reported are monomers in which the metal is coordinated to seven donor atoms. The nmr studies suggest that the OCH_3 ligands are probably equivalent. The environments on opposite ends of the essentially planar carbamate ligands seem to be different.

A model which is consistent with these observations and preliminary X-ray data has *trans* axial OCH_3 groups with the carbamate ligands and the halogen in the equatorial positions of a pentagonal bipyramid. A single-crystal X-ray study of $NbBr(OCH_3)_2(S_2CN(C_2H_5)_2)_2$ is in progress.

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Complexes of Titanium(IV) Containing the 3-Methyl-2,4-pentanedionate Anion

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Seven 3-methyl-2,4-pentanedionato complexes of titanium(IV) have been prepared and characterized. These include $X_2Ti(C_6H_9O_2)_2$ (X = F, Cl, Br), $X_3Ti(C_6H_9O_2)$ (X = Cl, Br), and $[Ti(C_6H_9O_2)_3]Y$ ($Y^- = FeCl_4^-, SbCl_6^-$). The dihalo and trihalo complexes are monomeric and nonionic; the trisubstituted complexes are 1:1 electrolytes. Nmr data show that the dihalo complexes have the *cis* configuration.

Introduction

The past few years have seen an interest in the reactions of titanium tetrahalides with β-diketones.[2–7] Complexes most frequently isolated are (1) simple Lewis acid–base adducts of the β-diketones, (2) monosubstituted X_3TiL enolate complexes, and (3) disubstituted X_2TiL_2 complexes. Further, tris-substituted complexes containing an L_3Ti^+ cation have been isolated mainly by the reaction of Cl_2TiL_2 complexes with a suitable Lewis acid such as antimony pentachloride or ferric chloride. In this paper we report the preparation and characterization of titanium(IV) complexes containing the 3-methyl-2,4-pentanedionate anion.

Experimental Section

Reagents.—Titanium tetrafluoride, titanium tetrabromide (Alfa Inorganics, Inc.), and titanium tetrachloride (Fisher Scientific Co., "purified") were purchased. Titanium tetrachloride was redistilled under nitrogen just prior to use; the other tetrahalides were used without further purification. 3-Methyl-2,4-pentanedione was prepared and characterized by a reported procedure.[2d,8]

All solvents were purified by distillation under nitrogen or vacuum from suitable dehydrating agents before use. Nitrobenzene was purified in a manner similar to that reported.[4b]

General Procedures.—All preparations were performed under an atmosphere of dry nitrogen by methods previously described.[2d] All compounds were washed thoroughly with hexane and dried under vacuum at room temperature. Physical measurements were made on samples prepared in a nitrogen-filled glove bag or a Vacuum Atmospheres Dri-Lab.

Preparation of Trichloro(3-methyl-2,4-pentanedionato)titanium(IV).—3-Methyl-2,4-pentanedione (2.5×10^{-2} mol) in methylene chloride (15 ml) was added dropwise to a solution of titanium tetrachloride (2.7×10^{-2} mol) in 40 ml of methylene chloride. A dark solution resulted. Approximately half the methylene chloride was boiled off under a slow stream of nitrogen. Hexane was then added; a dark red precipitate formed and was subsequently isolated. *Anal.* Calcd for $C_6H_9O_2Cl_3Ti$: C, 26.94; H, 3.40; Cl, 39.8. Found: C, 26.51; H, 3.58; Cl, 38.6.

Preparation of Tribromo(3-methyl-2,4-pentanedionato)titanium(IV).—This complex was prepared like trichloro(3-methyl-2,4-pentanedionato)titanium(IV). A dark crystalline solid was isolated. This complex was extremely moisture sensitive showing immediate decomposition on contact with air. *Anal.* Calcd for $C_6H_9O_2Br_3Ti$: C, 17.98; H, 2.26; Br, 59.8. Found: C, 17.99; H, 2.51; Br, 58.5.

Preparation of Difluorobis(3-methyl-2,4-pentanedionato)titanium(IV).—Titanium tetrafluoride (1.18×10^{-2} mol) was added to 20 ml of methylene chloride. 3-Methyl-2,4-pentanedione (2.23×10^{-2} mol) was added dropwise to the slurry. The reaction mixture was refluxed 4 hr. Hexane was then added, after which the methylene chloride was gently boiled off; an oil remained. Addition of dried ether with stirring gave a yellow precipitate. *Anal.* Calcd for $C_{12}H_{18}O_4F_2Ti$: C, 46.17; H, 5.81. Found: C, 46.30; H, 5.93.

Preparation of Dichlorobis(3-methyl-2,4-pentanedionato)titanium(IV).—This complex was prepared by a procedure similar to that reported by Fay and Lowry.[4b] A red-orange precipitate was

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isolated. *Anal.* Calcd for $C_{12}H_{18}O_4Cl_2Ti$: C, 41.76; H, 5.27; Cl, 20.6. Found: C, 41.72; H, 4.92; Cl, 20.4.

Preparation of Dibromobis(3-methyl-2,4-pentanedionato)titanium(IV).—This complex was prepared similarly to the dichloro analog. A deep red solid was isolated. The compound was recrystallized from a methylene chloride–hexane mixture. *Anal.* Calcd for $C_{12}H_{18}O_4Br_2Ti$: C, 33.21; H, 4.18; Br, 36.7. Found: C, 32.94; H, 4.52; Br, 36.7.

Reaction of Dichlorobis(3-methyl-2,4-pentanedionato)titanium(IV) with Titanium Tetrachloride.—Dichlorobis(3-methyl-2,4-pentanedionato)titanium(IV) and titanium tetrachloride were allowed to react in a 1:1.1 molar ratio in methylene chloride. After refluxing 4 hr, removing *ca.* two-thirds of the solvent, and adding hexane, a dark solid formed and was isolated. Color, thermal characteristics, and ir data showed the compound to be trichloro(3-methyl-2,4-pentanedionato)titanium(IV).

Reaction of Trichloro(3-methyl-2,4-pentanedionato)titanium(IV) with 3-Methyl-2,4-pentanedione.—Trichloro(3-methyl-2,4-pentanedionato)titanium(IV) and 3-methyl-2,4-pentanedione in a 1:1.2 molar ratio were refluxed in methylene chloride 2 hr. Removal of *ca.* half the methylene chloride followed by the addition of hexane gave a red-orange solid, mp 191–194°. The melting point and ir data showed the product to be dichlorobis(3-methyl-2,4-pentanedionato)titanium(IV).

Preparation of Tris(3-methyl-2,4-pentanedionato)titanium(IV) Hexachloroantimonate(V).—This compound was prepared by the procedure of Cox, Lewis, and Nyholm[8] for the acetylacetonate analog. An orange solid was isolated. *Anal.* Calcd for $C_{18}H_{27}O_6Cl_6SbTi$: C, 29.95; H, 3.77; Cl, 29.5. Found: C, 30.35; H, 3.72; Cl, 29.1.

Preparation of Tris(3-methyl-2,4-pentanedionato)titanium(IV) Tetrachloroferrate(III).—This compound was prepared by the above procedure. An orange solid was isolated. *Anal.* Calcd for $C_{18}H_{27}O_6Cl_4FeTi$: C, 36.96; H, 4.65; Cl, 24.2. Found: C, 35.41; H, 4.64; Cl, 23.7.

Conductance Measurements.—An Industrial Instruments Model RC-18 conductivity bridge operating at 3000 cps was used for all measurements. Measurements were made in nitrobenzene and acetonitrile at 22 ± 1° using a Freas-type cell (cell constant 0.17 cm^{-1}) with bright platinum electrodes (measurements with platinized electrodes were not significantly different).

Molecular Weight Measurements.—Molecular weights were determined cryoscopically under an atmosphere of dry nitrogen. The procedure was checked against recrystallized naphthalene.

Melting Points.—Melting points were measured in sealed capillaries with a Thomas-Hoover apparatus and are uncorrected.

Spectral Data.—Proton nmr spectra were run on a Perkin-Elmer R-20 spectrometer. Sample tubes were filled under nitrogen and sealed under vacuum.

Results and Discussion

The reaction of 3-methyl-2,4-pentanedione with the titanium tetrahalides TiX_4 (X = F, Cl, Br) in a molar ratio of 2:1 in methylene chloride leads to the formation of dihalobis(3-methyl-2,4-pentanedionato)titanium(IV) complexes in good yields. For the dichloro and dibromo complexes product formation is unaffected by the order of addition of the reagents. The properties of the dihalo complexes parallel those reported for the 2,4-pentanedionato analogs.[4b]

The facile formation of the dihalotitanium(IV) complexes with the 3-methyl-2,4-pentanedionate anion as a ligand is in marked contrast to the tin tetrachloride–3-methyl-2,4-pentanedione system. Smith and Wilkins[9] reported that they were unable to isolate any solid product from the reaction of 3-methyl-2,4-pentanedione and tin tetrachloride even though the acetylacetonate complex forms readily (results from this laboratory[10] confirm Smith and Wilkins' findings).

The reaction of titanium tetrachloride or titanium tetrabromide and 3-methyl-2,4-pentanedione in a molar ratio of 1:1 in methylene chloride leads to the formation of an enolate complex having a stoichiometry of $X_3Ti(C_6H_9O_2)$ (X = Cl, Br). For these 1:1 reactions no evidence even at low temperatures was found for a simple diketone–Lewis acid–base adduct such as forms with acetylacetone and titanium tetrachloride[2d] and which loses hydrogen chloride on refluxing in an inert solvent to give $Cl_3Ti(C_5H_7O_2)$. However, it is likely that adduct formation does precede formation of the enolate complex. Possibly the 3-methyl-2,4-pentanedione enolate anion being more basic than the acetylacetonate anion behaves as a stronger donor toward titanium(IV) favoring the formation of the enolate complex.

The trihalo complexes are much more sensitive to moisture than the dihalo complexes. The tribromo complex is soluble in nitrobenzene, benzene, and chlorinated hydrocarbons; the trichloro complex, however, although soluble in nitrobenzene, is only very slightly soluble in benzene.

No success was had in obtaining trisubstituted products as $[Ti(C_6H_9O_2)_3]_2TiCl_6$ from the direct reaction of titanium tetrachloride and 3-methyl-2,4-pentanedione even using an excess (4:1) of β-diketone. However, reaction of dichlorobis(3-methyl-2,4-pentanedionato)titanium(IV) with Lewis acid halides such as ferric chloride and antimony pentachloride leads to tris(3-methyl-2,4-pentanedionato)titanium(IV) salts with the anions $SbCl_6^-$ and $FeCl_4^-$. The lack of formation of a trisubstituted product is in contrast to the zirconium and hafnium tetrachlorides which readily substitute three chlorides to form seven-coordinate β-diketonate complexes.[11]

Conductivity and molecular weight data for some of the complexes prepared in this study are summarized in Table I. The results are consistent with the dihalo and trichloro complexes having nonionic and monomeric structures in nitrobenzene.[12] Nmr splitting patterns at low temperature are consistent with the dihalo complex being monomeric in methylene chloride as well. These findings are consistent with the results of others[2a–c,3,4] for analogous dihaloacetylacetonato complexes.

The molecular weight in benzene of the tribromo complex is concentration dependent (see Table I) with a monomeric species being favored at low concentration. The nmr spectrum in methylene chloride for $Br_3Ti(C_6H_9O_2)$ is complex and temperature-dependent splitting patterns are observed which we cannot at present explain with certainty. However, these data indicate an equilibrium of at least two species in solution. For trichloro(3-methyl-2,4-pentanedionato)-

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[10] Unpublished data.

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[12] We have also determined that trichloroacetylacetonatotitanium(IV) is monomeric in nitrobenzene. The complex is insoluble in benzene.

Table I

Complex	Mp, °C	Mol wt in nitrobenzene[a]			Conductivities (Λ_M[b])	
		Obsd	Calcd	Concn × 10^2, *M*	Nitrobenzene	Acetonitrile
$Ti(C_6H_9O_2)_2F_2$	203–205	317	314	1.47	<0.1 (2.1 × 10^{-2}) <0.1 (2.0 × 10^{-3})	1.0 (3.0 × 10^{-3})
$Ti(C_6H_9O_2)_2Cl_2$	195–198	325	345	3.79	0.09 (9.4 × 10^{-3})	1.3 (8.5 × 10^{-3})
		(321)		5.71	0.12 (2.5 × 10^{-3})	2.9 (2.1 × 10^{-3})
$Ti(C_6H_9O_2)_2Br_2$	191–193	412	436	4.28	0.36 (2.2 × 10^{-2})	6.6 (2.6 × 10^{-2})
					0.32 (2.6 × 10^{-3})	21.2 (3.1 × 10^{-3})
$Ti(C_6H_9O_2)Cl_3$	~170	262	267	(3.91)	0.63 (8.6 × 10^{-3})	2.4 (1.4 × 10^{-2})
		274		(6.12)	0.20 (2.3 × 10^{-3})	5.6 (2.5 × 10^{-3})
		[c]				
$Ti(C_6H_9O_2)Br_3$	148–150	411	401	3.86	0.73 (1.3 × 10^{-2})	33.3 (5.68 × 10^{-3})
		(417)		3.39	0.93 (4.4 × 10^{-3})	
		(438)		5.17		
$[Ti(C_6H_9O_2)_3]SbCl_6$	205–206				18.0 (7.4 × 10^{-3}) 25.9 (6.3 × 10^{-4})	82.4 (1.4 × 10^{-2}) 135 (1.1 × 10^{-3})
$[Ti(C_6H_9O_2)_3]FeCl_4$	185–188				23.8 (1.8 × 10^{-3})	88.3 (3.4 × 10^{-3})

[a] Molecular weights in parentheses are in benzene. [b] Molar concentrations are in parentheses. [c] Not sufficiently soluble in benzene.

Table II

Nmr Data[a]

Complex	Terminal CH_3	3-CH_3
$Ti(C_6H_9O_2)_2F_2$[d]	−2.13 (−2.16, −2.19)[b]	−1.96 (−1.97)[b]
$Ti(C_6H_9O_2)Cl_2$[e]	−2.18 (−2.19, −2.29)[c]	−2.06 (−2.07)[c]
$Ti(C_6H_9O_2)Br_2$[f]	−2.18 (−2.16, −2.29)[c]	−2.11 (−2.11)[c]
$Ti(C_6H_9O_2)Cl_3$	−2.36 (−2.31)[c]	−2.15 (−2.18)[c]
$Ti(C_6H_9O_2)_3SbCl_6$	−2.26	−2.09
$Ti(C_6H_9O_2)Br_3$	−2.41 (−2.41)[g]	...

[a] Chemical shifts are in ppm relative to internal tetramethylsilane (*ca.* 0.5% by volume). Concentrations are *ca.* 0.1 *M*. [b] Chemical shifts at −90°. [c] Chemical shifts at −75°. [d] Coalescence temperature <−80°. [e] Coalescence temperature <−35°. [f] Coalescence temperature <−40°. [g] Chemical shift at −40°. Except for the −2.41 ppm which can only be assigned to an enolate terminal methyl group peak, the spectrum is temperature dependent and complex, and thus the 3-CH_3 peak cannot be assigned with certainty.

titanium(IV) only the expected two-line (2:1) pattern was observed over a wide temperature range. Solubility limitations precluded molecular weight studies in benzene for the trichloro complex.

Spectral data (ir and nmr) are consistent with the complexes containing only oxygen-chelated enolate ligands.[13] Low-temperature nmr spectra of the dihalo complexes show that the terminal methyl signal of the 3-methylacetylacetonato ligand is split into two equally intense signals indicative of a *cis* configuration for the complexes.

In summation, the data suggest that the complexes $X_2Ti(C_6H_9O_2)_2$ (X = F, Cl, Br) are best formulated as neutral, monomeric *cis*-type six-coordinate complexes. Data for $X_3Ti(C_6H_9O_2)$ complexes (X = Cl, Br) are consistent with a nonionic five-coordinate structure at least in nitrobenzene in the concentration range studied. Further studies on trihalo(β-diketonato)titanium(IV) complexes are in progress and will be reported later. Complexes of the type $[Ti(C_6H_9O_2)_3]Y$ (Y^- = $SbCl_6^-$, $FeCl_4^-$) are 1:1 electrolytes having six-coordinate complex cations.

It has been found that titanium tetrachloride can be substituted in a stepwise manner. Product formation depends on the molar ratio of the tetrachloride to 3-methyl-2,4-pentanedione; *i.e.*, a 1:1 reaction yields $Cl_3Ti(C_6H_9O_2)$ and a 1:2 reaction yields $Cl_2Ti(C_6H_9O_2)_2$. However, a ≥3:1 reaction gives only the disubstituted product. Furthermore, it appears that $Cl_3Ti(C_6H_9O_2)$ is an intermediate in the 1:2 reaction since $Cl_3Ti(C_6H_9O_2)$ will react with 1 equiv of 3-methyl-2,4-pentanedione to give $Cl_2Ti(C_6H_9O_2)_2$ and since $Cl_2Ti(C_6H_9O_2)_2$ will react to give $Cl_3Ti(C_6H_9O_2)$ when refluxed with 1 equiv of titanium tetrachloride. The following reactions summarize what has been shown to occur in the titanium tetrachloride–3-methyl-2,4-pentanedione system

$$TiCl_4 + C_6H_{10}O_2 \longrightarrow TiCl_3(C_6H_9O_2) + HCl$$

$$TiCl_4 + 2C_6H_{10}O_2 \longrightarrow 2TiCl_2(C_6H_9O_2)_2 + 2HCl$$

$$Cl_3Ti(C_6H_9O_2) + C_6H_{10}O_2 \longrightarrow TiCl_2(C_6H_9O_2)_2 + HCl$$

$$Cl_2Ti(C_6H_9O_2)_2 + TiCl_4 \longrightarrow 2Cl_3Ti(C_6H_9O_2)$$

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(13) A listing of ir data from 2000 to 250 cm^{-1} is available on request.