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Proton Magnetic Resonance Studies of Ligand-Exchange Equilibria for Some Dihalo- and Diethoxybis(β-diketonato)titanium(IV) Complexes[1]

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Dihalo- and diethoxybis(β-diketonato)titanium(IV) complexes undergo rapid ligand-exchange reactions which exchange both monodentate (eq 1) and bidentate β-diketonate (eq 2) ligands: (1) $Ti(acac)_2X_2 + Ti(acac)_2Y_2 \rightleftarrows 2Ti(acac)_2XY$, where $X \neq Y = F, Cl, Br$, or OEt; (2) $Ti(dik)_2X_2 + Ti(dik')_2X_2 \rightleftarrows 2Ti(dik)(dik')X_2$, where X = F or OEt, and dik and dik' represent distinguishable diketonate ligands. Equilibrium constants (*K*) for these reactions in $CDCl_3$ (CH_2Cl_2) solution were determined by proton magnetic resonance (pmr) spectroscopy. For exchange of halogen atoms (eq 1), *K* is close to the statistical value of 4, but for F–OEt exchange, *K* exceeds the statistical value by $\sim 10^2$. *K* values for diketonate exchange (eq 2) are close to the statistical value when dik and dik' contain the same number of CF_3 substituents. However, *K* is 2–6 times the statistical value when dik and dik' differ by one CF_3 group, and $\sim 10^2$–10^3 times the statistical value when dik and dik' differ by two CF_3 groups. Deviations from random scrambling of diketonate ligands are discussed in terms of an electrostatic model. The temperature dependence of *K* for the $Ti(C_6H_5COCHCOCF_3)_2F_2$–$Ti(t\text{-}C_4H_9\text{-}COCHCO\text{-}t\text{-}C_4H_9)_2F_2$ system indicates that both enthalpy and entropy effects contribute to the nonstatistical distribution of ligands ($\Delta H = -0.50 \pm 0.27$ kcal/mol; $\Delta S = 4.9 \pm 0.8$ eu). Several of the $Ti(dik)_2F_2$ and $Ti(dik)_2(OEt)_2$ complexes are new compounds. Low-temperature pmr spectra show that $Ti(acac)_2F(OEt)$ exists in solution as the cis isomer.

Introduction

Previous papers from this laboratory have described the synthesis, properties, stereochemistry, and configurational rearrangements of dihalobis(β-diketonato)titanium(IV) complexes $Ti(dik)_2X_2$.[2-5] These compounds and the corresponding dialkoxybis(acetylacetonato) complexes $Ti(acac)_2(OR)_2$[6] exist in solution as stereochemically nonrigid cis octahedral isomers which rearrange *via* an intramolecular mechanism. In addition, the $Ti(dik)_2X_2$ and $Ti(dik)_2(OR)_2$ complexes undergo intermolecular ligand-exchange reactions (redistribution reactions) which scramble both monodentate and bidentate ligands.[1]

In view of continued interest in redistribution reactions[7-12] and the factors which determine the position of ligand-exchange equilibria, we report herein the results of our proton magnetic resonance (pmr) studies of ligand-exchange equilibria for the systems described by eq 1 and 2, where

$$Ti(acac)_2X_2 + Ti(acac)_2Y_2 \rightleftarrows 2Ti(acac)_2XY \qquad (1)$$

$$Ti(dik)_2X_2 + Ti(dik')_2X_2 \rightleftarrows 2Ti(dik)(dik')X_2 \qquad (2)$$

$X \neq Y = F, Cl, Br$, or OEt in eq 1; and X = F or OEt and dik ≠ dik' = acac, bzac, bzbz, dpm, tfac, bztf, thtf, or hfac in eq 2.[13] Several of the $Ti(dik)_2F_2$ and $Ti(dik)_2(OEt)_2$ complexes have been prepared for the first time.

Experimental Section

Reagents and Solvents. Titanium(IV) ethoxide (K & K Laboratories, Inc.) was vaccum distilled (100–105° ($\sim 10^{-3}$ Torr)) to give a colorless liquid. Titanium(IV) fluoride (K & K), benzoyltrifluoroacetone (4,4,4-trifluoro-1-phenyl-1,3-butanedione), and thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) (Eastman Organic Chemicals) were used without further purification. Dipivaloylmethane was prepared by the method of Adams and Hauser.[14] Trifluoroacetylacetone was synthesized by Claisen condensation of ethyl trifluoroacetate and acetone[15] and was distilled before use (bp 106.5–107°). Hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) obtained commercially (Columbia Organic Chemicals Co., Inc.) was quite impure; it was purified by conversion to hexafluoroacetylacetone dihydrate[16] (*vide infra*). $Ti(acac)_2Cl_2$ and $Ti(acac)_2Br_2$ were prepared according to published procedures.[2]

Solvents were dried by refluxing over an appropriate drying agent for at least 12 hr and distilling therefrom. Diethyl ether, toluene, and hexane were dried over lithium aluminum hydride; dichloromethane, and deuteriochloroform were dried over calcium hydride.

Purification of Hexafluoroacetylacetone. The impure diketone was treated with an equal volume of water which contained 1 drop of dilute NaOH. The mixture warmed and soon crystals of hexafluoroacetylacetone dihydrate formed at the water–diketone interface. The mixture was allowed to stand in the hood until the water and volatile impurities evaporated. The resulting solid, white cake of the dihydrate (174 g) was added to a mixture of toluene (~250 ml) and P_4O_{10} (100 g), and the mixture was shaken with periodic cooling until evolution of heat subsided. To complete the dehydration, the mixture was allowed to reflux for 12 hr, and then the fraction boiling below 73° was collected. This fraction was redistilled from a fresh portion of P_4O_{10} (50 g); 80 ml of hexafluoroacetylacetone was collected at 67–68° (80% yield based on the weight of the dihydrate).

Difluorobis(β-diketonato)titanium(IV) Complexes. The synthesis of $Ti(acac)_2F_2$, $Ti(bzac)_2F_2$, and $Ti(bzbz)_2F_2$ has been described previously.[2,3] Several new $Ti(dik)_2F_2$ complexes (Table I) were prepared by reaction, under dry nitrogen, of titanium(IV) fluoride with the appropriate β-diketone (1:2.1 molar ratio) in refluxing dichloromethane. Reaction times were 0.5 hr for dik = dpm, bztf, or thtf and 12–15 hr for dik = tfac or hfac. In each case a substantial amount of a white residue (unreacted TiF_4 and inert impurities) was separated from the dichloromethane solution before the product was isolated. $Ti(tfac)_2F_2$, $Ti(bztf)_2F_2$, and

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[1] Presented in part before the Division of Inorganic Chemistry, 154th National Meeting, American Chemical Society, Chicago, Ill., Sept. 1967.

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[13] The following ligand abbreviations are used throughout: acac, $CH_3COCHCOCH_3$ (acetylacetonate); bzac, $C_6H_5COCHCOCH_3$ (benzoylacetonate); bzbz, $C_6H_5COCHCOC_6H_5$ (dibenzoylmethanate); dpm, $t\text{-}C_4H_9COCHCO\text{-}t\text{-}C_4H_9$ (dipivaloylmethanate); tfac, $CF_3COCHCOCH_3$ (trifluoroacetylacetonate); bztf, $C_6H_5COCHCOCF_3$ (benzoyltrifluoroacetonate); thtf, $C_4H_3SCOCHCOCF_3$ (thenoyltrifluoroacetonate); hfac, $CF_3COCHCOCF_3$ (hexafluoroacetylacetonate); OEt, OC_2H_5 (ethoxide).

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Table I. Analytical Data, Melting Points, and Pmr Data for Difluoro- and Diethoxybis(β-diketonato)titanium(IV) Complexes

		% calcd		% found		Pmr chem shifts in $CDCl_3$[d]			
Compd	Mp, °C	C	H	C	H	$-CH_3$	$-CH=$	$-CH_3(OEt)$	$-CH_2(OEt)$
$Ti(acac)_2F_2$	165–166					−2.11	−5.87		
$Ti(bzac)_2F_2$	196–199					−2.23	−6.54		
$Ti(bzbz)_2F_2$	204–206						−7.18[e]		
$Ti(dpm)_2F_2$	142–144	58.40	8.47	58.60	8.50	−1.17	−6.07		
$Ti(tfac)_2F_2$[a]	121–123	30.63	2.06	30.75	2.21	−2.38	−6.32		
$Ti(bztf)_2F_2$	150–154	46.53	2.34	46.69	2.39		−6.95		
$Ti(thtf)_2F_2$	170–173	36.38	1.53	36.58	1.68		−6.73[e]		
$Ti(hfac)_2F_2$	39–41	24.02	0.40	22.34	0.34		−6.75		
$Ti(acac)_2(OEt)_2$	49–52[c]					−1.99	−5.54	−1.20	−4.45
$Ti(tfac)_2(OEt)_2$[b]	44–47	37.85	4.08	37.60	3.94	−2.20	−5.97	−1.23	−4.50
$Ti(hfac)_2(OEt)_2$	−13 to −11	30.45	2.19	30.58	2.07		−6.38	−1.29	−4.58

[a] Calcd for $Ti(C_5H_4F_3O_2)_2F_2$: F, 38.77; Ti, 12.22. Found: F, 38.54; Ti, 12.56. [b] Calcd for $Ti(C_5H_4F_3O_2)_2(OC_2H_5)_2$: F, 25.67; Ti, 10.78. Found: F, 25.42; Ti, 10.88. [c] Lit.[17] mp 48–52°. [d] Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). Concentration is 10 g/100 ml unless otherwise noted. Temperature is ~39°. [e] Concentration is 6 g/100 ml.

$Ti(thtf)_2F_2$ were isolated in 40–50% yields by reducing the volume of the solution, adding hexane, and allowing ~12 hr for crystallization. This procedure gave an oil in the case of $Ti(dpm)_2F_2$; consequently the dichloromethane was pumped off entirely and the residue was recrystallized from benzene–hexane (yield 53%). The resulting crystals contained dichloromethane, even after drying *in vacuo*; dichloromethane was removed by sublimation (95° (~10^{-3} Torr)). In the preparation of $Ti(hfac)_2F_2$ it was necessary to first remove HF from commercial samples of TiF_4 by heating *in vacuo* at ~130° for 12 hr; otherwise, negligible yields were obtained. $Ti(hfac)_2F_2$ was isolated by pumping off the dichloromethane solvent and unreacted hexafluoroacetylacetone. The resulting low-melting, crystalline mass was purified by vacuum distillation (58–62° (5 × 10^{-2} Torr)); yield 16%.

The $Ti(dik)_2F_2$ complexes are yellow and are, in general, moderately sensitive to hydrolysis. $Ti(hfac)_2F_2$ is extremely moisture sensitive, which may account for the low carbon analysis. Analytical data and physical properties are presented in Table I.

Diethoxybis(β-diketonato)titanium(IV) Complexes. $Ti(acac)_2(OEt)_2$ was prepared by reaction of titanium(IV) ethoxide and acetylacetone (1:2 molar ratio) as described by Yamamoto and Kambara[17] and was purified by recrystallization (three times) from diethyl ether at −28° (freezer). The new complexes $Ti(tfac)_2(OEt)_2$ and $Ti(hfac)_2(OEt)_2$ were synthesized in quantitative yield by the same procedure. $Ti(tfac)_2(OEt)_2$ was recrystallized from diethyl ether at −28° and $Ti(hfac)_2(OEt)_2$, which is a colorless liquid at room temperature, was purified by vacuum distillation (55° (~10^{-3} Torr)). Analytical data and physical properties are given in Table I.

Nmr Spectra and the Determination of Equilibrium Constants. Equilibrium concentrations were determined from the ring proton (-CH=) region of pmr spectra. Spectra were recorded with a Varian A-60 or A-60A spectrometer equipped with a Varian Model C-1024 time-averaging computer (CAT) to enhance the signal-to-noise ratio. In general, the ring proton region was scanned 20–50 times before the averaged spectrum was printed, and this process was repeated 2–3 times for each equilibrium mixture. Integrated intensities were measured with a planimeter. Care was taken to keep the radiofrequency power level below saturation. Probe temperatures were determined from the temperature-dependent chemical shift between the nonequivalent protons of ethylene glycol or methanol.[18]

The solutions used for determination of the equilibrium constants were equimolar mixtures of the two parent complexes in deuteriochloroform or dichloromethane; unless otherwise noted, the total complex concentration was 0.32 *M*. Solutions were prepared under dry nitrogen in a glove bag and transferred to nmr tubes, and the tubes were sealed with a flame. Because equilibrium is attained rapidly at room temperature (within minutes), solutions could be equilibrated in the probe of the nmr spectrometer.

Results and Discussion

Exchange of Monodentate Ligands. Pmr spectra for a solution containing equimolar amounts of $Ti(acac)_2F_2$ and $Ti(acac)_2Br_2$ are presented in Figure 1(a). The resonance lines at lowest and highest field may be assigned to $Ti(acac)_2Br_2$ and $Ti(acac)_2F_2$, respectively, by reference to spectra of solutions of the pure parent complexes (Table II), while the resonances at intermediate field may be attributed to the mixed-ligand complex $Ti(acac)_2FBr$. Only a single ring proton resonance and a single methyl resonance are observed for each compound in the mixture because intramolecular rearrangement is fast on the pmr time scale at ambient probe temperature.[2] The intermolecular ligand exchange $Ti(acac)_2F_2 + Ti(acac)_2Br_2 \rightleftarrows 2Ti(acac)_2FBr$, although slow on the pmr time scale, is fast on the laboratory time scale; a spectrum taken immediately after dissolution of the parent complexes indicates that equilibrium is attained in less than 1 min at room temperature.

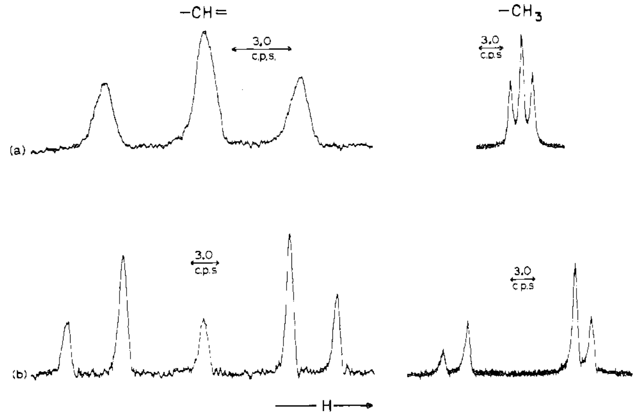

Figure 1. Ring proton (-CH=) and methyl regions of pmr spectra of (a) 0.158 *M* $Ti(acac)_2F_2$ + 0.158 *M* $Ti(acac)_2Br_2$ and (b) 0.158 *M* $Ti(acac)_2F_2$ + 0.158 *M* $Ti(tfac)_2F_2$ in dichloromethane solution at 31°. The -CH= regions were scanned 22 times using a CAT. Assignments (-CH= and $-CH_3$, in order of increasing field): (a) $Ti(acac)_2Br_2$, $Ti(acac)_2FBr$, $Ti(acac)_2F_2$; (b) $Ti(tfac)_2F_2$, Ti(*tfac*)(acac)F_2, Ti(tfac)(*acac*)F_2, $Ti(acac)_2F_2$. The dashed peak is a solvent spinning side band.

Similar results were obtained for $Ti(acac)_2F_2$–$Ti(acac)_2Cl_2$, $Ti(acac)_2F_2$–$Ti(acac)_2(OEt)_2$, and $Ti(acac)_2Cl_2$–$Ti(acac)_2Br_2$ mixtures, although resolution of the spectrum was poor in the latter case. As is shown in Table II, chemical shifts for the mixed-ligand complexes $Ti(acac)_2XY$ are intermediate between those for the $Ti(acac)_2X_2$ and $Ti(acac)_2Y_2$ parents; chemical shifts for the parent complexes are essentially unchanged (±0.02 ppm) on going from a pure solution to the equilibrium mixture. Because the ring proton resonances are better resolved than the methyl resonances (see Figure 1), the former were used in the determination of equilibrium constants.

Equilibrium constants for the reaction $Ti(acac)_2X_2$ +

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Table II. Chemical Shift Data for Parent $Ti(acac)_2X_2$ and Mixed-Ligand $Ti(acac)_2XY$ Complexes in $CDCl_3$ Solution[a]

Compd	$-CH_3$	$-CH=$	$-CH_3$- (OEt)	$-CH_2$- (OEt)
$Ti(acac)_2F_2$	−2.11	−5.87		
$Ti(acac)_2Cl_2$	−2.17	−6.00		
$Ti(acac)_2Br_2$	−2.16	−6.01		
$Ti(acac)_2(OEt)_2$	−1.99	−5.54	−1.20	−4.45
$Ti(acac)_2FCl$	−2.14	−5.94		
$Ti(acac)_2FBr^b$	−2.14	−5.94		
$Ti(acac)_2ClBr^b$	−2.17	−6.01		
$Ti(acac)_2F(OEt)$	−2.04	−5.67	−1.26	−4.53

[a] Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). Temperature is ~37°. Data for $Ti(acac)_2X_2$ refer to pure solutions: 10.0 g/100 ml for X = F, Cl, OEt; 3.5 g/100 ml for X = Br. Data for $Ti(acac)_2XY$ refer to equimolar equilibrium mixtures of $Ti(acac)_2X_2$ and $Ti(acac)_2Y_2$; total solute concentration is 0.32 *M* unless indicated otherwise. [b] Total solute concentration is 0.24 *M*.

Table III. Equilibrium Constants for the Reaction $Ti(acac)_2X_2 + Ti(acac)_2Y_2 \rightleftarrows 2Ti(acac)_2XY$

X	Y	$K(CDCl_3)^a$	$K(CH_2Cl_2)^a$
F	Cl	2.9	3.7
F	Br	2.5^b	2.9^b
Cl	Br	$\sim 4^{b,c}$	$\sim 4^{b,c}$
F	OEt	9×10^2	8×10^2

[a] At ~37°. The probable uncertainty in the equilibrium constants is ~±10%. Total solute concentration is 0.32 *M* unless indicated otherwise. [b] Total solute concentration is 0.24 *M*. [c] Resolution of resonance lines is too poor for quantitative measurement, but signal peak heights indicate that *K* is near the statistical value of 4.

$Ti(acac)_2Y_2 \rightleftarrows 2Ti(acac)_2XY$ in deuteriochloroform and dichloromethane solution are presented in Table III. When both of the monodentate ligands are halogen atoms, the equilibrium constants are close to the statistical value of 4 expected for random scrambling of ligands. However, when X = F and Y = OEt, the equilibrium constant exceeds the statistical value by a factor of $\sim 10^2$. The difference between halogen-halogen exchange and halogen-alkoxide exchange is further illustrated in Figure 2 wherein is plotted, for the $Ti(acac)_2F_2$-$Ti(acac)_2Cl_2$ and $Ti(acac)_2F_2$-$Ti(acac)_2(OEt)_2$ systems, the fractional concentration of the various complexes in the equilibrium mixture as a function of ligand composition. It is evident that the data for the $Ti(acac)_2F_2$-$Ti(acac)_2Cl_2$ system lie close to the calculated curves for random scrambling whereas, for the $Ti(acac)_2F_2$-$Ti(acac)_2(OEt)_2$ system, the mixed-ligand complex is favored at the expense of the parent complexes. Nonstatistical behavior for halogen-alkoxide exchange has been reported previously by Van Wazer and coworkers[19,20] for the $TiCl_4$-$Ti(OR)_4$ and $SiCl_4$-$Si(OR)_4$ systems; it can probably be understood in terms of the difference in ligand electronic structure.[20]

Exchange of Bidentate Ligands. Pmr spectra for a typical equimolar mixture of two different β-diketonate complexes, $Ti(acac)_2F_2$ and $Ti(tfac)_2F_2$, are shown in Figure 1(b). The resonances at lowest and highest field are due to the parent complexes, $Ti(tfac)_2F_2$ and $Ti(acac)_2F_2$, respectively, while the two lines at intermediate field are assigned, in order of increasing field, to the tfac and acac resonances, respectively, of the mixed-ligand complex $Ti(tfac)(acac)F_2$. Again, the spectra are simplified because intramolecular rearrangement is rapid on the pmr time scale.

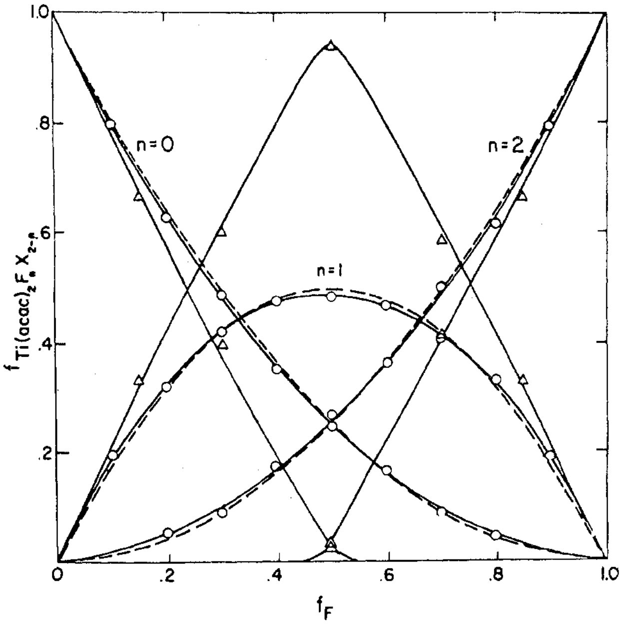

Figure 2. Ligand-exchange equilibria for the $Ti(acac)_2F_2$-$Ti(acac)_2X_2$ (X = Cl, ○–○; X = OEt, △–△) systems in dichloromethane solution at 31°. The molar fraction of total solute as $Ti(acac)_2F_nX_{2-n}$ at equilibrium, $f_{Ti(acac)_2F_nX_{2-n}}$, is plotted *vs.* the molar fraction of total ligand as fluorine, f_F. Broken lines are calculated curves assuming a random statistical distribution of ligands.

Table IV. Chemical Shift Data for Mixed-Ligand $Ti(dik)(dik')X_2$ Complexes in $CDCl_3$ Solution[a]

Compd	dik		dik′	
	$-CH_3$	$-CH=$	$-CH_3$	$-CH=$
$Ti(acac)(bzac)F_2$	−2.09	−5.86	−2.24	−6.53
$Ti(acac)(bzbz)F_2$	−2.07	−5.84		−7.20
$Ti(acac)(dpm)F_2$	−2.06	−5.82	−1.17	−6.11
$Ti(bzac)(bzbz)F_2$	−2.20	−6.51		−7.18
$Ti(bzbz)(dpm)F_2$		−7.13	−1.14	−6.11
$Ti(tfac)(acac)F_2$	−2.34	−6.24	−2.12	−5.94
$Ti(tfac)(bzac)F_2$	−2.32	−6.24	−2.27	−6.60
$Ti(tfac)(bzbz)F_2$	−2.28	−6.23		−7.29
$Ti(bztf)(acac)F_2$		−6.87	−2.12	−5.93
$Ti(bztf)(bzac)F_2$		−6.88	−2.26	−6.60
$Ti(bztf)(dpm)F_2$		−6.83	−1.17	−6.18
$Ti(thtf)(acac)F_2^{\ b}$		−6.68	−2.11	−5.92
$Ti(thtf)(bzac)F_2^{\ b}$		−6.68	−2.25	−6.58
$Ti(thtf)(dpm)F_2^{\ b}$		−6.65	−1.17	−6.16
$Ti(tfac)(thtf)F_2^{\ b}$	−2.36	−6.30		−6.75
$Ti(tfac)(bztf)F_2$	−2.36	−6.33		−6.97
$Ti(bztf)(thtf)F_2^{\ b}$		−6.95		−6.75
$Ti(tfac)(hfac)F_2$	−2.44	−6.41		−6.63
$Ti(acac)(hfac)F_2$	−2.16	−6.01		−6.53
$Ti(acac)(tfac)(OEt)_2$	−2.00	−5.59	−2.18	−5.90
$Ti(tfac)(hfac)(OEt)_2$	−2.23	−6.04		−6.29
$Ti(acac)(hfac)(OEt)_2$	−2.03	−5.66		−6.22

[a] Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). Temperature is ~39°. Data refer to equimolar equilibrium mixtures of $Ti(dik)_2X_2$ and $Ti(dik')_2X_2$; total solute concentration is 0.32 *M* unless indicated otherwise. [b] Total solute concentration is 0.24 *M*.

Chemical shift data for the mixed-ligand complexes in the $Ti(dik)_2X_2$-$Ti(dik')_2X_2$ mixtures studied are presented in Table IV. The assignments are straightforward because, again, chemical shifts for the parent complexes (Table I) are, in general, unaltered (±0.02 ppm) on going to the equilibrium mixtures. The only exception to this generalization is that, in mixtures containing $Ti(bzbz)_2F_2$, the resonances of the other parent complex are shifted upfield by as much as 0.03-0.04 ppm. Ordinarily, the ring proton resonances of the parent complexes are found at highest and lowest field with the two signals of the mixed-ligand

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(20) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 3, 268 (1964).

complex at intermediate field; however, there are a few exceptions where just the reverse occurs. Additional aids in making assignments are the relative intensities, which differ appreciably for mixtures which deviate from random scrambling (see Figure 1(b)).

Equilibrium constants for the reaction $Ti(dik)_2X_2 + Ti(dik')_2X_2 \rightleftarrows 2Ti(dik)(dik')X_2$ (X = F, OEt) in $CDCl_3$ solution are presented in Table V. The time required to reach equilibrium at room temperature was investigated for a majority of the mixtures; in no case did this time exceed 35 min.

The exchange reactions can be classified into three categories, depending on the relative number of CF_3 groups on the β-diketonate ligands. (1) Reactions which exchange ligands that contain the same number of CF_3 groups or no CF_3 groups (*e.g.*, tfac-bztf or acac-bzac) have equilibrium constants close to the statistical value of 4 expected for random scrambling. (2) Reactions which exchange ligands that differ by one CF_3 group (*e.g.*, acac-tfac or tfac-hfac) display *K* values which are 2-6 times the statistical value. (3) Reactions which exchange ligands that differ by two CF_3 groups (*e.g.*, acac-hfac) exhibit equilibrium constants which exceed the statistical value by a factor of $\sim 10^2$-10^3. The reactions can be assigned to these categories independent of the nature of the monodentate ligand (X = F, OEt), although the deviations from random scrambling appear to be somewhat larger when X = F. These results are in full accord with previous studies of β-diketonate exchange on Zr(IV),[21-23] Hf(IV),[21,22] Al(III),[23,24] Ga(III),[25] and Y(III),[26,27] which have established, for a smaller range of ligands, that equilibrium constants depend primarily on the relative number of CF_3 substituents on the exchanging ligands.

The observed deviations from random scrambling can be rationalized in terms of an electrostatic model.[23,25,28] Kida[29] and Marcus and Eliezer[30] have shown that electrostatic effects always stabilize mixed-ligand complexes relative to the parent complexes whenever the charges on the two exchanging ligands are unequal. (In that case, the average ligand-ligand repulsion energy is less for the mixed complexes than for the parents.) The effective charges on the donor oxygen atoms of β-diketonate ligands which carry zero, one, and two CF_3 groups will differ because of the inductive effect of the fluorine atoms. Consequently, the mixed complex, $Ti(dik)(dik')X_2$, and the corresponding parent complexes will have comparable stability when dik and dik′ contain the same number of CF_3 groups, but the mixed complex will be more stable than the parents when dik and dik′ have a different number of CF_3 groups. Moreover, the mixed complexes will be most stable (*K* largest) when dik and dik′ differ by two CF_3 groups (*e.g.*, acac-hfac). These predictions of the electrostatic model are in accord with the equilibrium constants in Table V and also with available data for β-diketonate exchange on other metal atoms.[21-28,31]

Table V. Equilibrium Constants for the Reation $Ti(dik)_2X_2 + Ti(dik')_2X_2 \rightleftarrows 2Ti(dik)(dik')X_2$ (X = F or OEt)[a]

dik	dik′	Terminal groups dik	Terminal groups dik′	*K*
		X = F		
acac	bzac	CH_3, CH_3	CH_3, C_6H_5	~4[b]
acac	bzbz	CH_3, CH_3	C_6H_5, C_6H_5	3.7
acac	dpm	CH_3, CH_3	$t\text{-}C_4H_9, t\text{-}C_4H_9$	2.2
bzac	bzbz	CH_3, C_6H_5	C_6H_5, C_6H_5	~4[b]
bzbz	dpm	C_6H_5, C_6H_5	$t\text{-}C_4H_9, t\text{-}C_4H_9$	3.8
tfac	acac	CF_3, CH_3	CH_3, CH_3	15
tfac	bzac	CF_3, CH_3	CH_3, C_6H_5	16
tfac	bzbz	CF_3, CH_3	C_6H_5, C_6H_5	15
bztf	acac	CF_3, C_6H_5	CH_3, CH_3	10
bztf	bzac	CF_3, C_6H_5	CH_3, C_6H_5	11
bztf	dpm	CF_3, C_6H_5	$t\text{-}C_4H_9, t\text{-}C_4H_9$	23
thtf	acac	CF_3, C_4H_3S	CH_3, CH_3	7.1[c]
thtf	bzac	CF_3, C_4H_3S	CH_3, C_6H_5	7.4[c]
thtf	dpm	CF_3, C_4H_3S	$t\text{-}C_4H_9, t\text{-}C_4H_9$	22[c]
tfac	thtf	CF_3, CH_3	CF_3, C_4H_3S	~4[b,c]
tfac	bztf	CF_3, CH_3	CF_3, C_6H_5	~4[b]
bztf	thtf	CF_3, C_6H_5	CF_3, C_4H_3S	~4[b,c]
tfac	hfac	CF_3, CH_3	CF_3, CF_3	17
acac	hfac	CH_3, CH_3	CF_3, CF_3	3.2×10^3
		X = OEt		
acac	tfac	CH_3, CH_3	CF_3, CH_3	9.2
tfac	hfac	CF_3, CH_3	CF_3, CF_3	13
acac	hfac	CH_3, CH_3	CF_3, CF_3	2.8×10^2

[a] Data refer to equimolar equilibrium mixtures of $Ti(dik)_2X_2$ and $Ti(dik')_2X_2$ in $CDCl_3$ solution at ~39°; total solute concentration is 0.32 *M* unless indicated otherwise. Probable uncertainty in the equilibrium constants is ~±10%. [b] Resolution of resonance lines is too poor for quantitative measurement, but signal peak heights indicate that *K* is near the statistical value of 4. [c] Total solute concentration is 0.24 *M*.

In order to assess the relative importance of enthalpy and entropy contributions to the nonstatistical equilibria, we have measured the temperature dependence of the equilibrium constant for the reaction $Ti(bztf)_2F_2 + Ti(dpm)_2F_2 \rightleftarrows 2Ti(bztf)(dpm)F_2$. Among the reactions which exchange ligands that differ by one CF_3 group, this is the reaction which exhibits the greatest deviation from random scrambling. The equilibrium constant was determined three times at each temperature using 25 CAT scans per determination. Average values of $K(CDCl_3$ solution) were 25.7 (44.1°), 24.0 (51.5°), 24.4 (61.1°), 25.4 (68.4°), 24.5 (81.1°), and 21.9 (91.8°). The following values of ΔH and ΔS ($\pm 1\sigma$) were determined from a least-squares plot of $\log K$ *vs.* $1/T$ including all three values of $\log K$ at each temperature: $\Delta H = -0.50 \pm 0.27$ kcal/mol and $\Delta S = 4.9 \pm 0.8$ eu. The observed exothermic value of ΔH differs from the statistical value (zero) at the 90% confidence limit, and the observed value of ΔS exceeds the statistical value (2.75 eu) at the 98% confidence limit. Thus, both ΔH and ΔS contribute to the greater stability of the mixed-ligand complex.

The enthalpy change is expected to be more exothermic for the $Ti(acac)_2F_2$-$Ti(hfac)_2F_2$ system.[23,31] However, very small concentrations of the parent complexes in this equilibrium mixture deterred us from attempting quantitative ΔH measurements.

Stereochemistry. Since $Ti(dik)_2X_2$ (X = F, Cl, Br) and $Ti(acac)_2(OR)_2$ complexes exist in solution exclusively as cis geometrical isomers,[2-4,6] mixed complexes of the type $Ti(dik)_2XY$ ($X \neq Y$ = F, Cl, Br, OEt) are expected to have

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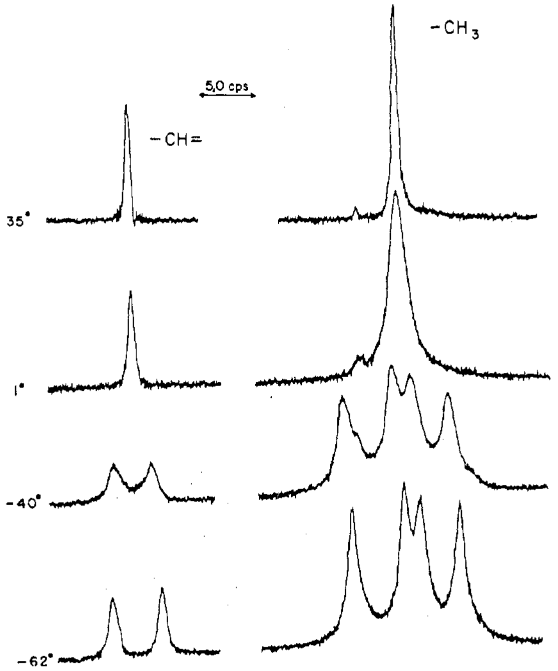

Figure 3. Variable-temperature pmr spectra of an equimolar mixture of $Ti(acac)_2F_2$ and $Ti(acac)_2(OEt)_2$ in dichloromethane solution; total solute molarity is 0.32 *M*. The weak peak on the low-field side of the methyl resonance in the 35° spectrum and the very weak, broad shoulder on the high-field side of this resonance are due to $Ti(acac)_2F_2$ and $Ti(acac)_2(OEt)_2$, respectively. The intense lines are all due to the mixed complex $Ti(acac)_2F(OEt)$.

the same configuration. This was checked for $Ti(acac)_2F(OEt)$ by low-temperature nmr. Pmr spectra of an equimolar mixture of $Ti(acac)_2F_2$ and $Ti(acac)_2(OEt)_2$ (Figure 3) are dominated by the resonance lines of $Ti(acac)_2F(OEt)$ because of the large value of *K* (Table III) for F-OEt exchange; resonances of the parent complexes are weak and do not complicate interpretation of the spectra. The low-temperature spectra exhibit four equally intense methyl resonances and two equally intense -CH= resonances, as expected for the cis isomer (point group C_1). There is no evidence for any appreciable concentration of the trans isomer. Above −40°, rapid intramolecular rearrangement collapses the spectrum to a single, time-averaged methyl resonance and a single, time-averaged -CH= line.

Thompson, *et al.*,[32] have recently reported the preparation and isolation of the mixed chloroalkoxy complexes, $Ti(acac)_2Cl(OR)$. These compounds also exist in solution as stereochemically nonrigid cis isomers.

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Registry No. $Ti(acac)_2F_2$, 16986-93-9; $Ti(bzac)_2F_2$, 51064-85-8; $Ti(bzbz)_2F_2$, 17967-65-6; $Ti(dpm)_2F_2$, 51022-45-8; $Ti(tfac)_2F_2$, 51022-46-9; $Ti(bztf)_2F_2$, 51022-47-0; $Ti(thtf)_2F_2$, 51022-48-1; $Ti(hfac)_2F_2$, 51025-52-6; $Ti(acac)_2(OEt)_2$, 23072-30-2; $Ti(tfac)_2(OEt)_2$, 51022-49-2; $Ti(hfac)_2(OEt)_2$, 51022-50-5; $Ti(acac)_2Cl_2$, 16986-94-0; $Ti(acac)_2FCl$, 51025-53-7; $Ti(acac)_2FBr$, 51022-51-6; $Ti(acac)_2ClBr$, 51025-54-8; $Ti(acac)_2F(OEt)$, 51022-52-7; $Ti(acac)_2Br_2$, 16986-95-1; $Ti(acac)(bzac)F_2$, 51022-53-8; $Ti(acac)(bzbz)F_2$, 51022-54-9; $Ti(acac)(dpm)F_2$, 51022-55-0; $Ti(bzac)(bzbz)F_2$, 51022-26-5; $Ti(bzbz)(dpm)F_2$, 51022-27-6; $Ti(tfac)(acac)F_2$, 51022-28-7; $Ti(tfac)(bzac)F_2$, 51022-29-8; $Ti(tfac)(bzbz)F_2$, 51022-30-1; $Ti(bztf)(acac)F_2$, 51022-31-2; $Ti(bztf)(bzac)F_2$, 51022-32-3; $Ti(bztf)(dpm)F_2$, 51022-33-4; $Ti(thtf)(acac)F_2$, 51022-34-5; $Ti(thtf)(bzac)F_2$, 51022-35-6; $Ti(thtf)(dpm)F_2$, 51022-36-7; $Ti(tfac)(thtf)F_2$, 51022-37-8; $Ti(tfac)(bztf)F_2$, 51022-38-9; $Ti(bztf)(thtf)F_2$, 51022-39-0; $Ti(tfac)(hfac)F_2$, 51022-40-3; $Ti(acac)(hfac)F_2$, 51022-41-4; $Ti(acac)(tfac)(OEt)_2$, 51022-42-5; $Ti(tfac)(hfac)(OEt)_2$, 51022-43-6; $Ti(acac)(hfac)(OEt)_2$, 51022-44-7.

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Reduction of Vanadium Tetrachloride by Tetrakis(dimethylamino)diborane(4). Preparation of Bis(dimethylaminomethane)vanadium(III) Chloride

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Treatment of vanadium tetrachloride, VCl_4, with excess tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, affords bis(dimethylaminomethane)trichlorovanadium(III), $VCl_3\cdot[N(CH_3)_2]_2CH_2$ (I). Reaction of I with pyridine, py, quantitatively displaces $CH_2[N(CH_3)_2]_2$ and affords $VCl_3\cdot 3py$. Treatment of I with gaseous HCl results in the formation of the cationic species $(CH_3)_2N{=}CH_2^+$ and $(CH_3)_2NH^+$ and liberation of VCl_3. For comparison, the reaction of HCl with $CH_2[N(CH_3)_2]_2$ is also described. Electronic and infrared spectral data for I are consistent with vanadium in the five-coordinate state, and the magnetic moment is normal for a V(III) d^2 system.

Introduction

The reduction of anhydrous metal halides (periodic groups IVb, Vb) by tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, has led to the formation of metal halide complexes involving bridging and chelate groups derived from oxidation of $B_2[N(CH_3)_2]_4$, *i.e.*, $B[N(CH_3)_2]_2X$, X = Cl and Br. Reduction of $TiCl_4$ affords the ligand-bridged species $(TiCl_4)_3\{[N(CH_3)_2]_2BCl\}_2$ and the binuclear antiferromagnetic complex $(TiCl_3)_2[N(CH_3)_2]_2BCl$.[2] A similar reaction with $TiBr_4$ results in the formation of $(TiBr_4)_3\{[N(CH_3)_2]_2Br\}_2$ and $(TiBr_3)_2\{B_2Br_2[N(CH_3)_2]_2\}_2$.[3] In an effort to prepare binuclear V(III) complexes the reduction of VCl_4 with $B_2[N(CH_3)_2]_4$ was investigated.

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