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Tris(trifluoro and difluorobutane-2,4-dionato)aluminum(III) Complexes

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Eight tris(β-diketonate)aluminum(III) complexes having various fluoro and aryl substituents have been studied by nuclear magnetic resonance spectroscopy. The complexes are all nonrigid (fluxional) and their ^{19}F nuclear magnetic resonance spectra show four resonances in the nonexchanging region due to cis *and* trans *isomers. A variable high temperature ^{19}F NMR study of these complexes was done and activation parameters are calculated.*

Introduction

The classic ^{19}F NMR study of tris(1,1,1-trifluoropentanedionato) complexes of aluminum, gallium and indium [M(tfac)$_3$] established the utility of nuclear magnetic resonance spectroscopy as being a convenient method for the study of fluxional β-diketonate metal complexes [1, 2]. Their ^{19}F NMR spectral study showed that each complex gave four fluorine resonances which coalesce into one resonance as the temperature is increased. These resonances are attributed to the three nonequivalent trifluoromethyl fluorines of the *trans* isomer and to the equivalent trifluoromethyl fluorines of the *cis* isomer. We have recently done a ^{13}C NMR study on tris(trifluoropentanedionato)aluminum [3].

We have now prepared a series of fluxional tris-(1,1,1-trifluoro-4-substituted-butane-2,4-dionato)aluminum complexes where the 4-substituent is phenyl, 2′-thienyl, *p*-methylphenyl, *p*-fluorophenyl, *p*-methoxylphenyl and 2′-naphthyl. The tris(1,1-difluoro-4-(phenyl)butane-2,4-dionato)aluminum complex is also included in this study. The ^{19}F and ^{13}C NMR spectra of these β-diketonates are discussed in this report. Nuclear magnetic resonance spectroscopy has been shown to be a convenient method for the study of stereochemically nonrigid metal β-diketonate complexes [4, 5].

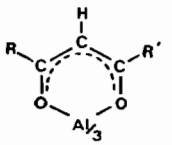

TABLE I. ^{19}F NMR Chemical Shift Data (ppm) for Al(RCOCHCOR′)$_3$ Complexes.

Compound (No.)	R	R′	Relative Chemical Shift (ppm)[a]			
1	CH_3	CF_3	76.35	76.44	76.47	76.48
2	C_6H_5	CF_3	76.03	76.09	76.14	76.21
3	C_6H_5	CHF_2	124.93	125.09	125.23	125.27
4	2′-C_4H_3S	CF_3	75.98	76.13	76.15	76.29
5	*p*-$CH_3C_6H_4$	CF_3	76.00	76.08	76.12	76.23
6	*p*-FC_6H_4	CF_3	[b]76.07	76.12	76.17	76.22
			[c]102.67	102.80	102.88	103.01
7	*p*-$CH_3OC_6H_4$	CF_3	75.89	75.98	76.02	76.12
8	2′-$C_{10}H_7$	CF_3	75.85	75.90	75.93	76.00

[a]Upfield from $CFCl_3$. [b]Chemical shift for CF_3 fluorines. [c]Chemical shift for *p*-fluorophenyl fluorines.

TABLE II. Exchange Parameters for $Al(RCOCHCOR')_3$ Complexes.

Compound (No.)	$\Delta\nu$ (Hz)	k_c (sec^{-1})	T_c (°C)	$\Delta G^{\ddagger}$ (kcal/mol)
1	6.92	5.4	106	20.3
2	6.88	15.3	128	21.5
3	14.65	32.5	133	21.2
4	12.41	27.6	115	20.3
5	8.79	19.5	105	20.1
6(CF_3)	6.02	13.4	113	20.8
6(*p*-F)	13.67	30.4	138	21.5
7	9.12	20.3	97	19.6
8	5.45	12.1	104	20.4

Experimental

Preparation of the β-Diketones

The β-diketones ($RCOCH_2COCF_3$) with R as methyl and 2'-thienyl were obtained from the commercial sources. Other trifluoromethy β-diketones were prepared by Claisen condensation of the methyl ketone ($RCOCH_3$) and ethyl trifluoroacetate ($CF_3COOC_2H_5$), catalyzed by sodium methoxide. The difluoromethy-β-diketone was prepared by a similar condensation of acetophenone and ethyl difluoroacetate.

Preparation of the Complexes

9 mmol of β-diketone was added to the solution of 3 mmol of aluminium nitrate in 50 ml abs. alcohol. The pH of the solution was raised to 5 by adding conc. NH_3. The solution was then filtered and cooled in an ice-bath for one hour. The solid was filtered and washed with ice-cold abs. alcohol. The solutions were kept in the refrigerator for crystallization for 24 hours when R = *p*-methylphenyl and *p*-methoxyphenyl and for four days when R = CH_3 and *p*-fluorophenyl groups.

Nuclear Magnetic Resonance Spectral Measurements

NMR spectra were taken on a JEOL FX60Q NMR Spectrometer. ^{13}C NMR spectra were run in deuteriochloroform using TMS as an internal standard. ^{19}F NMR spectra were run in 1,1,2,2-tetrachlorethane d_2 with $CFCl_3$ used as an internal standard. Variable temperature spectra (^{19}F NMR) were run over a 50 Hz sweep width with a pulse width of 10 us using 8 K data points.

Results and Discussion

The ^{19}F NMR spectra of all complexes taken at ambient temperatures gave four resonances indicating the presence of *cis* and *trans* isomers for each complex. The *cis* isomer having a C_3 axis of rotation show all fluorines to be equivalent; whereas, in the *trans* isomer this axis of symmetry is absent and the three fluoro groups are nonequivalent. In Table I is presented the chemical shifts of the four nonequivalent resonances (ppm) for each complex in the nonexchanging region (33 °C). Table I includes the parent compound $Al(CH_3COCHCOCF_3)_3$ (No. 1) which was originally studied by ^{19}F NMR by Fay and Piper [2]. Also included in Table I are the fluorine resonances of the *p*-fluoro group of $Al(p\text{-}FC_6H_4COCHCOCF_3)_3$. All four resonances due to the CF_3-fluorines occur in range of 8–14 Hz over the 500 Hz sweep width. Both the CHF_2-fluorine (No. 3) and the *p*-fluorophenyl fluorine resonances (No. 6) occur over *ca.* 20 Hz range. The least intense resonance is assigned to the *cis*-isomer and the three resonances of larger and about equal intensity are due to the *trans* isomers. These data show the *cis–trans* equilibrium to favor the *trans* isomer with about 15–20% *cis* isomer. In most cases the low field fluoromethyl resonance is of low intensity (*cis* isomer) except for complexes No. 1 and 3. The CF_3, *p*-fluoro and CHF_2 fluorine resonances of all compounds are *ca.* 76, 103 and 125 ppm upfield from $CFCl_3$, respectively.

As the temperature is increased the four ^{19}F NMR resonances coalesce into one peak. Table II shows the coalescence temperature, chemical shift difference ($\Delta\nu$), exchange rate (k_c) and the free energy of activation ($\Delta G^{\ddagger}$). The chemical shift difference in the nonexchanging region was taken as the average separation in Hertz between the low field resonance and the other three resonances at higher fields [2]. From this data the rate constants at the coalescence temperatures are obtained (eqn. 1) and the free energy of activation is calculated from eqn. 2 [6].

$$k_c = \frac{\pi(\Delta\nu)}{\sqrt{2}} \quad (1)$$

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

The stereochemical barrier is *ca.* 21 kcal for all the complexes. While the mechanism for this intra-

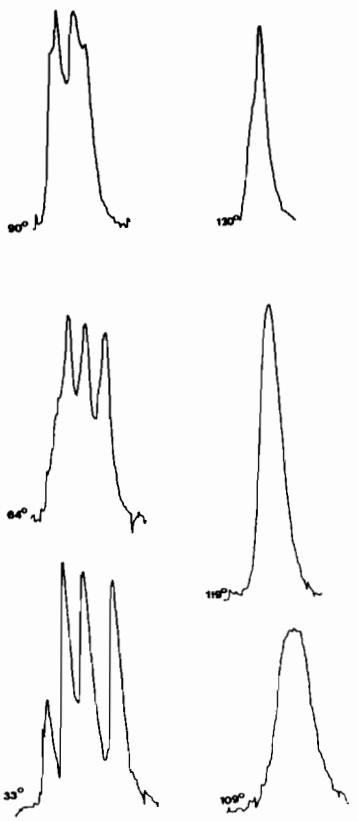

Fig. 1. Temperature dependence of the trifluoromethyl region of the ^{19}F NMR spectra for $Al(C_6H_5COCHCOCF_3)_3$. Relative to the low field *cis* resonance the resonances occur at 0.00, 3.42, 6.47 and 10.74 Hz at 33 °C. The small shoulder at 130 °C is due to decomposition of the complex.

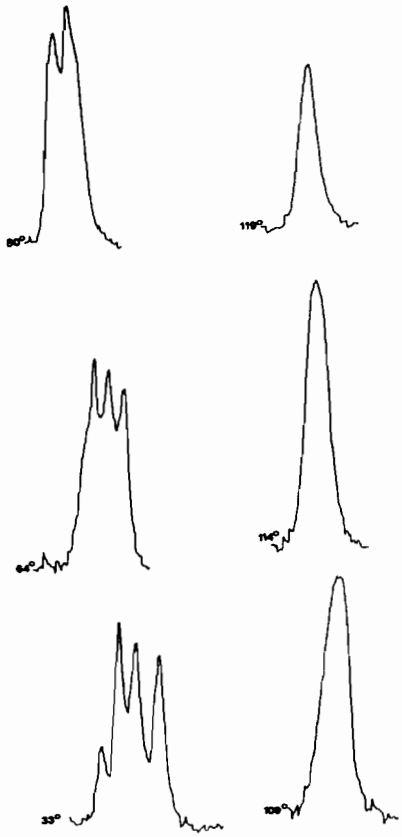

Fig 2. Temperature dependence of the trifluoromethyl region of the ^{19}F NMR spectra for $Al(p\text{-}FC_6H_4COCHCOCF_3)_3$. Relative to the low field *cis* resonance the resonances occur at 0.00, 3.05, 5.74 and 9.28 Hz at 33 °C.

molecular rearrangement is unknown, Fay and Piper have cited evidence in favor of a one-bond rupture mechanism *versus* a trigonal twist mechanism to account for the racemization and isomerization of the two delta and lambda confirmations for each *cis* and *trans* isomer of $Al(tfac)_3$ [2]. Our present data for $Al(tfac)_3$ taken in $C_2Cl_4D_2$ and our previously reported ^{13}C NMR data of $Al(tfac)_3$ [3] agree with the coalescence temperature (103 °C) and free energy of activation (19.6 kcal) taken in $CDCl_3$ by Fay and Piper [2]. A detailed topological analysis of β-diketonates with fluoro substituents suggest a bond rupture mechanism for complexes of this type through a square-pyramidal intermediate. This bond rupture is thought to take place at the CF_3 end of the bidentate ligand [7]. Studies of stereochemical nonrigid tristropolonato complexes of aluminum and gallium have shown a smaller stereochemical barrier and a lower coalescence temperature than their β-diketonate or trifluoro-β-diketonate complexes [8]. Here a rhombic twist mechanism is believed to be the most likely pathway for rearrangement [7]. In view of the evidence cited above the smaller coalescence temperature (104 °C) of the bulky 2-naphthyl substituents (No. 8) it is not too surprising when a bond rupture mechanism is considered to be the sole pathway as compared to twist mechanisms.

Figures 1 and 2 shows the temperature dependence of the methyl fluorines region of the ^{19}F NMR spectra of $Al(C_6H_5COCHCOCF_3)_3$ and $Al(p\text{-}FC_6H_4COCHCOCF_3)_3$ respectively and Fig. 3 shows the temperature dependence of the *p*-fluoro fluorine in the latter compound (No. 6). The free energies of activation in Table II indicates that the CF_3 and *p*-F moieties of complex No. 6 are exchanging at the same rate.

At 30 °C the ^{13}C NMR of these complexes all showed splitting or line broading due to the *cis–trans* isomers for each respective carbon atom. Spin-coupling with fluorine and splitting (or line broading) was also observed for the $CF_3(CHF_2)$, CH, and $F_3C–C^*–O$ ($F_2HC–C^*–O$) carbons. No detectable line broading was observed for the *p*-methyl (No. 5) and *p*-methoxy carbons (No. 7). The aryl substituents all gave R–C–O carbon resonances at high field

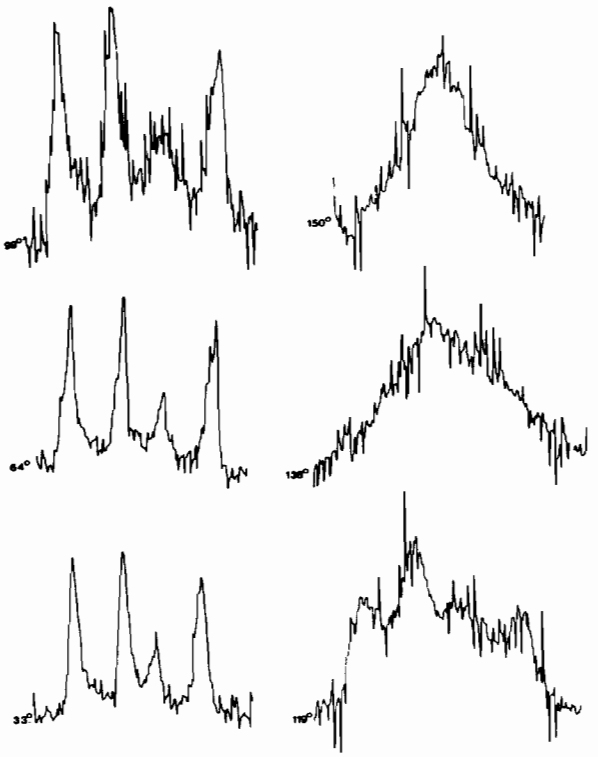

Fig. 3. Temperature dependence of the *para*-fluorophenyl region of the ^{19}F NMR spectra for $Al(p\text{-}FC_6H_4COCH\text{-}COCF_3)_3$. Relative to the low field *trans* resonance the resonances occur at 0.00, 8.06, 12.57 and 20.38 Hz at 33 °C.

(*ca.* 190 ppm) as compared to the parent (No. 1) compound (*ca.* 201 ppm) [3]. The $F_3C\text{–}C^*\text{–}O$ carbons are all more shielded (*ca.* 171 ppm) than those in $Al(acac)_3$ [9]. The CF_3 group has been suggested to give an increase in the quasi-aromatic character of the β-diketonate ring [10]. A similar shielding trend is seen in the methine carbon resonance in these complexes (*ca.* 93 ppm) as compared to methine carbon in $Al(acac)_3$ (101.0 ppm) [9].

The data reported herein gives further evidence that nonrigid (fluxional) molecules containing substituted β-diketonate ligands can also be followed by ^{19}F NMR spectroscopy. Exchange parameters by ^{13}C NMR spectroscopy may not be conveniently obtained as all of the aluminum complexes showed some decomposition when kept at or above temperatures of 140 °C for 3 to 4 hours. Reproducible ^{13}C NMR spectra usually required 3000 to 8000 transients (PR time of 1.8 sec). The data reported herein compliments that found by ^{19}F NMR for $Al(tfac)_3$ [2].

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