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Reactions of Coordinated Molecules. 8. Geometrical Isomerization of Tris(acetyl(phenylacetyl)tetracarbonylmanganato)aluminum: an Unsymmetrical Metallo-β-diketonate Complex

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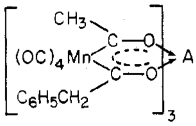
Received July 6, 1977

The intramolecular geometrical isomerization of the cis and trans isomers of the unsymmetrical tris-chelate metallo-β-diketonate complex [*cis*-$(OC)_4Mn(CH_3CO)(C_6H_5CH_2CO)]_3Al$ was followed as a function of time by ^1H NMR in CCl_4 solution at 16, 29, and 36 °C. The first-order rate constant for this isomerism at 298 K is $(0.76 \pm 0.04) \times 10^{-3}\ s^{-1}$, and the values of the activation parameters are $\Delta H^{\ddagger} = 30.2 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = 28.8 \pm 2.6$ eu. The equilibrium constant, defined by [cis]/[trans], was determined at 9, 15, 36, and 45 °C. The calculated ground-state thermodynamic parameters are $\Delta H° = -1.8 \pm 0.6$ kcal/mol, $\Delta S° = -9.0 \pm 2.1$ eu, and $\Delta G°_{298} = 0.89 \pm 0.03$ kcal/mol.

The geometrical isomerization of tris-chelate complexes containing unsymmetrical, β-diketonate ligands has been investigated extensively in recent years.[1,2] Although the elucidation of the mechanism of this isomerization is an exceedingly difficult and usually futile task, the observation of discrete geometrical isomers does confirm the essentially octahedral coordination of the chelating ligands.

In a previous paper of this series the preparation and molecular structure of the first metallocetylacetonate complex, [*cis*-$(OC)_4Mn(CH_3CO)_2]_3Al$, was reported.[3] This complex is a close structural analogue to tris(acetylacetonate)aluminum, $Al(acac)_3$, where the methine group of each acac ligand is replaced formally by the organometallic group, $Mn(CO)_4$. Several other tris-chelate complexes of aluminum and gallium containing a variety of metallo-β-diketonate ligands have been prepared.[4] Also, the preparation and molecular structure of the first metallo-β-diketone molecule were reported recently.[5]

In this paper we wish to substantiate the solution-phase structural similarity of the tris-chelate complexes which contain β-diketonate ligands to those complexes which contain metallo-β-diketonate ligands, since such a comparison of a closely analogous metallo-β-diketonate complex has been reported in the solid state.[3] This solution-phase structural similarity was established by demonstrating the geometrical isomerization of a tris-chelate complex having unsymmetrical metallo-β-diketonate ligands. By use of ^1H NMR spectroscopy, the cis–trans isomerization of tris(acetyl(phenylacetyl)tetracarbonylmanganato)aluminum, $Al(abtm)_3$ (**1**), was followed as a function of time in carbon tetrachloride solution at three temperatures. The values of the rate of isomerization and the activation parameters are consistent with an intramolecular rearrangement which may occur by a mechanism similar to that proposed for the geometrical isomerization of tris(1-phenyl-5-methylhexane-2,4-dionato)aluminum, $Al(pmhd)_3$,[6] although this comparison is highly tenuous. However, the interconversion of the optical isomers of complex **1** was not studied and such a comparison may be fortuitous. The trans to cis equilibrium constant was recorded at four temperatures and indicated a slightly negative $\Delta H°$ for the isomerization.



1, $Al(abtm)_3$

Experimental Section

Complex **1**, $Al(abtm)_3$, was prepared by a literature method[4] and was recrystallized from a hexane/methylene chloride (1:1) solution at −20 °C affording crystals of the trans isomer only. All kinetic and equilibrium data were recorded on a Joel MH-100 ^1H NMR spectrometer equipped with a Model JES-VI-3B variable-temperature unit using the resonances of the methyl substituent of the metallo-β-diketonate ligand as a probe to the isomerization and equilibrium.

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All spectra were recorded as dry, spectrograde CCl_4 solutions.

The crystalline trans isomer (25 mg) was dissolved in 0.4 mL of CCl_4 and the resulting yellow solution was filtered rapidly in air into a ^1H NMR tube. The rate data were collected beginning within 90 s of the dissolution of the sample by following the change in intensity, estimated by peak height times peak width at half-height, of the methyl resonances. Integration by this method gave values for the relative isomer population within 10% of the values obtained by instrumental integration and permitted a more rapid data collection. Kinetic data were collected over a minimum of 70% of the isomerization reaction prior to equilibration. Some paramagnetic decomposition appeared in the samples after prolonged periods although the infrared spectra of these solutions showed no change. Therefore, the equilibrium measurements were recorded from samples prepared under an argon atmosphere with dried, degassed CCl_4. The isomerization was studied at three temperatures (16, 29, 36 °C) over a 20 °C range, and all rate constants were determined in triplicate. Probe temperature was measured using a standard methanol calibration sample and temperature graph. These values were within 1.5° of the temperatures calculated from the Van Geet equations.

The equilibrium constant, K_{eq} = [cis]/[trans], was evaluated at four temperatures (9, 15, 36, 45 °C) over a 36 °C range which included the temperature range used for the collection of the kinetic data. The sample solutions were prepared under argon and were placed into septum-capped ^1H NMR tubes which had been flushed with argon. These samples were stored at 25 °C for 8 h and then were placed into a regulated, constant-temperature bath for 12 h at the desired temperature prior to recording the spectrum of the equilibrium mixture. The probe temperature was adjusted to the appropriate value, and peak areas were obtained by instrumental integration.

The kinetic data were treated by standard methods,[7] and the activation parameters were calculated from the Eyring equation for reactions performed in solution[8]

$$k_{\mathrm{soln}} = e\frac{kT}{h}e^{-E_a/RT}e^{\Delta S^{\ddagger}/R}$$

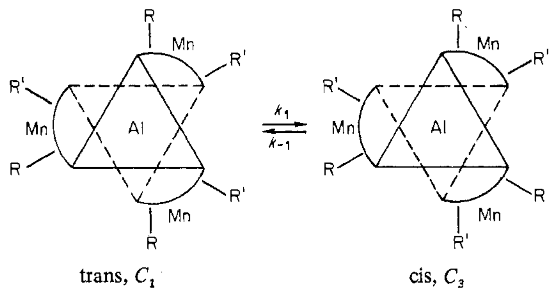
where E_a is the experimental activation energy and all values for the reported activation parameters are normalized to 298 K. The thermodynamic parameters were determined using the standard free

$$\Delta H^{\ddagger} = E_a - RT$$

energy equations, and all uncertainties were determined graphically from least-squares plots.

Results and Discussion

The two geometrical isomers of $Al(abtm)_3$ are shown below for the same optical configuration.



trans, C_1 cis, C_3

$R = CH_3$, $R' = C_6H_5CH_2$

Since both geometrical isomers are chiral, the prochiral[9] benzyl protons afford a complex multiplet which is of relatively low intensity in the ^1H NMR spectrum due to the limited solubility of $Al(abtm)_3$.[4] For this reason the methyl substituent was used as a probe to the isomerization. All three methyl groups of the cis isomer are equivalent (C_3 symmetry) and, therefore, will give a single resonance in the ^1H NMR spectrum. However, the three methyl groups of the trans isomer are nonequivalent (C_1 symmetry) and will afford, ideally, three distinct single resonances of equal intensity.

When a crystalline sample of $Al(abtm)_3$ is dissolved in CCl_4 and placed immediately into the ^1H NMR probe, the spectrum at expanded scale shows only three sharp resonances of nearly equal intensity for the methyl substituent. This set of resonances is centered at δ 2.60. Within 2 min at 36 °C, a sharp resonance begins to appear at δ 2.72 (12 Hz to lower field) concomitant with a decrease in intensity of the initial set of three resonances. These spectral changes indicate that a trans to cis isomerization is occurring and that the ^1H NMR resonance of the methyl group of the cis isomer is sufficiently separated from the resonances of the methyl group of the trans isomer that the relative concentration of each isomer could be determined directly from the experimental spectra. This is the second metallo-β-diketonate complex prepared at present where such a fortuitous separation of resonances occurs, thus facilitating the study of the geometrical isomerization.[13]

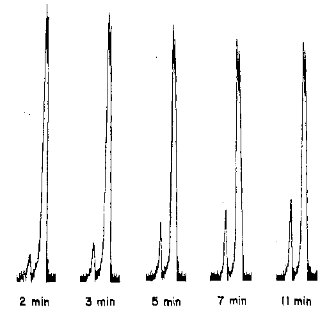


Figure 1. A partial set of ^1H NMR spectra of the methyl region of $Al(abtm)_3$ at 36 °C as an ca. 2.5×10^{-5} M solution in CCl_4 showing the appearance of the cis isomer at δ 2.72 concomitant with the disappearance of the trans isomer at δ 2.60 as a function of time.

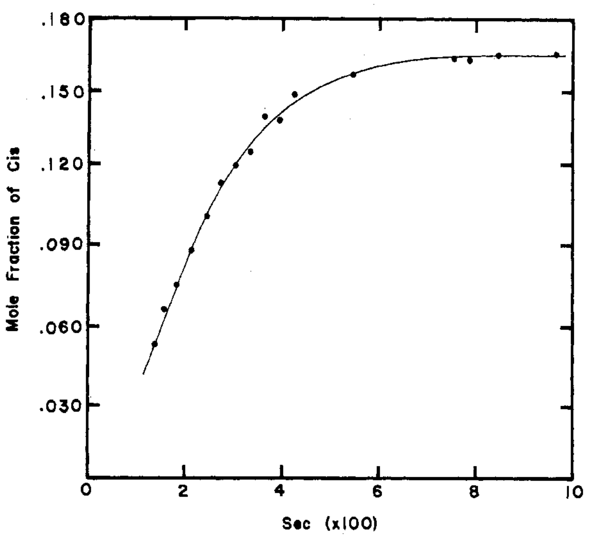


Figure 2. Increase in the mole fraction of the cis isomer of $Al(abtm)_3$ as a function of time in CCl_4 solution at 36 °C.

Figure 1 shows a partial ^1H NMR spectrum of $Al(abtm)_3$ as a function of time at 36 °C showing the appearance of the cis isomer along with the disappearance of the trans isomer. The set of resonances assigned to the methyl group of the trans isomer is observed as two single resonances of nearly equal intensity. The expanded-scale spectrum of these resonances has been reported previously.[4]

Figure 2 is a plot of the appearance of the cis isomer as its mole fraction vs. time for the isomerization at 36 °C. The equilibrium mixture is ca. 16% cis and 84% trans giving a value of 0.19 ± 0.01 for the trans to cis equilibrium constant at this temperature. Similar plots are obtained at 29 and 16 °C. However, the rate of isomerization at these lower temperatures is sufficiently slow that the appearance of trace paramagnetic impurities prevented the determination of the equilibrium constants.

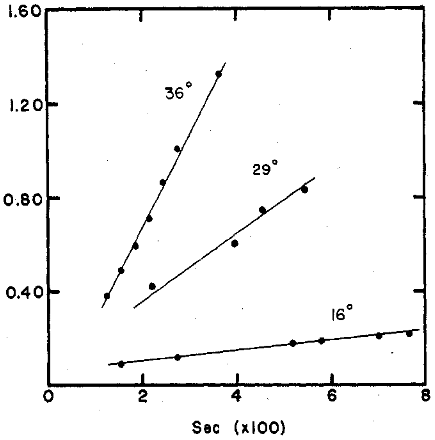


Figure 3. Logarithmic plots assuming first-order kinetics for the trans to cis isomerization of $Al(abtm)_3$ in CCl_4 solution at three temperatures. A is the mole fraction of cis at equilibrium and B is A minus the mole fraction of cis at time *t*.

The equilibrium constant was evaluated at four temperatures using sample solutions which were prepared under an argon atmosphere. The equilibrium data are shown below:

T, °C	K_{eq} ([cis]/[trans])	T, °C	K_{eq} ([cis]/[trans])
45	0.18 ± 0.01	15	0.24 ± 0.01
36	0.19 ± 0.01	9	0.26 ± 0.01

The calculated values of the ground-state thermodynamic parameters are $\Delta H° = -1.8 \pm 0.6$ kcal/mol, $\Delta S° = -9.0 \pm 2.1$ eu, and $\Delta G°_{298} = 0.89 \pm 0.03$ kcal/mol. The small negative value of $\Delta H°$ and the negative $\Delta S°$ value are consistent with the reported thermodynamic parameters for the geometrical isomerization (trans to cis) of several alkyl- and aryl-substituted nonmetallo tris(β-diketonate) complexes.[10]

The plot of the averaged rate data vs. time at each temperature assuming first-order kinetics involving an equilibrium is shown in Figure 3. Although the solubility of $Al(abtm)_3$ prevented an extensive dilution study, a twofold dilution of the sample concentration did not affect the rate of isomerization. Addition of the lithium salt of abtm to the ^1H NMR solution of $Al(abtm)_3$ did not alter either the spectrum or the isomerization. Also, all synthetic attempts to effect ligand exchange between $Al(abtm)_3$ and other $M(\beta\text{-diketonate})_3$ complexes in solution at 25 °C have been unsuccessful. Thus, the isomerization is assumed to be intramolecular. The values of the activation parameters are calculated from a standard Eyring plot. These values and the overall rate constants, $k_t = k_1 + k_{-1}$, for the isomerization are shown here: $10^3k_t = 0.16 \pm 0.02$ s^{-1} at 16 °C, 1.4 ± 0.1 s^{-1} at 29 °C, and 5.6 ± 0.9 s^{-1} at 36 °C; $E_a = 30.8 \pm 0.8$ kcal/mol, $\Delta H^{\ddagger} = 30.2 \pm 0.8$ kcal/mol, and $\Delta S^{\ddagger} = 28.8 \pm 2.6$ eu. The overall rate constant at 298 K is $(0.76 \pm 0.04) \times 10^{-3}$ s^{-1}, and the value of $\Delta G^{\ddagger}$ at 298 K is 21.6 ± 1.6 kcal/mol.

When comparing the geometrical isomerization of tris(β-diketonate) complexes to discern a common mechanism, it is very important to use only very similar complexes for the comparison. The isomerization parameters depend strongly upon the nature of the metal atom and the substituents of the chelate ring.[10] The most extensively studied complex which is also a close analogue to $Al(abtm)_3$ is $Al(pmhd)_3$. The only differences between these complexes are the $Mn(CO)_4$ substitution for the methine group and that $Al(pmhd)_3$ has benzyl and isopropyl substituents on the chelate ring whereas $Al(abtm)_3$ has benzyl and methyl substituents.

The detailed analysis of the geometrical isomerization of $Al(pmhd)_3$ in chlorobenzene solution has been reported.[6] Although a detailed comparison of this isomerism to that of $Al(abtm)_3$ is not warranted since the optical isomerization of $Al(abtm)_3$ was not studied, there are some intriguing similarities. The overall rate constant at 298 K of $Al(pmhd)_3$, 0.40×10^{-3} s^{-1},[11] is very similar to the value observed for $Al(abtm)_3$, $(0.76 \pm 0.04) \times 10^{-3}$ s^{-1}. Also, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the isomerization of $Al(abtm)_3$ agree well with the calculated values of the activation parameters of $Al(pmhd)_3$ undergoing geometrical isomerization via various bond-rupture mechanisms.

An interesting difference between the geometrical isomerism of $Al(abtm)_3$ and $Al(pmhd)_3$ or other alkyl- or aryl-substituted tris(β-diketonate) complexes is the reversal of isomer stability. For these complexes having nonmetallo ligands, the cis isomer is slightly more stable than the trans isomer.[10] The value of K_{eq} ([cis]/[trans]) for $Al(pmhd)_3$ is 0.40 ± 0.05 whereas the statistical value is 0.33. However, the value of $K_{eq}{}^{298°C}$ for $Al(abtm)_3$ is 0.22 ± 0.01 which indicates that the trans isomer has the lower free energy. This accounts for the isolation of only the trans isomer of $Al(abtm)_3$.[12] The thermodynamic preference of the trans isomer is observed in a number of trifluoroacetylacetonate complexes. The value of $\Delta H°$ for $Al(tfac)_3$ is essentially zero, 0.24 ± 0.19 kcal/mol, and the value of K_{eq} is 0.22. Since $Al(tfac)_3$ and $Al(abtm)_3$ have chelating ligands which are presumably much more electronegative than alkyl- or aryl-substituted β-diketonate ligands, this similarity in K_{eq} values may lend support to the dependence of isomer stability on electronic rather than steric factors.

Acknowledgment. We thank the Research Corporation, the University Research Council of Vanderbilt University, and the generous funding of the National Science Foundation, Grant No. 76-14304, for support of this research.

Registry No. **1**, trans,, 59839-85-9; **1**, cis,, 59839-96-2.

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