Direct Measurement of Enantiomerization of Labile Aluminium(III) β-Diketonates

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Summary Dynamic n.m.r. studies of tris-(2,6-dimethylheptane-3,5-dionato)aluminium(III), and bis(pentane-2,4-dionato)-(2,6-dimethylheptane-3,5-dionato)aluminium(III) give proof of the rapid enantiomerization of these complexes.

WE report dynamic n.m.r. studies of tris-(2,6-dimethylheptane-3,5-dionato)aluminium(III), $Al(dibm)_3$, and bis-(pentane-2,4-dionato)-(2,6-dimethylheptane-3,5-dionato)-aluminium(III), $Al(acac)_2(dibm)$.

The methyl proton resonance of the protonated form of the ligand, H(dibm), gives the expected simple spin-coupled doublet for the isopropyl groups [1·11 p.p.m. downfield from Me_4Si in CCl_4 J ($CH–CH_3$) 6·4 Hz]. This resonance in $Al(dibm)_3$, however, appears as a quartet (Figure 1) at ambient probe temperatures in every solvent we have used. The geminal methyls of the isopropyl groups in the complex are diastereotopic and anisochronous[1] at these temperatures (61·9 and 64·8 Hz downfield from Me_4Si at 60 MHz, respectively, 0·294 M in PhCl at 37°, both coupling constants 6·6 Hz).

Two sources of this splitting might be considered; (i) the existence of one or more rotamers in which the methyls are diastereotopic because of restricted rotation of the isopropyl group about the C-2–C-3 bond, or (ii) the total molecular dissymmetry which is centred at the aluminium.

Source (i) can be effectively ruled out since the spectrum of tris-(2,2,6,6-tetramethylheptane-3,5-dionato)aluminium(III), $Al(thd)_3$, in many solvents,[2,3] reveals a singlet at these temperatures. Also, the spectrum of 2,4,6-trimethylisopropylbenzene, in which the rotation of the isopropyl group about the sp^3–sp^2 bond is restricted,[4] shows no splitting of the isopropyl methyl doublet even at $-60°$.[4b] Source (ii) then remains as the only plausible cause of the spectral splitting. Other investigators have also recently attributed similar nonequivalences to molecular dissymmetry in six-coordinate Al^{III} and Fe^{II} complexes.

An increase in the temperature of the sample causes the individual components of the quartet to broaden and coalesce (Figure 1). Above 120° in chlorobenzene, a doublet is observed which sharpens as the temperature is raised further. The two low-field resonances have coalesced with one another and this can be regarded as reflecting the increased rate of the process:

$$CH_3(1)^{\delta}|\alpha> + CH_3(2)^{\lambda}|\alpha> \rightleftarrows CH_3(2)^{\delta}|\alpha> + CH_3(1)^{\lambda}|\alpha>$$

where (1) and (2) simply label methyl groups, the superscripts δ and λ designate the two diastereotopic environments, and $|\alpha>$ represents the spin function of the methine proton. A similar process causes collapse of the two high-field lines due to methyls in isopropyl groups with the opposite methine spin function. The most plausible cause for the exchange of the diastereotopic environments is the enantiomerization of the complex.† Thus, the dynamic n.m.r. of either of the coalescing pairs can yield direct kinetic information on the enantiomerization. The isopropyl group acts as a probe for measuring the average

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† Inversion of the methine carbon or exchange of methyl groups would not be expected to proceed, if at all, at rates fast enough to cause coalescence.

lifetime of the molecule in one enantiomeric form. Preliminary analysis of the low-field pair using the simplified Gutowsky–Holm equation[7] indicates an activation energy of 14·7 ± 0·5 kcal/mole and a free energy of activation at the coalescence temperature,‡ 120°, $\Delta G_c^{‡}$, of 21·8 kcal/mole. These values are unchanged on reducing the concentration of $Al(dibm)_3$ in PhCl, indicating that the reaction is unimolecular. The data were corrected for the very slight temperature dependence of the splitting due to non-exchange effects (*i.e.*, changes in solvation, temperature dependence of rotomer populations, *etc.*) evident in Figure 1.[9]

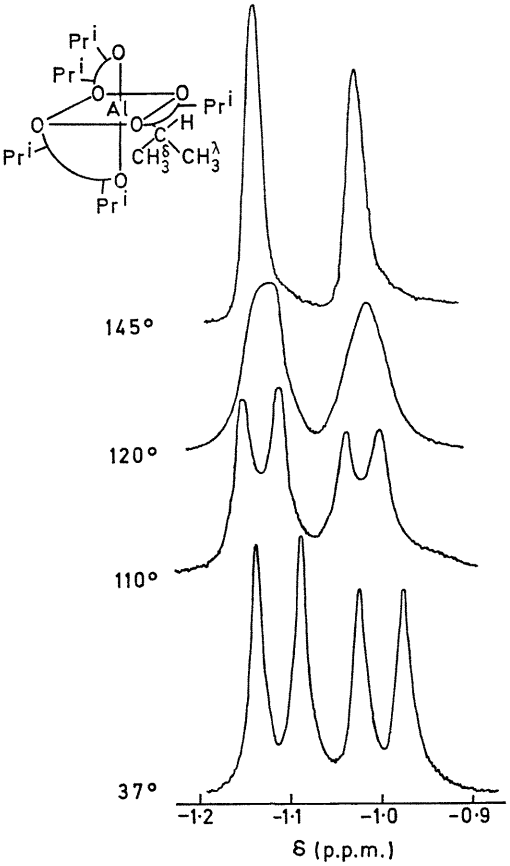

FIGURE 1. *The proton dynamic n.m.r. of the isopropyl methyl groups of* $Al(dibm)_3$ *in* PhCl *with temperature. Concentration,* 0·294 M; *frequency,* 60 *MHz.*

Mixed-ligand complexes of the formula $M(AA)_2(BB)$, where AA and BB are different symmetrical bidentate β-diketonate ligands, often reveal anisochronous resonances for the diastereotopic terminal substituents on the AA ligands.[3] LaMar has claimed to have obtained a lower limit to the rate of optical inversion of (4,7-dimethyl-1,10-phenanthroline)bis(acetylacetonato)cobalt(II) by studying the dynamic n.m.r. of the acac doublet.[10] However, the coalescence of such peaks need not necessarily be caused by an enantiomerization of the complex. A diastereotopomerization[8] which exchanges the environments of the methyl groups without inverting the complex could account for the phenomenon. Fortman and Sievers have depicted a possible mechanism for such a process.[2] In order to determine whether enantiomerization does in fact accompany diastereotopomerization in such complexes, we have investigated the $Al(acac)_2(dibm)$ complex.

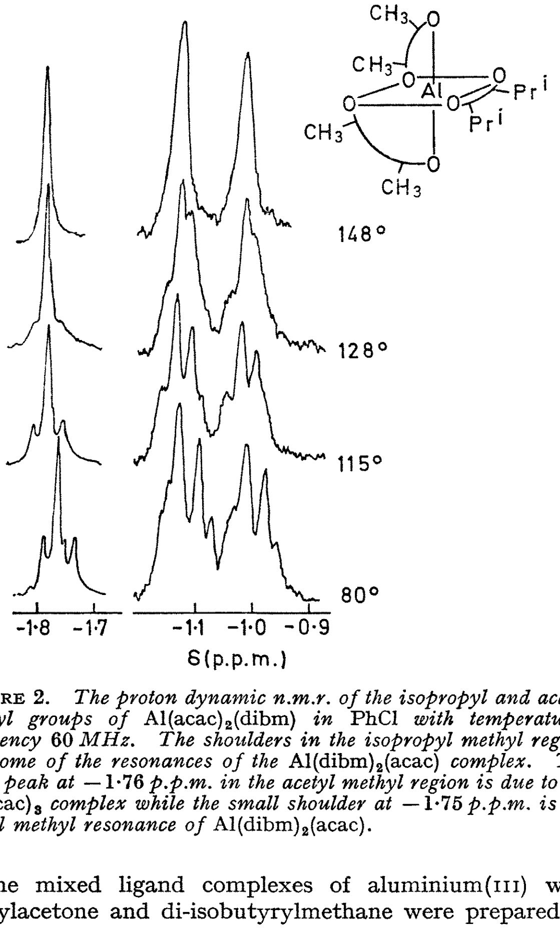

FIGURE 2. *The proton dynamic n.m.r. of the isopropyl and acetyl methyl groups of* $Al(acac)_2(dibm)$ *in* PhCl *with temperature: frequency* 60 *MHz. The shoulders in the isopropyl methyl region are some of the resonances of the* $Al(dibm)_2(acac)$ *complex. The large peak at* −1·76 *p.p.m. in the acetyl methyl region is due to the* $Al(acac)_3$ *complex while the small shoulder at* −1·75 *p.p.m. is the acetyl methyl resonance of* $Al(dibm)_2(acac)$.

The mixed ligand complexes of aluminium(III) with acetylacetone and di-isobutyrylmethane were prepared *in situ* by allowing chlorobenzene solutions of $Al(acac)_3$ and $Al(dibm)_3$ to react at *ca.* 75° for *ca.* 13 h in a sealed n.m.r. tube. The spectral assignments of all the peaks of the $Al(acac)_3$, $Al(dibm)_3$, $Al(acac)_2(dibm)$, and $Al(acac)(dibm)_2$ complexes in the acac methyl, dibm methyl, and ring CH regions were made with the aid of integration and by running the reaction with several different starting ratios of $Al(acac)_3$ and $Al(dibm)_3$. Heating for the above mentioned length of time produced an equilibrium mixture not significantly different from that at room temperature. The equilibrium constant for the reaction

$$Al(acac)_3 + Al(dibm)_3 \rightleftarrows Al(acac)_2(dibm) + Al(acac)(dibm)_2$$

was 5·0 ± 0·8, not far from the statistical value of 9. A solution with a solute mole ratio of 1·67 [$Al(acac)_3/Al(dibm)_3$] gave the best spectral resolution of the peaks of $Al(acac)_2(dibm)$ (Figure 2). As in $Al(dibm)_3$, the isopropyl methyl resonances appear as two doublets (62·1 Hz and 64·2 Hz downfield from Me_4Si at 60 MHz, both coupling constants 6·8 Hz; 37°, 46·4 mg total solute in 0·517 ml of solution) because of the dissymmetry of the complex. The acetyl methyl resonance is also split into the expected

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‡ The greater reliability of this activation parameter has recently been discussed (ref. 8).

doublet ($-1{\cdot}78$ and $-1{\cdot}73$ p.p.m.). As the temperature of the solution is raised, the latter doublet coalesces to a singlet while the dibm methyl quartet coalesces to a doublet (Figure 2). Thus, enantiomerization *is* occurring simultaneously with the acac methyl exchange. However, an analysis of the splitting data similar to that mentioned above indicates that, while the energy of activation for the methyl group environmental exchange is *ca.* 18 kcal/mole, a value in good agreement with the corrected value of *ca.* 19 kcal/mole for the similar exchange of Bu^t groups in $Al(thd)_2(acac)$,[9] the activation energy for the enantiomerization is lower, perhaps by as much as a factor of two. Furthermore, the Arrhenius plots for the two processes indicate that completely independent mechanisms may be involved. In the study of the dynamic n.m.r. of tris-(α-isopropyltropolonato)aluminium(III),[5b] the authors observe that enantiomerization, as detected by the coalescence of anisochronous isopropyl methyl doublets "appears to be faster than *cis–trans*-isomerization." These labile aluminium complexes may be undergoing the same rearrangement mechanisms.

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