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# Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$ and *cis*-$M(AB)_2X_2$ Complexes. 8. The *cis*-$M(AA)_2XY$ System, Y = $O^iC_3H_7$ and 2,6-$(^iC_3H_7)_2C_6H_3O$

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*The diastereotopic nmr probe in the complexes Ti(acac)$_2$XY (X = Cl or Br; Y = $O^iC_3H_7$ or 2,6-$(^iC_3H_7)_2C_6H_3O$; acac = anion of 2,4-pentanedione) has been positioned on the monodentate Y ligand in our quest to follow the course of the configurational rearrangements in these and analogous complexes. Where Y is the isopropoxide ligand, the isopropyl methyl nmr resonance remains a sharp doublet even at −63 °C. Diastereotopic splitting is observed when Y is 2,6-$(^iC_3H_7)_2C_6H_3O$. The pertinent activation parameters for enantiomerization in Ti(acac)$_2$Cl(2,6-$(^iC_3H_7)_2C_6H_3O$) are ($CH_2Cl_2$ and 25 °C): $\Delta H^{\neq}$ = 3.7 ± 0.6 kcal/mol, $\Delta S^{\neq}$ = −41.5 ± 2.2 eu, and* k = *10 sec$^{-1}$. It is argued, on the basis of previous work, that rearrangements probably occur* via *twist processes.*

## Introduction

In our last paper in this series [1] we had positioned the diastereotopic nmr probe on the AA ligand of a *cis*-$M(AA)_2XY$ complex. Those studies indicated that rearrangements occur with inversion of the molecular configuration of these dissymmetric *cis* complexes. It was also shown that substitution of a halo group by an alkoxy ligand in *cis*-$M(AA)_2X_2$ decreases the stereochemical lability of the AA ligand. We further argued that the averaging set defining the observed permutations [2] in the complex Ti(dibm)Cl($OCH_3$) [dibm = anion of diisobutyrylmethane] is $A'_{13}$; this set scrambles all the groups (both –CH= and isopropyl methyls) amongst all the nonequivalent sites of the *cis*-$C_1$ isomer and, furthermore, leads to $\Delta \rightleftarrows \Lambda$ interconversions.

In their report of the preparation and characterization of several *cis*-Ti(acac)$_2$Cl(OR) complexes [acac = anion of 2,4-pentanedione and R = $CH_3$, $C_2H_5$, n-$C_3H_7$, i-$C_3H_7$, or $C_3H_5$], Thompson and co-workers [3] reported that the acetylacetonate methyl proton nmr resonance of Ti(acac)$_2$Cl($O^iC_3H_7$) splits into three resonances at low temperature; no nmr information was given regarding the diastereotopic isopropyl methyl group signals.

The Ti(acac)$_2$X($O^iC_3H_7$) (X = Cl or Br) complexes were unexpected products from the reaction of the appropriate Ti(acac)$_2X_2$ complex and titanium(IV) isopropoxide, and thus presented a further opportunity to investigate enantiomerization processes in these Ti(acac)$_2$X(OR) complexes, where R is also 2,6-$(^iC_3H_7)_2C_6H_3$.

## Experimental

Reagent grade dichloromethane, hexane, and benzene were dried for at least 12 hr over $CaH_2$ chips just prior to use. Titanium(IV) isopropoxide was used as received from the supplier (Research Organic/Inorganic). The Ti(acac)$_2X_2$ complexes (X = Cl or Br) were either available from previous studies or were prepared fresh by standard procedures [4]. Chemicals and reactions were handled under a dry nitrogen atmosphere in a glove bag. Analyses were performed by Galbraith Laboratories of Knoxville, Tennessee, U.S.A. Melting points are not corrected.

The Ti(acac)$_2$X($O^iC_3H_7$) (X = Cl or Br) complexes were synthesized by reacting the parent Ti(acac)$_2X_2$ complexes with titanium(IV) isopropoxide in dichloromethane. Stirring overnight at room temperature followed by removal of solvent under reduced pressure gave a yellow oil. After dissolving this oil in a minimum amount of hexane and on cooling to 0 °C a yellow powder was recovered. The crude products were recrystallized from a benzene-hexane solution. For X = Cl, mp 106–108 °C, lit. [3] mp 110–114 °C (dec); for X = Br, mp 105–107 °C. The purity of the complexes was further verified by infrared and proton nmr spectroscopy.

Chloro(2,6-diisopropylphenoxy)bis(2,4-pentanedionato)titanium(IV) was prepared from Ti(acac)$_2$-

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TABLE I. Temperature Dependence of Mean Residence Times, $\tau$, of Isopropyl Methyl Group Exchange in $Ti(acac)_2Cl(2,6\text{-}(^iC_3H_7)_2C_6H_3O)$.[a]

| Temp.[b], °C | $10^2\ \tau$, sec | Temp., °C | $10^2\ \tau$, sec |
|---|---|---|---|
| −18.7 | 16 | 3.1 | 8.4 |
| −17.4 | 16 | 4.8 | 8.3 |
| −14.9 | 15 | 5.7 | 7.4 |
| −11.7 | 14 | 7.1 | 7.0 |
| −7.6 | 11 | 7.3 | 8.9 |
| −3.0 | 11 | 10.0 | 7.8 |
| −1.5 | 11 | 10.2 | 6.6 |
| 1.1 | 10 | 10.6 | 7.3 |

[a]0.300 *M* in dichloromethane. [b]Calculated from the Van Geet equation for methanol [7].

TABLE II. Concentration Dependence of Mean Residence Times for Isopropyl Methyl Group Exchange in $Ti(acac)_2Cl(2,6\text{-}(^iC_3H_7)_2C_6H_3O)$ in $CH_2Cl_2$.

| Temp., °C | Concentration, *M* | $\tau$, sec |
|---|---|---|
| −17.4 | 0.300 | 0.162 |
| | 0.150 | 0.161 |
| −1.5 | 0.300 | 0.113 |
| | 0.150 | 0.115 |
| 1.1 | 0.300 | 0.100 |
| | 0.150 | 0.095 |
| 10.6 | 0.300 | 0.073 |
| | 0.150 | 0.064 |

$Cl(O^iC_3H_7)$ [1.50 g, 4.40 mmol] and 2,6-diisopropylphenol (1.02 g, 5.72 mmol) in benzene. The resulting blood-red solution was stirred overnight at ~20 °C, after which removal of the solvent under reduced pressure produces a viscous red residue. Dissolving this residue in hexane and cooling the solution produces a red solid which was collected, washed with hexane, and dried in air. The crude product was subsequently recrystallized from benzene–hexane solutions and dried at 80 °C *in vacuo* for ~4.5 hr; mp 125–127 °C (dec). Analysis gave C, 57.81; H, 7.13 *versus* C, 57.59 and H, 6.81 for $TiC_{22}H_{31}O_5Cl$.

The $^1H$ nmr spectral techniques employed, treatment of the data and methods of calculating relaxation times, $\tau$, were analogous to those used previously [5, 6].

Mean residences times, $\tau$, for exchange of isopropyl methyl groups in the complex $Ti(acac)_2Cl(2,6\text{-}(^iC_3H_7)_2C_6H_3O)$ are presented in Table I; Table II summarizes the concentration dependence of $\tau$ at various temperatures. Arrhenius and Eyring activation parameters were obtained from the slopes and intercepts of a least-squares treatment of log k *vs.* $10^3/T$ (see Fig. 1) or of log (k/T) *vs.* $10^3/T$.

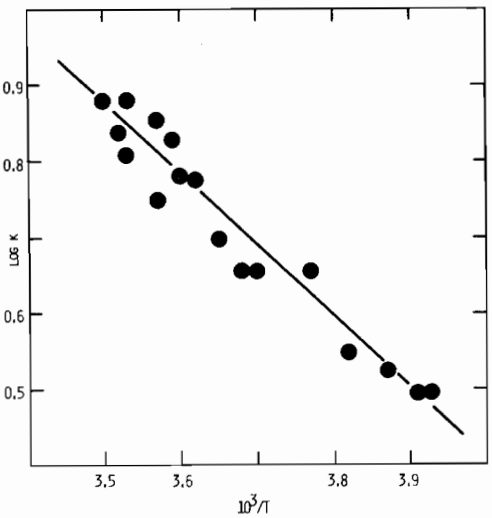


Fig. 1. Arrhenius (log k *versus* 1/T) least-squares plot for isopropyl methyl group exchange in the $Ti(acac)_2Cl(2,6\text{-}(^iC_3H_7)_2C_6H_3O)$ complex in dichloromethane solution.

## Results and Discussion

The nmr spectrum of a dichloromethane solution of $Ti(acac)_2Cl(O^iC_3H_7)$ reveals a single acetylacetonate methyl, ring proton, and isopropyl methyl doublet resonance at room temperature (~37 °C). By ~−10 °C the acetylacetonate methyl resonance appears as three peaks in a 1:1:2 intensity ratio, while the –CH= resonance appears as two equally intense absorptions. These results agree with those of Thompson and co-workers [3] and the identical behaviour is observed for the acetylacetonate methyl and ring proton resonances of the $Ti(acac)_2Br(O^iC_3H_7)$ complex; the bromo complex possesses slightly larger chemical shift separations. However, the isopropyl methyl resonance for these $Ti(acac)_2X(O^iC_3H_7)$ (X = Cl, Br) complexes remains a sharp doublet down to ~−60 °C. The $W_{1/2}$ (full width at half maximum amplitude) values for the isopropyl methyl doublet of the $Ti(acac)_2Cl(O^iC_3H_7)$ complex vary from 0.61 Hz (39.6 °C) to 1.49, 1.57 Hz (−62.7 °C); the bromo complex has similar values of 0.62, 0.65 Hz (39.6 °C) and 1.59, 1.63 Hz (−62.7 °C). These changes in linewidths probably reflect changes in solvation and increased solvent viscosity at the lower temperatures.

The failure to detect optical inversion processes in these $Ti(acac)_2X(O^iC_3H_7)$ (X = Cl, Br) complexes is surprising in light of the observed [8–10] non-

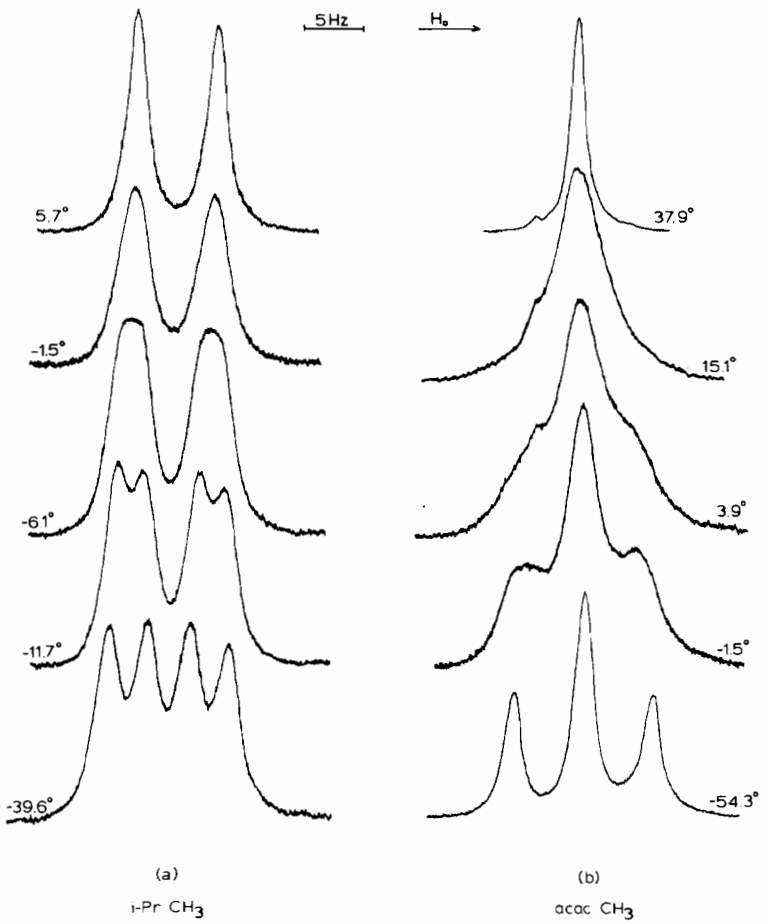


Fig. 2. Temperature dependence of the (a) isopropyl methyl and (b) acetylacetonate methyl resonances of the $Ti(acac)_2Cl(2,6\text{-}^iPr_2C_6H_3O)$ complex in dichloromethane solution.

equivalence of isopropyl methyl groups in the $Ti(acac_2(O^iC_3H_7)_2$ complex. Introduction of a halogen into the complex is expected to increase the lability [1], but not to an extent so as to render inversion processes rapid even at −60 °C. That the diastereotopic isopropyl methyl groups in the mixed haloisopropoxy complexes exhibit chemical shift degeneracy cannot be precluded.

Consulting Table V of ref. 2 with the observed changes in signal multiplicities of 4 → 1 for nondiastereotopic terminal groups on the A–A ligand and 2 → 1 for nondiastereotopic –CH= groups leads to a choice of $A'_6$ or $A'_{13}$ as the averaging set responsible for the rearrangement. Assuming optical inversion occurs during the rearrangement, $A'_{13}$ remains as the only viable averaging set and arguments presented earlier [1] suggest that $A'_{13}$ correlates with a twist mechanism. Arguments suggestive of a twist mechanism assume the rearrangements occur *via* a single physical pathway.

The reaction of 2,6-diisopropylphenol with the $Ti(acac)_2Cl(O^iC_3H_7)$ complex yields the $Ti(acac)_2Cl(2,6\text{-}(^iC_3H_7)_2C_6H_3O)$ complex. The temperature dependence of the isopropyl methyl and acetylacetonate methyl resonances for this complex is illustrated in Fig. 2. A single isopropyl methyl doublet is observed at ambient temperature but below *ca.* −10 °C two doublets are observed. A total lineshape analysis of this exchange process has been carried out and the results are summarized in Table I. The exchange process was also verified to be a first-order process (see Table II). A linear least-squares analysis of the data of Table I (see also the experimental section) gives the following activation parameters ($CH_2Cl_2$ and 25 °C): $E_a$ = 4.3 ± 0.6 kcal/mol, $\Delta H^{\neq}$ = 3.7 ± 0.6 kcal/mol, $\Delta S^{\neq}$ = −41.5 ± 2.2 eu, $\Delta G^{\neq}$ = 16.08 ± 0.06 kcal/mol, and $k$ = 10 $sec^{-1}$. The rates of isopropyl methyl group exchange in the related complexes $Ti(acac)_2(2,6\text{-}(^iC_3H_7)_2C_6H_3O)_2$ and $Ti(acac)_2Cl_2$ are (also in $CH_2Cl_2$) respectively, 8.3 $sec^{-1}$ [6] and 670 $sec^{-1}$ [4]. These data support our earlier [1] conclusions that successive replacement of a chloride in $Ti(AA)_2Cl_2$ by an alkoxy group *decreases* the stereochemical lability of the complex,

in the present case the enantiomerization process. Replacement of the first chloride appears to have the most dramatic effect. This suggests that electronic effects probably play a major role in the rearrangement processes [6].

The acetylacetonate methyl proton region reveals a single resonance at ~37 °C, but on cooling this resonance broadens and, by ~−30 °C, three sharp resonances are observed with an intensity ratio of 1:2:1. In contrast to the $Ti(acac)_2X(O^iC_3H_7)$ species, the 2,6-diisopropylphenoxy complex does not reveal two acetylacetonate ring proton (–CH=) resonances at low temperature. The $W_{1/2}$ value for the –CH= resonance of the $Ti(acac)_2Cl(2,6\text{-}^iPr_2C_6H_3O)$ complex varies from 0.52 Hz (41.9 °C) to 1.55 Hz (−57.9 °C), which presumably also reflects solvation and viscosity changes at the lower temperature and the two nonequivalent –CH= groups probably possess nearly identical chemical shifts.

No attempts were made to perform a detailed total lineshape analysis of the exchange of acetylacetonate methyl groups as this presents a four-site exchange problem, which requires six first-order rate constants to completely describe the system [11]. In addition, the relaxation times $T_2$ appear to be temperature dependent.

The changes in signal multiplicities in the temperature-dependent nmr spectra of the $Ti(acac)_2Cl(2,6\text{-}(^iC_3H_7)_2C_6H_3O)$ complex, and the assumption that –CH= group exchange occurs indicate, also, that the averaging set responsible for the permutation of nuclei is $A'_{13}$. Extending the arguments put forward previously [1], leads us to conclude that a twist mechanism may also be operative in the rearrangement phenomena observed in the 2,6-diisopropylphenoxy complex. The averaging set $A'_{13}$ predicts a ratio of unity for the rate of inversion to the rate of terminal group exchange in the AA ligands [12]. Unfortunately, the unavailability of the rate of terminal group exchange precludes an operational test for $A'_{13}$.

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