 °C. Further addition of dodecanal at −80 °C does not cause significant changes, while increasing the temperature of such a mixture to −60 °C results in a broadening of the carbonyl peak, which becomes almost invisible at tem-

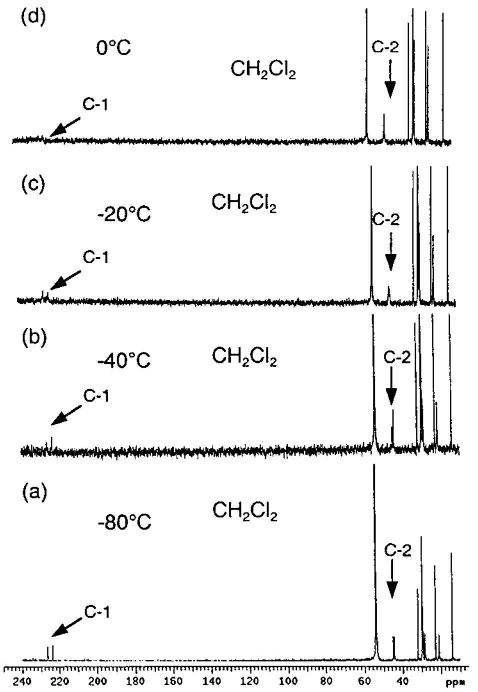

Figure 9. ^{13}C NMR spectra of a 1:1.5 $ZrCl_4$/dodecanal mixture in CH_2Cl_2 recorded at (a) −80, (b) −40, (c) −20, and (d) 0 °C.

peratures higher than −20 °C. The C-1 signal of the free aldehyde cannot be detected in any case, even in the presence of 5% mole of $ZrCl_4$.[23] It is also worth noting that no chemical change other from complexation occurs from the interaction of $ZrCl_4$ and both dodecanal or benzaldehyde below 0 °C. In fact, upon quenching with water, all of the above solutions showed only the presence of the free aldehydes and no trace of other products as evidenced by TLC and GC analysis.

The trend observed for the $ZrCl_4$−dodecanal adducts parallels the trend observed by Denmark[24] for the $TiCl_4$ complexes with heptanal and 4-(*n*-heptyl)-benzaldehyde. In that case the two sets of signals observed at −80 °C were associated with two different species whose relative concentration was determined by the Lewis acid/aldehyde molar ratio. The two species were characterized by ^{13}C chemical shifts that are comparable to those reported here for the $ZrCl_4$−dodecanal complexes. Denmark associated these species with 1:1 and 1:2 $TiCl_4$−aldehyde complexes even if no structural information could be inferred from the spectroscopic data.

Experimental Section

A Varian Gemini 300 instrument was used to obtain ^{13}C NMR spectra (75.5 MHz) at variable temperatures. Chemical shifts are reported in ppm downfield from internal tetramethylsilane (TMS). Anhydrous CH_2Cl_2 containing less than 0.005% water was obtained from Fluka and stored over molecular sieves under argon; CD_2Cl_2 was dried and stored over activated molecular sieves under argon. $ZrCl_4$ was obtained from Fluka and transferred under argon atmosphere into carefully dried glass vials that were successively sealed. Dodecanal and benzaldehyde were distilled and stored under argon. The glassware was dried by heating under vacuum and cooling under a gentle flow of argon. All of the manipulations were carried out under strictly anhydrous conditions with needle techniques. NMR samples were prepared by drying the NMR tube through heating under vacuum and filling with argon (three times); the tubes were maintained in a Schlenk bottle under argon during the transfer of the sample solution, immediately closed with appropriate seal, and briefly maintained at −20 °C in an argon atmosphere until transferred into the NMR probe where anhydrous nitrogen was flowing.

$ZrCl_4$−Dodecanal (1:1 Molar Ratio). A stirred suspension of zirconium tetrachloride (304 mg, 1.3 mmol) in CH_2Cl_2 (3 mL) was treated dropwise at 0 °C under argon with dodecanal (290 μL, 1.3 mmol). The mixture was stirred at 0 °C for 1 h and filtered under argon. CD_2Cl_2 (0.3 mL) and a small amount of TMS were added to the obtained pale yellow solution, which after addition was transferred in a NMR tube under argon atmosphere at 0 °C. The ^{13}C NMR spectrum was recorded immediately at −80 °C. δ_c (ppm): 14.70; 21.42; 23.34; 28.81; 29.77; 29.99; 30.20; 32.48; 45.75; 226.96.

$ZrCl_4$−Dodecanal (1:1.5 Molar Ratio). A similar procedure, but with 1.95 mmol (435 μL) of dodecanal, provided the desired sample.

$ZrCl_4$−Dodecanal (1:2 Molar Ratio). A similar procedure, but with 2.6 mmol (580 μL) of dodecanal, provided the desired sample. δ_c (ppm): 14.67; 22.78; 23.33; 29.08; 30.18; 32.52; 44.98; 224.30.

For comparison, the spectrum of dodecanal in the same experimental conditions is also reported. **Dodecanal** δ_c (ppm): 14.58; 22.15; 23.22; 29.24; 29.45; 29.97; 30.13; 35.13; 44.31; 204.00.

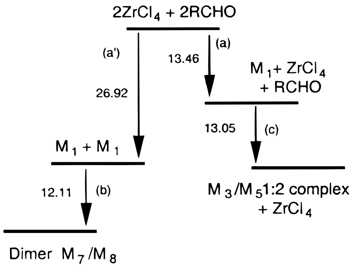

Figure 10. Energy diagram for the formation of the 1:1, 2:1, and dimer complexes for a 1:1 $ZrCl_4$/aldehyde molar ratio.

Discussion

We believe that our spectroscopic data clearly indicate for the $ZrCl_4$−dodecanal system the existence of two complexes with different stoichiometry (A and B complexes) and that their relative concentrations depend only on the Lewis acid/aldehyde molar ratio. The computational results previously discussed can be of great help to rationalize the spectroscopic evidences. Let us analyze first the case where the $ZrCl_4$/aldehyde molar ratio is 1:1. A schematic representation of this situation is given in Figure 10 where we assume as a reference level (asymptotic limit) two noninteracting $ZrCl_4$ units and two noninteracting aldehyde molecules (RCHO). The assumption made in our model and concerning the reference level is useful to simplify the discussion, but in a way, it is a quite rough approximation. In the real system $ZrCl_4$ is initially in a polymeric crystalline form,[25] and we ignore here the energy required to obtain a single $ZrCl_4$ unit (monomer). However, this energy is approximately a constant term and should only shift the asymptotic limit without affecting significantly the relative energies of the various species and the meaning of the discussion. The interaction between zirconium tetrachloride and one aldehyde molecule leads to the formation of the coordinatively unsaturated M_1 complex (paths a or a′). This process is exothermic by 13.46 kcal mol^{-1}. In a subsequent step (path b) two M_1 complexes can interact to afford the coordinatively saturated dimeric species (M_7 or M_8, which are almost degenerate). This process is also exothermic (12.11 kcal mol^{-1}), and consequently, the overall process that leads to a dimer from two $ZrCl_4$ units and two free aldehyde molecules is highly favored since it is exothermic by 39.03 kcal mol^{-1}. Alternatively (path c), one M_1 complex can react with a free formaldehyde molecule and give the 2:1 complex (M_3 or M_5). However, this process is disfavored with respect to the formation of the dimer since the overall exothermicity is 26.51 kcal mol^{-1}. Thus complex A observed at 226.96 ppm should correspond to the 1:1 dimeric species (M_7/M_8) that we have located on the potential surface.

Let us consider now a $ZrCl_4$/aldehyde molar ratio equal to 1:2. This situation is represented in Figure 11, where the asymptotic limit corresponds to four noninteracting RCHO molecules and two noninteracting $ZrCl_4$ units. After formation of the 1:1 complex (M_1) and of the dimeric species M_7/M_8 (paths a + b), in the presence of an aldehyde excess, one of the zirconium atoms of the dimer

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[23] The C-1 peak of the aldehyde cannot be detected in any case if $ZrCl_4$ is present. Solutions containing 20-fold excess aldehyde with respect to the Lewis acid also did not show this peak in a −80 to 0 °C temperature range. The reason for this is, at present, not well understood; excessive broadening or reversible Lewis acid catalyzed polymerization could be invoked.

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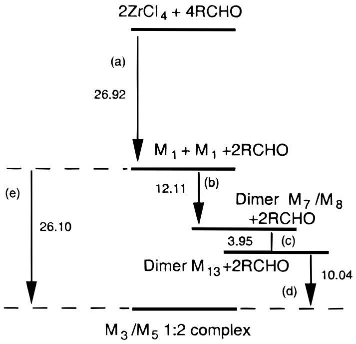

Figure 11. Energy diagram for the formation of the 1:1, 2:1, and dimer complexes for a 1:2 $ZrCl_4$/aldehyde molar ratio.

can react with an additional aldehyde molecule and afford the second dimeric species M_{13} reported in Figure 7 (path c). A further reaction of M_{13} with another aldehyde (path d) causes the breaking of the remaining Zr−Cl bridge in M_{13} and the simultaneous binding of the aldehyde to the zirconium atom that has lost the Cl ligand (the process can be thought as a nucleophilic displacement). This process leads to the formation of two coordinatively saturated monometallic 2:1 complexes (M_3/M_5) and is exothermic by 10.04 kcal mol^{-1}. Thus in the presence of an excess of aldehyde the formation of the 2:1 aldehyde−$ZrCl_4$ complex is favored with respect to the formation of the dimeric species. This finding suggests that this 2:1 monometallic complex (M_3/M_5) should correspond to complex B that has been observed at 224.30 ppm.

When the molar ratio is in the range 1:1 to 1:2 the two complexes, i.e., M_3/M_5 and M_7/M_8, are simultaneously present as indicated by the two sets of signals in the NMR spectra recorded when a 1:1.5 molar ratio is used. In these conditions the two observed species coexist in a slow equilibrium on the NMR time scale at a temperature of −80 °C, while over −20 °C the equilibrium becomes fast.

Conclusion

In this paper we have carried out a combined theoretical−experimental study of the structures and energies of $ZrCl_4$−aldehyde complexes. The system that we have experimentally investigated using ^{13}C NMR spectroscopy is represented by the adducts that can form from $ZrCl_4$ and dodecanal in various molar ratios. In our computations we have emulated the real system by replacing dodecanal with formaldehyde. The computational investigation that we have carried out using a DFT (B3LYP) approach has demonstrated the existence of different types of complexes. A 1:1 complex (H_2CO−$ZrCl_4$) can originate from one $ZrCl_4$ unit and one aldehyde molecule. This complex in still coordinatively unsaturated and after interaction with an additional aldehyde molecule can form a 2:1 complex (($H_2CO)_2$−$ZrCl_4$). The formation of both complexes is significantly exothermic if we assume as the asymptotic limit noninteracting $ZrCl_4$ and formaldehyde (13.46 kcal mol^{-1}) and noninteracting aldehyde and H_2CO−$ZrCl_4$ complex, respectively (13.05 kcal mol^{-1}). Alternatively, two unsaturated 1:1 complexes can interact and afford a dimeric species where the two metal atoms are bonded through two bridged Cl atoms in a four-centered cycle. The formation of the lowest energy dimeric species is also exothermic (12.11 kcal mol^{-1}) if we assume two noninteracting H_2CO−$ZrCl_4$ complexes as a reference. The analysis of the energies involved in the formation of the various complexes (1:1 and 2:1 complexes and dimers) has indicated that, when the $ZrCl_4$/aldehyde molar ratio is 1:1, the formation of the dimer is favored, and this complex should be responsible of the signal recorded at 226.96 ppm in these stoichiometric conditions. On the other hand, when the molar ratio is 1:2 or lower the $(H_2CO)_2$−$ZrCl_4$ complex should be the dominant species and should correspond to the complex that has been observed at 224.30 ppm in the ^{13}C NMR spectra. This $(H_2CO)_2$−$ZrCl_4$ complex is characterized by a *cis* arrangement of the two aldehyde molecules, and its structures is in quite good agreement with that determined in the X-ray study of the octahedral 1:2 adduct of $ZrCl_4$ with pinacolone.[14]

Finally, it is worth pointing out an important computational aspect concerning the level of accuracy used in our computations that we have already discussed elsewhere.[26] Our results have demonstrated that the ECP basis set is able of providing geometrical parameters in good agreement both with the experiment (comparison with the X-ray study on the $ZrCl_4$−pinacolone adducts) and with the results obtained with all-electron basis sets such as DZVP. As a consequence the energetic obtained by means of single-point computations with the DZVP basis on the ECP optimized structures is very close to that obtained using the DZVP optimized structures. This evidence suggests that this computational approach (single-point computation with all-electron basis sets on ECP optimized structures) can represent a reliable and cheaper computational strategy for describing larger systems involving carbonyl compounds and zirconium atoms.

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Supporting Information Available: H−C HETCOR spectrum of the 1:1.5 $ZrCl_4$−dodecanal mixture at −80 °C. This material is available free of charge at the Internet address http://pubs.acs.org.

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