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SHORT COMMUNICATION

Additional NMR Data on Compounds of the Type cis-Ti(AA)₂X₂

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Previous work has shown that cis-disubstituted(acac)₂titanium(IV) complexes exist in solution as nonrigid molecules[1]. These studies were followed by variable temperature ¹H NMR spectroscopy. The spectra shows that for the dialkoxy and dihalo complexes the acetylacetonate(acac) rings exchange the methyl groups between the two nonequivalent sites of the cis isomer. These rearrangements take place via an intramolecular rearrangement: both twisting and one bond rupture mechanisms have been suggested for these stereochemical rearrangements [2-4].

Recently we have reported on a ¹³C NMR study of molecules of the type Ti(acac)₂X₂ (X is F, Cl, Br, OPrⁱ) [5,6]. The ¹³C NMR results show that the acetylacetonate ring carbonyl and methyl carbons of these complexes are involved in the exchange process as are the methyl protons of the acetylacetonate ring. From the chemical shift differences ($\Delta\nu$) in the nonexchanging region for each type of carbon, an exchange rate, k_c , can be calculated, eq. 1. From this number the free energy of activation, ΔG^\ddagger , can be calculated, eq. 2, where T is the coalescence temperature [7].

$$k_c = \frac{\pi(\Delta\nu)}{2} \quad [\text{eq. 1}]$$

$$\Delta G^\ddagger = 4.57 T (10.32 + \log T/k_c) \quad [\text{eq. 2}]$$

The free energy of activation is the same for the methyl and carbonyl carbons as well as the methyl hydrogens from proton data, indicating that all of these moieties in any given compound are exchanging at the same rate.

We now wish to report additional ^{13}C NMR data on compounds of the type $\text{Ti}(\text{bzac})_2\text{X}_2$ and $\text{Ti}(\text{bzbz})_2\text{X}_2$ and $\text{Ti}(\text{tfac})_2\text{X}_2$ where X is F, Cl and Br as well as ^{19}F NMR data on $\text{Ti}(\text{tfac})_2\text{F}_2$.

^{13}C NMR chemical shift data obtained for these complexes is shown in Table 1. The chemical shift data for each type of

TABLE 1

^{13}C NMR chemical shift data on various cis- $\text{Ti}(\text{AA})_2\text{X}_2^*$

Compound	CH_3	CO	CH
$\text{Ti}(\text{acac})_2\text{X}_2$	25.8	191.7	109.0
$\text{Ti}(\text{bzbz})_2\text{X}_2$		184.3	100.5
$\text{Ti}(\text{bzac})_2\text{X}_2$	26.7	193.1(ac) 182.5(bz)	104
$\text{Ti}(\text{tfac})_2\text{X}_2$	27.5	201.6(ac) 170.7(tf)	102.5

*In ppm downfield from TMS, X is F, Cl, Br.

carbon in each series of compounds shows only a small variation (± 0.1 ppm) with F, Cl or Br. This trend was also observed in our ^{13}C NMR data on $\text{Ti}(\text{acac})_2\text{X}_2$ [6] and in proton data for $\text{Ti}(\text{acac})_2\text{X}_2$ and $\text{Ti}(\text{bzbz})_2\text{X}_2$ [3,4]. In general the chemical shifts for each type of carbon in any of the series examined is more deshielded than the corresponding carbon in the free ligand (enol form). The methine carbon experiences the greatest electronic effect (~ 6 to 9 ppm) with the carbonyl carbons (~ 1 to 2 ppm) and the methyl and phenyl carbons (~ 0.5 to 1.0 ppm) having less deshielding than the free ligand.

Spin-spin coupling of ^{13}C with ^{19}F was observed in the $\text{Ti}(\text{tfac})_2\text{X}_2$ complexes not only for the carbon of the CF_3 group but also for the carbonyl carbon bonded to the CF_3 group and the methine (C-H) carbon. A typical spectrum of $\text{Ti}(\text{tfac})_2\text{F}_2$ gave the following chemical shift data (ppm) in CDCl_3 : 27.5 (CH_3); 102.5 (CH, q, $J=2.44$ Hz); 117.6 (CF_3 , q, $J=281.7$ Hz); 170.7 ($\text{CF}_3\text{-C}^*\text{-O}$, q, $J=37.9$ Hz); 201.6 ($\text{CH}_3\text{-C}^*\text{-O}$). No spin coupling of the methyl carbon with fluorine was observed; however, an off resonance ^{13}C NMR spectrum of tfac ligand showed each quartet of the methyl carbon resonance to be slightly split into a doublet (0.01 Hz) apparently by fluorine. A noticeable electronic effect (170.7 ppm) as compared to the free ligand (176.3 ppm) can be seen in the carbonyl carbon of $\text{Ti}(\text{tfac})_2\text{X}_2$ which is bonded to CF_3 .

The ^{19}F NMR of $\text{Ti}(\text{tfac})_2\text{F}_2$ showed two resonances, -74.5 ppm and -239.7 ppm from CFCl_3 . The -74.5 ppm resonance is assigned to the fluorines of the CF_3 group and the resonance at -239.7 ppm is typical of a Ti-F resonance which we have also observed for $\text{Ti}(\text{acac})_2\text{F}_2$ (-239.7 ppm), $\text{Ti}(\text{bzac})_2\text{F}_2$ (-239.8 ppm) and $\text{Ti}(\text{bzbz})_2\text{F}_2$ (-239.6 ppm) and which has been reported [3,4].

Variable temperature ^{13}C NMR spectra of $\text{Ti}(\text{bzbz})_2\text{F}_2$ and $\text{Ti}(\text{bzbz})_2\text{Cl}_2$ was obtained in CDCl_3 . The carbonyl carbon of the compounds showed line broadening with decreasing temperature, then splitting into two resonances at $-16 \pm 2^\circ\text{C}$ ($\Delta\nu = 3.20$ Hz) and $-5 \pm 2^\circ\text{C}$ ($\Delta\nu = 2.19$ Hz) for the fluoro and chloro compounds, respectively. The coalescence temperatures (T_c) gave an exchange rate, k_c , of 7.11 and 4.86 sec^{-1} with the free energy of activation (ΔG^\ddagger) as 13.9 and 14.6 kcal/mol for the fluoro and chloro compounds, respectively. No splitting of the phenyl carbons was observed down to -45°C . Evidently the splitting is smaller than the natural line width; the point to point resolution is approximately 1/16 Hz for the ^{13}C NMR spectra. While line broadening in the ^1H NMR spectra has been observed for these compounds no kinetic data was reported [4]. A ^{13}C NMR variable temperature study of the $\text{Ti}(\text{bzbz})_2\text{Br}_2$ complex was not attempted due to its limited solubility.

The phenyl carbons of $\text{Ti}(\text{bzbz})_2\text{Cl}_2$ showed four distinct resonances: 128.0, 128.4, 132.9 and 134.9 ppm downfield from TMS. The two latter resonances are of lower intensity and they are assigned to the phenyl carbon bonded to the carbonyl carbon and to the para phenyl carbon. An off-resonance study showed no splitting of the 132.9 resonance indicating this is the phenyl carbon bonded to the carbonyl ring carbon. The IR of $\text{Ti}(\text{bzbz})_2\text{Cl}_2$ gave a $\nu_{\text{Ti-Cl}}$ at 384 cm^{-1} and $\text{Ti}(\text{bzbz})_2\text{Br}_2$ gave a $\nu_{\text{Ti-Br}}$ at 305 cm^{-1} . This agrees with our previous study of $\text{Ti}(\text{acac})_2\text{X}_2$ [6] and with a recent report by Serpone [8]. The $\nu_{\text{Ti-F}}$ in $\text{Ti}(\text{bzbz})_2\text{F}_2$ was obscured by the many absorbances in the $500\text{--}800$ cm^{-1} range due to phenyl and acac ring vibrations.

An intramolecular exchange mechanism is proposed for $\text{Ti}(\text{bzbz})_2\text{F}_2$ and $\text{Ti}(\text{bzbz})_2\text{Cl}_2$ since these rates are independent of concentration. It is interesting to note that the rate of exchange decreases from acac to bzbz. This dependence is in accord with both twisting and bond rupture mechanisms. Strong support for a twist mechanism has been reported as a result of Fay's inversion and R-group exchange data [9] and it is also suggested by Jennings' data [10] from their dynamic ^1H NMR studies taken on various bulky alkoxide ligands in cis-dialkoxybis(acac)titanium(IV) complexes. We agree with Fay that no NMR experiment has as yet settled the question of bond rupture versus a twisting mechanism for complexes of this type.

Experimental

The ^{13}C and ^{19}F NMR spectra were taken on a JEOL-FX 100 NMR spectrometer. All samples were run in CDCl_3 with TMS (^{13}C NMR) and CFCl_3 (^{19}F NMR) used as internal standards. The compounds were prepared from known literature reports [4]. The following abbreviations are used: acac, acetylacetonate; bzbz, dibenzoyl methanate; bzac, benzoyl methanate and tfac, trifluoromethyl methanate.

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