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Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ Complexes. 4. The *cis*-$M(AA)_2X_2$ System: $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$

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In a preceding paper [1] we reported the results of incorporating a diasterotopic isopropyl group at the terminal AA positions of complexes of the type *cis*-$M(AA)_2X_2$. It was argued, on permutational grounds, that the steric course of the configurational changes in these C_2-type complexes can be rationalized in terms of the A_5 averaging set [2]. Placement of the prochiral isopropyl group in the γ- or (3-) position of the acetylacetonate (acac) ring in a $M(AA)_2X_2$ complex can, in principle, provide an opportunity to study the environmental averaging of terminal A groups, and the inversion of the molecular configuration *independently*.

The present work reports on our investigations of the configurational changes taking place in the complex $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$ using the variable temperature nuclear magnetic resonance method.

Experimental

The synthesis and the handling of compounds were carried out under anhydrous nitrogen as described earlier [1].

The complex dichlorobis(3-isopropylacetylacetonato)titanium(IV) was prepared by the general procedure outlined earlier [1], refluxing the reaction mixture for 3.5 hr. Yield was 73%. Recrystallization from dichloromethane–hexane solutions gave a red solid. M.p. 170–172 °C (dec.) *Anal.* Calcd for $TiC_{16}H_{26}O_4Cl_2$: C, 47.90; H, 6.53. Found: C, 47.69; H, 6.58%.

In another preparation of this complex, titanium (IV) chloride and 3-isopropylacetylacetone (1:2 mol ratio) were mixed in dichloromethane. Standing at ambient temperature for *ca.* 2 hr, addition of hexane and cooling produces an orange solid. M.p. 102–104 °C (dec). The infrared spectrum (Nujol) of this orange solid exhibits a strong band at 1670 cm^{-1} and a medium–weak band at *ca.* 800 cm^{-1}, not expected for a complex containing a chelated 1,3-diketonate anion. The orange product is identified as the titanium(IV) chloride 1:2 adduct of the keto tautomer of 3-isopropylacetylacetone. Similar adducts have been isolated with acetylacetone and 3-methylacetylacetone with titanium tetrachloride [3].

Room-temperature and variable-temperature proton NMR spectra were recorded in dichloromethane solutions as described earlier [1]. Van Geet [4] equations were used to estimate the sample temperature (± 0.5°) from the CH_3OH chemical shifts.

The data were treated by a total lineshape (TLS) calculation by a method analogous to one described earlier [5]. The pertinent parameters are collected in Table I.

Arrhenius activation parameters were calculated from the slope and intercept of a linear least-squares plot of ln $1/2\tau$ *vs.* $10^3/T$. The entropy of activation, $\Delta S^{\neq}$, was obtained from the expression $\Delta S^{\neq} = R(\ln A - \ln RT/Nh) - R$.

TABLE I. Terminal Methyl PMR Lineshape Parameters and Values of τ for $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$.

Temp.,[b] °C	R[c]		$\delta\nu_e$,[d] Hz	Linewidths,[e] Hz						$\tau \times 10^2$, sec
	LF[f]	HF[f]		$W_{1/4}$		$W_{1/2}$		$W_{3/4}$		
				LF	HF	LF	HF	LF	HF	
–52.2	4.60	4.71	7.82	4.88	4.69	2.58	2.56	1.50	1.50	12
–49.8	3.51	3.65	7.65	–	–	2.92	2.86	1.68	1.67	9.7
–46.2	2.14	2.22	7.22	–	–	4.46	4.20	2.22	2.17	6.6
–42.6	1.41	1.43	6.33	–	–	–	–	3.68	3.33	4.7
–40.0	1.09	1.09	4.64	–	–	–	–	–	–	3.6
–38.9	1.01	1.02	2.94	–	–	–	–	–	–	3.2
–35.4	–		–	10.60		7.37		4.84		2.4
–33.5	–		–	8.79		5.39		3.27		1.9
–31.3	–		–	7.23		4.27		2.52		1.5
–27.3	–		–	5.32		3.09		1.82		1.1

[a] 0.300 *M* in dichloromethane. [b] Calculated using the Van Geet equation for methanol. [c] Ratio of the maximum amplitude to the central minimum. [d] Observed frequency separation. [e] Full line width at designated fraction of maximum amplitude. [f] LF = low field signal; HF = high field signal.

Results and Discussion

The room-temperature spectrum reveals a single terminal methyl resonance, which on cooling broadens and eventually splits into two equally-intense resonances below *ca.* –40 °C. At all accessible temperatures, a single isopropyl methyl doublet is observed on the 60-MHz instrument and at –80 °C on the 100-MHz instrument. This resonance is considerably broadened at low temperatures: width at half-height, $W_{1/2}$, is 0.8 Hz at room temperature and 3.0 Hz at –69.6 °C. The concentration dependence of the mean residence times, τ, is presented in Table II.

TABLE II. Concentration Dependence of Mean Residence Times for Terminal Group Exchange in $Ti(3\text{-}^{i}C_3H_7\text{-acac})_2Cl_2$ at Selected Temperatures.[a]

Temp., °C	τ, sec	
	0.300 *M*	0.150 *M*
–33.5	0.019	0.018
–35.4	0.024	0.024
–42.6	0.047	0.048
–46.2	0.066	0.067

[a] In dichloromethane solution.

Arrhenius and Eyring activation parameters are collected in Table III, and for comparison the corresponding values for the exchange process in $Ti(dik)_2X_2$ (dik = acac, dpm; X = halogen or pseudohalogen) complexes [6, 7]. The errors in the activation parameters for $Ti(3\text{-}^{i}C_3H_7\text{-acac})_2Cl_2$ represent the random scatter of the data points. Inasmuch as T_2 is temperature dependent, a reasonable uncertainty in this parameter may lead to systematic errors of the order of ±1 kcal/mol in the activation energy and ±4 eu in the activation entropy [8, 9].

Stereochemistry and Lability

Observation of two terminal methyl group resonances indicates that this complex adopts the *cis* geometry and is stereochemically nonrigid. Analogous observations were made by Thompson and coworkers [10] in a study of $Ti(3\text{-}CH_3\text{-acac})_2X_2$ (X = F, Cl, Br) complexes. Failure to observe two isopropyl methyl doublets could be a result of either a chemical shift degeneracy or a very rapid enantiomerization process still occurring at –70 °C. The concentration dependence data demonstrate that the environmental averaging process is independent of concentration and is first order.

Comparison of the kinetic data for terminal methyl group exchange of $Ti(3\text{-}^{i}C_3H_7\text{-acac})_2Cl_2$ with data (Table III) of other $Ti(dik)_2X_2$ complexes reveals no startling differences. The largest differences appear to be in the entropies of activation; however, since this parameter has the largest determinate error and probably contains more indeterminate errors, the differences may be of little validity [11]. The more interesting comparisons are amongst the $Ti(acac)_2Cl_2$, $Ti(3\text{-}^{i}C_3H_7\text{-acac})_2Cl_2$, and $Ti(dpm)_2Cl_2$ complexes, lability increasing in this order. Inasmuch as the same solvent was employed for the study of these three complexes, solvation differences are expected to be small. Placement of an inductive electron-donating alkyl group on the acetylacetonate ring would be expected to increase the electron density within the ring, and hence result in stronger Ti–O bonds. Should a bond-rupture mechanism be operative, the $Ti(dpm)_2Cl_2$ complex would be expected to be less labile (higher E_a) than the acetylacetonate analogue; similar arguments prevail for the $Ti(3\text{-}^{i}C_3H_7\text{-acac})_2Cl_2$ complex. However, the latter complex reveals a slightly lower E_a relative to that for $Ti(acac)_2Cl_2$. The $Ti(dpm)_2Cl_2$ complex shows no change in activation energy from that of the acetylacetonate analogue.

Somewhat enigmatic also is the expected slight increase in steric hindrance to the operation of a twist mechanism when the more bulky isopropyl or t-butyl groups are substituted onto the acetylacetonate framework. The experimental results for the $Ti(dik)_2Cl_2$ series indicate that the rates and energetics of the rearrangement process are not dependent, to any significant degree, on the nature of the β-diketonate ring. Even the *cis*-$Ti(hfac)_2Cl_2$ complex (hfac is the anion of hexafluoroacetylacetone) [7, 12] does not

TABLE III. Kinetic Data for Terminal Group Exchange in $Ti(dik)_2X_2$ Complexes.[a]

Compound	k_{298} (sec^{-1})	$\Delta H^{\neq}_{298}$ (kcal/mol)	$\Delta S^{\neq}_{298}$ (eu)	E_a (kcal/mol)	log A	Ref.
$Ti(acac)_2Cl_2$	6.7×10^2	10.7 ± 0.6	–9.7 ± 2.3	11.2 ± 0.6	11.03 ± 0.51	6
$Ti(acac)_2(NCO)_2$	1.1×10^3	10.5 ± 0.6	–9.3 ± 2.4	11.0 ± 0.6	11.08 ± 0.52	7
$Ti(3\text{-}^{i}C_3H_7\text{-acac})_2Cl_2$	1.9×10^3	9.8 ± 0.3	–10.4 ± 1.5	10.4 ± 0.3	10.94 ± 0.33	This work
$Ti(acac)_2Br_2$	2.3×10^3	11.0 ± 0.5	–6.2 ± 2.0	11.6 ± 0.4	11.85 ± 0.36	6
$Ti(dpm)_2Cl_2$	3.5×10^3	10.9 ± 0.4	–5.6 ± 1.5	11.4 ± 0.4	11.91 ± 0.33	7
$Ti(dpm)_2(NCO)_2$	6.7×10^3	9.4 ± 0.3	–9.5 ± 1.5	9.8 ± 0.3	11.04 ± 0.32	7
$Ti(acac)_2F_2$	1.6×10^4	11.1 ± 0.4	–2.2 ± 2.0	11.6 ± 0.5	12.70 ± 0.49	6

[a] In dichloromethane solution. [b] All errors are random errors estimated at the 95% confidence level.

exhibit the usual rate enhancement of *ca.* 10^4 observed for tris-chelates of Al(III) and Ga(III) on introduction of hexafluoroacetylacetonate ligands [13].

Permutational Considerations

Referring to the expected changes in signal multiplicities generated for the allowed averaging sets of a *cis*-$M(AA)_2X_2$ complex (see Table IV of ref. 2) our data can be interpreted in terms of the A_2, A_3, A_5 and A_6 averaging sets. Inasmuch as the related complexes [1] which possess the prochiral group at the terminal position of the AA chelate ring undergo exchange of terminal groups along with reversal of helicity, the present system is also expected to reverse its helicity (see below) during the exchange process. Therefore the A_2 and A_3 sets are eliminated since they provide no path for inversion of the molecular configuration. A_5 and A_6 need to be distinguished. The A_5 set predicts a ratio of rates of inversion to terminal group exchange of 2:1, while A_6 predicts a ratio of unity. For the $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$ complex, no splitting of the isopropyl methyl doublet was observed for a dichloromethane solution even at –80 °C on a 100-MHz instrument [14]. It is not unreasonable to expect smaller diastereotopic splittings for this complex compared to the $Ti(dibm)_2Cl_2$ analogue [1] inasmuch as the isopropyl methyl groups are further away from the metal and the chlorine atoms in the former complex. This would result in a lower temperature being necessary to observe any splitting in the $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$ complex relative to $Ti(dibm)_2Cl_2$ (T_c *ca.* –25 °C, ref. 1). As noted above, the isopropyl methyl doublet for $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$ broadens from a $W_{1/2}$ of 0.8 Hz at ambient temperature to 3.0 Hz at –70 °C in a dichloromethane solution. The acac methyl resonance of the related $Zr(acac)_2Cl_2$ complex in a dichloromethane solution broadens from a $W_{1/2}$ of 0.5 Hz at room temperature to *ca.* 1.2 Hz at –65 °C [6]. Thus, the broadening observed for the isopropyl methyl resonance of the complex $Ti(3\text{-}^iC_3H_7\text{-acac})_2Cl_2$ is probably real and appears to be greater than that expected for viscosity broadening in dichloromethane solutions. This broadening is therefore rationalized in terms of a greater rate of inversion as compared to the rate of terminal group exchange (ratio $>$ 1), thereby favouring the A_5 set over the A_6 averaging set.

This A_5 set also correlates with the A'_{13} set of a *cis*-$M(AA)_2XY$ in which the permutational degeneracy in A_5 is lifted [2]. As suggested earlier [1], the likely sole reaction pathways consistent with A_5 are identified as twist motions about the $C_3(i')$ and $C_3(i''')$ axes of the octahedral framework (see *e.g.* Table I of ref. 15). An implicit assumption here is that site interchange in *cis*-$M(AA)_2X_2$ complexes probably result from a single averaging set. Unfortunately true is the fact that a mixture of physical motions can also generate a mixture of averaging sets that may not be distinguishable from averaging sets operating individually.

Acknowledgments

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