THE PREPARATION, STEREOCHEMISTRY, AND LABILITY OF SOME TITANIUM(IV) AND GERMANIUM(IV) B-DIKETONATES

> Thests for the Degree of M. S. MICHIGAN STATE UNIVERSITY Luis J. Matienzo 1969

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ABSTRACT

THE PREPARATION, STEREOCHEMISTRY, AND LABILITY OF SOME TITANIUM(IV) AND GERMANIUM(IV) β -DIKETONATES

By

Luis J. Matienzo

Several new dichlorobis(diketonato) titanium(IV) and germanium(IV) complexes have been prepared by reaction of the anhydrous metal halide and the free diketone. The reactions for germanium are slower and the complexes are thermodynamically less stable. Possible reasons for the kinetic and thermodynamic differences are discussed briefly. Nuclear magnetic resonance studies show that the stereochemistry of the $Ti(dik)_2Cl_2$ complexes in solution is based almost exclusively on a cis octahedral geometry, whereas the Ge(dik)₂Cl₂ complexes exhibit both <u>cis</u> and <u>trans</u> isomers. The rate of isomerization for $trans-Ge(dpm)_2Cl_2$, where dpm is dipivaloylmethanate, was studied in benzene solution in the temperature range 16-37°. The reaction follows firstorder reversible kinetics, with $E_a = 30.6 \pm 5.4 \text{ kcal/mole}$ and $\triangle S^* = 23.2 \pm 8.1$ eu. A dissociative mechanism is favored based on the values obtained for the activation energy and activation entropy and the solvent dependence of the rate of isomerization.

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Luis J. Matienzo

Several new titanium(IV) and germanium(IV) complexes of the type $[M(dik)_3][SbCl_6]$ were prepared by reaction of $M(dik)_2Cl_2$ and $SbCl_5$ in anhydrous organic solvents. The reaction of $Ge(dpm)_2Cl_2$ and $SbCl_5$ was studied in detail in an attempt to understand the role of $SbCl_5$ in the reaction. The results suggest that an addition compound, $Ge(dpm)_2Cl_2$. $SbCl_5$, is formed, which then disproportionates. Nmr studies of germanium(IV) complexes containing asymmetric diketonate ligands, such as pivaloylacetonate, show that both <u>cis</u> and <u>trans</u> isomers are present at room temperature.

In the course of studying the reaction of SbCl₅ and Ge(dpm)₂Cl₂ some new reactions of SbCl₅ were discovered. The first of these is the reaction of SbCl₅ and tetramethyl-silane (TMS) at room temperature:

 $SbCl_5 + (CH_3)_4Si \longrightarrow (CH_3)_3SiCl + CH_3Cl + SbCl_3.$ Also, $SbCl_5$ was found to form an addition compound $(SbCl_5 \cdot H(dpm))$ with dipivaloylmethane. A possible structure is suggested based on nmr data. The reaction of the adduct and TMS is also described.

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THE PREPARATION, STEREOCHEMISTRY, AND LABILITY OF SOME TITANIUM(IV) AND GERMANIUM(IV) β -DIKETONATES

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Luis J. Matienzo

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1969

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ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Thomas J. Pinnavaia for his encouragement, guidance and friendship throughout the course of this work.

Financial support from Ford Foundation through La Molina Project is very highly appreciated. A man should never be ashamed to own he has been in the wrong, which is but saying in other words, that he is wiser today than he was yesterday.

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I. INTRODUCTION

Metal complexes with β -diketones have been reported for all of the non-radioactive elements of the periodic table¹. Acetylacetone (2,4-pentanedione) is the simplest β -diketone. Replacement of the methyl groups or the y-proton by various organic groups leads to a large variety of derivatives. Because metal β -diketonates have been studied for almost 100 years, several reviews have been written. The first extensive review was published by Morgan and Moss² in 1914. During the following years these compounds received more attention. Synthetic techniques improved, new ligands have become available, and new analytical tools have helped to understand the nature of these compounds. Fernelius and Bryant³ have summarized the various procedures used prior to 1957. Since 1957, new synthetic methods have appeared which have some general utility, especially for the preparation of organometallic compounds containing B-diketonate groups⁴,⁵. Other reviews which bridge the gap since the work of Morgan and Drew have been written by Fackler¹, Collman⁶,⁷, and Selbin⁸.

This thesis concerns the preparation and characterization of several germanium (IV) and titanium (IV) β -diketonates. Therefore only the chemistry of group IV metal β -diketonates

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relevant to this area will be reviewed. The β -diketonate ligands of interest are listed in Table I, along with their abbreviations and formulas.

The complexes formed between Group IV metals and β -diketones can be classified according to the following general types:

A. <u>Trihalo (β-diketonato)</u> Metal (IV) Complexes.

The reaction of one mole of β -diketone and one mole of a metal(IV) chloride may in some cases give a penta-coordinate species. For example, Puri, Pande and Mehrotra⁴² have prepared Ti(acac)Cl₃. Yamamoto and Kambarg have assigned a penta-coordinate structure for this compound by infrared studies. Ti(bzac)Cl₃⁴³ and Zr(acac)Cl₃⁴⁴ have also been claimed.

B. Dikalobis (β-diketonato) Metal (IV) Complexes.

The reaction of two moles of ligand and one mole of certain Group IV metal halides generally yields an octahedral compound with the general formula $M(dik)_2X_2$. The elements that form these compounds are titanium^{11,12}, germanium^{12,13}, zirconium^{14,15}, hafnium¹⁵ and tin¹⁶.

C. <u>Tris (β-diketonato)</u> Metal (IV) Cations.

Reaction of dikalobis (β -diketonato) metal (IV) complexes with a Lewis acid such as SbCl₅, PtCl₄, AuCl₃, or FeCl₃, normally yields salts containing M(dik)₃⁺, where M = Ti, Ge,

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Table I.

Abbreviat
acac
bzac
bzbz
dpm
pvac
tfac
hfac
dik

Abbreviation	Ligand	Formula
acac	acetylacetonate	[H ₃ CCOCHCOCH ₃]
bzac	benzoylacetonate	[H ₃ CCOCHCOC ₆ H ₅]
bzbz	dibenzoylmethanate	[H ₅ C ₆ COCHCOC ₆ H ₅]
dpm	dipivaloylmethanate	$[H_9C_4COCHCOC_4H_9]^-$
pvac	pivaloylacetonate	[H ₃ CCOCHCOC ₄ H ₉]
tfac	trifluoroacetylacetonate	[F ₃ CCOCHCOCH ₃]
hfac	hexafluoroacetylacetonate	[F ₃ CCOCHCOCF ₃]
dik	any diketonate	[R'COCHCOR]

Table I. Abbreviations and formulas for some $\beta\text{-diketonate}$ ligands.

Zr, or Hf. firmed by studies¹², with acety S1 (acac) 2C complexes dihalobis (ketonato) Pe(acac)₃ species. group IV e question. D. <u>Halotr</u> ketona Sever plexes of known only chemistry and Hf (aca ^{squa}re and ^{but the me} E. Adduc The ; and metal ètoms of .

Zr, or Hf. The formulation of these cations has been confirmed by ultraviolet spectral studies¹⁷ and conductivity studies^{12,15}. It is interesting to note that SiCl₄ reactions with acetylacetone to give [Si(acac)₃][HCl₂], instead of Si(acac)₂Cl₂¹⁸. Another way of preparation of these cationic complexes is by ligand exchange of diketone groups of the dihalobis (β -diketonato) metal (IV) complex with tris (β -diketonato) iron (III)¹². Sn(acac)₂Cl₂ when treated with Fe(acac)₃ does not yield the expected tris (β -diketonato) species. The reason for the difference in behavior of the group IV elements is not apparent and poses and interesting question.

D. <u>Halotris (β-diketonato) Metal (IV)</u> and Tetrakis (β-diketonato) Metal (IV) Complexes.

Seven- and eight-coordinated group IV metal(IV) complexes of the type $M(dik)_3X$ and $M(dik)_4$, respectively, are known only for zirconium and hafnium^{11,15}. The stereochemistry of these complexes is unknown, except for $Zr(acac)_4$ and $Hf(acac)_4$, which have stereochemistries based on a square antiprism¹⁹. $Zr(acac)_3Cl \cdot THF$ has been reported⁴⁶ but the metal atom is probably six-coordinated.

E. Adducts of the Group IV Tetrahalides with β -diketonates.

The addition compounds of acetylacetone-type ligands and metal(IV) halides are formed by bonding of the oxygen atoms of the β -diketone to the metallic halide without

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replacement of the halide groups. $TiCl_4Hacac^{20}$ and $ZrCl_4Hacac^{14}$ have been characterized only by elementary analyses. Recently, the complexes SiF_4Hacac , GeF_4Hacac and SnF_4Hacac^{21} were listed in a nmr study but they were neither isolated nor analyzed. Allred and Thompson²² have reported the reactions of acetylacetone and 3,3-dimethylacetylacetone with several metal(IV) halides. They concluded that the tendency of formation of addition compounds for the elements followed the sequence:

Zr > Ti, Sn > > Ge, Si

and for the halides:

Infrared spectroscopy readily allows one to distinguish adduct formation with enolizable β -diketones from the formation of substitution complexes through the elimination of hydrogen halide. Characteristic regions of absorption of chelated acac ligands are well known²³.

Group (IV) metal β -diketonates have been studied by a variety of physical techniques. Nuclear magnetic resonance spectroscopy should certainly be classified among the most important techniques. It has been used to study stereoisomerism²⁴⁻²⁸, kinetics of configurational rearrangement^{29,30} and ligand exchange reactions^{31,32}. The present work reports the preparation of some new β -diketonates of titanium(IV) and germanium(IV) of the type $M(dik)_2X_2$ and $[M(dik)_3]^+$. The stereochemistry of these complexes has been studied by nmr. In addition, the rate of trans \rightarrow cis isomerization of

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Ge $(dpm)_2Cl_2$ has been determined. During the course of an nmr investigation of the reaction between Ge $(dpm)_2Cl_2$ and SbCl₅ for the preparation of Ge $(dpm)_3^+$, a new ligand exchange reaction between SbCl₅ and Si(Me)₄ was discovered. Also, some new antimony(V) β -diketonates were prepared.
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II. EXPERIMENTAL

A. Preparation of Compounds

1. Reagents and Solvents

Anhydrous titanium(IV) chloride (99.5 + % Baker), anhydrous antimony(V) chloride (99 + % Baker), anhydrous germanium(IV) chloride (99.99% Alfa Inorganics) and anhydrous germanium(IV) iodide (99.99% K & K Laboratories) were used without further purification. Dow-Corning chemicals trimethylchlorosilane and dimethylchlorosilane were used as purchased.

Acetylacetone was purchased from Matheson, Coleman and Bell. The ligand was freshly distilled before use, and the absence of organic impurities was checked by nmr spectroscopy. Eastman Organic Chemicals 1,3-diphenyl-1,3-propanedione was used as purchased without further purification. Trifluoroacetylacetone and hexafluoroacetylacetone were purchased from Columbia Organic Chemicals Company and were freshly distilled before use. Hexafluoroacetylacetone was purified by formation of its solid dihydrate, and subsequent dehydration with P_2O_5 . Dipivaloylmethane and pivaloylacetone were synthesized in our laboratories according to Adams and Hauser's methods³⁴. The purity of these ligands was checked by nmr spectroscopy.

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All organic solvents used in the synthesis and purification of products were reagent grade and were dried over suitable desiccants. Glacial acetic acid was the only exception; it was used as it was purchased. Carbon tetrachloride, benzene, hexane and methylene chloride were distilled from calcium hydride. Solutions of methylene chloride, chloroform and benzene with 1% of tetramethylsilane to be used as nmr solvents were prepared with solvents refluxed for 100 hrs over their respective drying agents. When benzene was used an an nmr solvent, it was further distilled from lithium aluminum hydride. Hexadeuterobenzene (99.5%, Diaprep Corporation) was used as purchased. Deuterochloroform and deuteroacetone were prepared according to the procedures described by Paulsen and Cooke³⁵. Nitrogen, which was used as a purging agent, was "Hi-Pure" nitrogen purchased from the liquid carbonic division of General Dynamics and is referred to herein as "dry nitrogen".

2. General Techniques

Since the compounds reported here are hydrolyzed very easily, all operations involved in syntheses, purification, and subsequent handling were conducted under anhydrous conditions. The preparations were carried out in a similar system to that shown in Figure 1. During some preparations, a stream of dry nitrogen was passed through the reaction mixture; in others, a P_2O_5 drying tube attached to the reflux condenser prevented hydrolyzation. All of the

Figure 1. Apparatus used for the preparation of dihalobis(diketonato)M(IV) and tris- (diketonato)M(IV) hexachloroantimonate(V) complexes.

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transferences to the reaction vessel were conducted inside a glove bag, and the weight of material delivered to the flask was determined by difference. Filtrations were carried out using a specially designed glass frit büchner funnel similar to that described by Holah³⁶. Recrystallizations were performed in a glass stoppered erlenmeyer flask fitted with a side arm and stopcock. During crystallizations, solutions were freed of moist air by passing dry nitrogen over the solution.

All glassware was dried at 180° for several hours and cooled in a desiccator whenever possible. Ground glass joints were usually greased with silicone grease.

Compounds were stored in screw cap vials fitted with teflon liners and were kept in a calcium sulphate desiccator.

B. Titanium Complexes.

1. Dichlorobis (2,4-pentanedionato) titanium (IV)²⁹

Titanium(IV) chloride (5.8 ml, 0.053 mole) was added slowly to a solution of acetylacetone (13.1 ml, 0.128 mole) in 150 ml of dichloromethane. The red solution was purged for 40 min with a low stream of dry nitrogen to remove evolved hydrogen chloride. The solution was then boiled down to <u>ca</u> 75 ml, and 100 ml of hexane was added. After 8 hr the red orange product was filtered and dried <u>in vacuo</u>. The yield of the crude product was 15.1 g (90%). Recrystallization from methylene chloride-hexane gave a product with mp 190-193°; lit.²⁹ 191-192°.

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2. <u>Tris(2,4-pentanedionato)titanium(IV)</u> Hexachloroantimonate(V)¹²

Dichlorobis(2,4-pentanedionato) titanium(IV) (3.62 g, 0.0114 mole) was dissolved in 50 ml of glacial acetic acid by heating the mixture for 30 min at reflux temperature. A solution of antimony(V) chloride (1.48 ml, 0.0114 mole) in 30 ml of glacial acetic acid was added dropwise to the hot titanium(IV) solution while the solution was being stirred. A gental stream of dry nitrogen was passed through the solution to avoid any hydrolysis. After 30 minutes, the volume of the mixture was reduced to <u>ca</u>. 40 ml by vacuum distillation at room temperature. The precipitate was filtered and dried <u>in vacuo</u> at room temperature for 6 hr. The orange product (4.54 g, 88.0% theoretical) was recrystallized from boiling glacial acetic acid and dried <u>in vacuo</u>, mp 165°, lit. 153-155°¹², 167.5-169.5°³⁷.

3. <u>Dichlorobis(1,3-diphenyl-1,3-propanedionato)-</u> titanium(IV)

A solution of titanium(IV) chloride (1.66 ml, 0.0150 mole) in 10 ml of benzene was added dropwise to a solution of 1,3-diphenyl-1,3-propanedione (8.10 g, 0.0361 mole) in 60 ml of benzene at room temperature. The mixture was stirred vigorously for 1 hr and the volume was reduced to <u>ca</u> 30 ml by passing a stream of nitrogen across the surface of the solution. The product was filtered and dried in vacuo

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for 4 hr. The yield of crude product was 7.96 g (94.0%). The bright red product was recrystallized from benzenehexane, mp 261.5-262°; lit.³⁰ 262.5-263.5°.

4. <u>Tris(1,3-diphenyl-1,3-propanedionato)titanium(IV)</u> <u>Hexachloroantimonate(V)</u>

Dichlorobis (1,3-diphenyl-1,3-propanedionato)titanium(IV) (2.91 g, 0.00515 mole) was dissolved in 200 ml of glacial acetic acid by heating the mixture at 95-100° for 1 hr under a N₂ atmosphere. A solution of antimony(V) chloride (10.7 ml, 0.00515 mole) in 20 ml of glacial acetic acid was added dropwise. The color of the solution became less intense red. Heating was continued an additional 15 min. Then the mixture was allowed to cool at room temperature. The red product was filtered and dried <u>in vacuo</u> for 6 hr and was recrystallized from acetic acid, mp 227-227.5°.

<u>Anal</u>. Calcd. for C₄₅H₃₃Cl₆O₆SbTe: C, 51.42; H, 3.17; Cl, 20.34. Found: C, 51.34; H, 3.20; Cl, 20.65.

5. <u>Dichlorobis(1,1,1-trifluoro-2,4-pentanedionato)-</u> titanium(IV)

A solution of titanium(IV) chloride (6.08 ml, 0.0554 mole) in 25 ml of methylene chloride was added dropwise to a solution of trifluoroacetylacetone (16.0 ml, 0.132 mole) in 25 ml of methylene chloride. The reaction mixture was heated at reflux temperature for 3 hrs. The solvent was distilled in vacuo and an orange foamy oil was obtained.

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The oil was slurried in 50 ml of freshly distilled diethyl ether, and the ether was removed by vacuum distillation at room temperature. When this procedure was repeated, a solid yellow residue was obtained. The residue was slurried in 50 ml of diethyl ether, filtered, and dried <u>in vacuo</u> at room temperature for 4 hr. Recrystallization of the product from methylene chloride-hexane yielded fine yellow crystals with mp 179-181.5°.

<u>Anal</u>. Calcd for $C_{10}H_8F_6O_4Cl_2Ti$: C, 28.3; H, 1.90. Found for a crude product: C, 30.2; H, 2.21. The nmr spectrum of the product indicates the presence of some free ligand, which probably accounts for the high C, H analysis.

6. <u>Attempted Preparation of Tris(1,1,1-trifluoro-2,4</u>pentanedionato) <u>Titanium(IV)</u> hexachloroantimonate(<u>V</u>)

Dichlorobis(trifluoroacetylacetonate)titanium(IV) (1.60 g, 0.00376 mole) was dissolved in 100 ml of dichloromethane. A solution of antimony(V) chloride (0.50 ml, 0.00376 mole) in 20 ml of dichloromethane was added dropwise. The mixture was stirred at room temperature for 2 hrs. After distillation of the solvent an orange oil was obtained. This product was washed with 50 ml of diethyl ether. The color of the material in the reaction flask suddenly changed to dark brown. The solvent was pumped out and the presence of tiny crystals was noted. A mixture of methylene chloride-ethylether (1 to 1 by volume) was added. After 5 minutes of stirring a light yellow precipitate was obtained. The volume

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of the solvent was reduced to <u>ca</u> 20 ml by evaporation under a stream of nitrogen. The solid was filtered and dried <u>in</u> <u>vacuo</u> at room temperature for 3 hr. Recrystallization of the product with methylene chloride-ether yielded white crystals with mp 142-143°. The nmr spectra of the product did not show the expected methyl line of the ligand, but rather the characteristic peaks of diethyl ether. The mp of the product is in agreement with the mp of TiCl₄·SbCl₅· $2(C_2H_5)_2O$ obtained in the attempted preparation of [Ti(hfac)₃⁺][SbCl₆⁻].

7. <u>Dichlorobis(1,1,1,5,5,5-hexafluoro-2,4-pentane-</u> dionato)titanium(IV)

Titanium(IV) chloride (4.56 ml, 0.0415 mole) was added dropwise to a solution of hexafluoroacetylacetone (15.0 ml, 0.106 mole) in 50 ml of methylene chloride at room temperature. The addition of the first drops of the titanium tetrahalide to the free ligand caused boiling of the mixture. Therefore, the rate of addition was maintained at 0.5 ml per minute. The mixture was refluxed for 20 hr. Then the volume of the solvent was reduced to <u>ca</u> 20 ml by evaporation under a stream of nitrogen and <u>ca</u> 20-30 ml of diethyl ether was distilled from lithium aluminum hydride directly into the reaction flask. The mixture was cooled in a dry iceacetone bath for 3 hr. The yellow orange solid which formed was filtered on a cold (-80^{0}) frit. The separated product was dried in vacuo at room temperature. The material was

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recrystallized by adding hexane and cooling in a dry iceacetone bath for 1 hr. The product was filtered and dried <u>in vacuo</u> for 3 hr. A second crop of crystals was obtained by addition of more hexane to the mother liquid. The total yield was 2.65 g (12.0%), mp 81° . Proton nmr showed only one γ -H line, as expected. The filtered solution was treated with a mixture of hexane-tetrahydrofuran(THF). A yellow precipitate was immediately formed. The product was filtered and dried <u>in vacuo</u>, mp $164-165^{\circ}$.

Analysis of the product with mp 81^{0} was as follows: Calcd. for $C_{10}H_{2}F_{12}O_{4}Cl_{2}Ti$: C, 22.38; H, 0.38. Found: C, 22.54; H, 0.39.

Analysis of the product with mp 164⁰ gave the following results: C, 26.05; H, 1.95. The nmr spectrum of the product did not indicate presence of THF.

8. <u>Attempted Preparation of Tris(1,1,1,5,5,5-hexafluoro-</u> 2,4-pentanedionato) <u>Titanium(IV)</u> <u>Hexachloroanti-</u> monate(V)

Dichlorobis(hexafluoroacetylacetonato) titanium(IV) (2.80 g, 0.0470 mole) was dissolved in 60 ml of dichloromethane by heating the mixture at reflux temperature for two hours. A solution of antimony(V) chloride (0.85 ml, 0.047 mole) in 20 ml of dichloromethane was added slowly after 0.5 hr, the volume was reduced to 20 ml by blowing a stream of dry nitrogen across the surface of the solution. Freshly distilled diethyl ether was added and some precipitate

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formed. The gray precipitate was recrystallized from a mixture of methylene chloride-diethyl ether, mp 141.5°.

<u>Anal</u>. Calcd for $C_{15}H_3F_{18}O_6Cl_6SbTi$: C, 17.95; H, 0.30; F, 34.08; Cl, 21.19. Found: C, 15.1; H, 3.18; F, 0.00; Cl, 49.85.

The absence of fluorine in the product obtained by reaction of dichlorobis(hexafluoroacetylacetonato) titanium(IV) and antimony(V) chloride suggested that the isolated product could be an addition compound, formed by reaction of $TiCl_4$, SbCl₅ and diethyl ether.

Titanium chloride (1.73 ml, 0.0156 mole) was added slowly to a solution of antimony(V) chloride (2.04 ml, 0.0156 mole) in 25 ml of dichloromethane. Diethyl ether (3.26 ml, 0.0312 mole) added to the stirred mixture, and a white precipitate formed. It was filtered and dried <u>in</u> <u>vacuo</u>. The crude product was recrystallized from methylene chloride-ether. The white crystals gave a mp of 141.5^{0}

<u>Anal</u>. Calcd for $C_8H_{20}O_2Cl_9SbTi$: C, 15.58; H, 3.54; Cl, 49.85. Found: C, 15.1; H, 3.18; Cl, 50.0.

9. <u>Dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)</u>titanium(IV)

A solution of titanium(IV) chloride (1.24 ml, 0.0116 mole) in 20 ml of methylene chloride was added dropwise to a mixture of dipivaloylmethane (5.00 ml, 0.0272 mole) and 30 ml of methylene chloride. The mixture was stirred for 2 hr at reflux temperature. The volume of solution was

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reduced to <u>ca</u> 30 ml and 30 ml of hexane added, but no product was obtained. Again, the volume was reduced to <u>ca</u> 30 ml and the solution was cooled in a dry ice-acetone bath overnight. The crystals were filtered and dried <u>in</u> <u>vacuo</u> for 4 hr. The yield of crude product was 4.97 g (88.0%). Recrystallization was carried out with a mixture of methylene chloride-hexane (1 to 10 by volume), mp 117-118°.

<u>Anal</u>. Calcd for $C_{22}H_{38}O_4Cl_2Ti$: C, 54.44; H, 7.90; Cl, 14.60; Ti, 9.84. Found: C, 54.32; H, 8.06; Cl, 14.88; Ti, 10.13.

10. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium(IV) hexachloroantimonate(V)

Dichlorobis(dipivaloylmethanato) titanium(IV) (2.09 g, 0.00430 mole) was dissolved in 25 ml of glacial acetic acid heated at reflux temperature. A mixture of antimony(V) chloride (0.55 ml, 0.0043 mole) and 25 ml of acetic acid was added. The reaction yielded a yellow precipitate, which was separated from the mother liquid by filtration and dried <u>in vacuo</u> for 5 hr. The yield of crude product was 1.22 g (90.0%). The compound was recrystallized from methylene chloride-hexane (1 to 10 by volume); mp 239^{0} .

<u>Anal</u>. Calcd for $C_{33}H_{57}Cl_6O_6SbTi$: C, 42.50; H, 6.17; Cl, 22.99. Found: C, 42.32; H, 6.10; Cl, 22.99.

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11. <u>Dichlorobis(5,5-dimethyl-2,3-hexanedionato)</u>-<u>titanium(IV)</u>

A solution of titanium(IV) chloride (3.18 ml, 0.0114 mole) in 40 ml of dichloromethane was mixed with pivaloylacetone (10.0 ml, 0.0269 mole) and 40 ml of dichloromethane. The mixture was stirred and heated at reflux temperature for 1 hr. The volume of solvent was reduced to <u>ca</u> 30 ml by evacuation, and hot hexane was added. The mixture was cooled in a dry ice-acetone bath overnight. The orange crystals formed were separated by filtration, and the product was dried <u>in vacuo</u> for 4 hr. The yield of crude product was 4.09 g (89.0%). The compound was twice recrystallized from methylene chloride-hexane (1 to 20 by volume); mp 195°.

<u>Anal</u>. Calcd for $C_{16}H_{26}O_4Cl_2Ti$: C, 47.89; H, 6.55; Cl, 17.67; Ti, 11.93. Found: C, 47.89; H, 6.54; Cl, 17.67; Ti, 11.93.

12. Tris(5,5-dimethyl-2,3-hexanedionato) titanium(IV) Hexachloroantimonate(V)

Dichlorobis(pivaloylacetonato) titanium(IV) (4.99 g, 0.0124 mole) was dissolved in 40 ml of boiling glacial acetic acid. A solution of antimony(V) chloride (1.54 ml, 0.0124 mole) in 20 ml of glacial acetic acid was added. The mixture was heated at reflux temperature for 1.25 hr. The volume was reduced to ca 35 ml by vacuum distillation,

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<u>Anal</u>. Calcd for $C_{24}H_{39}O_6Cl_6SbTi$: C, 35.76; H, 4.88. Found: C, 35.68; H, 4.92.

C. Germanium Complexes

1. Dichlorobis(2,4-pentanedionato)germanium(IV)¹²

Germanium(IV) chloride (4.03 ml, 0.0241 mole) was added slowly to a solution of acetylacetone (4.88 g, 0.0481 mole) in 40 ml of dichloromethane. The mixture was heated at reflux temperature. During the course of the reaction, the flask was purged 5 times with dry nitrogen to remove evolved hydrogen chloride. The crystals formed were removed from the mother liquid by filtration and dried <u>in vacuo</u> for 1 hr. The product was recrystallized from dichloromethane-hexane; mp $241-242^0$, lit¹²: $236-240^0$.

2. <u>Tris(2,4-pentanedionato)germanium(IV) Hexachloro-</u> antimonate(V)¹²

A mixture of dichlorobis(acetylacetonatq)germanium(IV) (3.41 g, 0.0100 mole) and antimony(V) chloride (1.28 ml, 0.100 mole) in 50 ml of boiling chloroform produced a white precipitate upon the addition of diethyl ether (<u>ca</u> 20 ml). The product was recrystallized from chloroform-ether; mp, 161-162°; lit¹² 161-163°.

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3. Dichlorobis(5,5-dimethyl-2,3-hexanedionato)germanium(IV)

A mixture of pivaloylacetone (10.0 ml, 0.0691 mole) and germanium(IV) chloride (3.29 ml, 0.0289 mole) in 60 ml of chloroform was heated at reflux temperature for 110 hrs. The volume of the mixture was reduced to 20 ml by vacuum distillation, and hexane was added. White crystals were formed. The mother liquid was flitered three times to collect all the obtained product, which was very soluble even in hexane. The collected fractions were dried <u>in vacuo</u> for several hours. The yield in crude product was 6.67 g (54.0%). The product was recrystallized from hexanemethylene chloride; mp, 177-178.5⁰.

<u>Anal</u>. Calcd for C₁₆H₂₆O₄Cl₂Ti: C, 45.11; H, 6.16; Cl, 16.67; Ge, 17.04. Found: C, 45.11; H, 6.16; Cl, 16.67; Ge, 17.04.

4. <u>Tris(5,5-dimethyl-2,3-hexanedionato)germanium(IV)</u> hexachloroantimonate(V)

Dichlorobis(pivaloylacetonato) germanium(IV) (0.669 g, 0.00157 mole) was dissolved in 30 ml of glacial acetic acid. A solution of antimony(V) chloride (0.174 ml, 0.00157 mole) in 10 ml of glacial acetic acid was added with stirring. A crude precipitate formed immediately, it was collected and dried overnight <u>in vacuo</u>. The yield in crude product was 0.680 g (78.0%). Recrystallization from methylene chloridehexane gave a product with mp 117-120°.

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<u>Anal</u>. Calcd for $C_{24}H_{39}O_6Cl_6SbGe$: C, 34.60; H, 5.09. Found: C, 34.30; H, 5.00.

5. <u>cis-Dichlorobis (2,2,6,6-tetramethyl-3,5-heptane-</u> <u>dionato)germanium(IV)</u>

A mixture of germanium(IV) chloride (2.58 g, 0.0120 mole) and dipivaloylmethane (4.22 ml, 0.0240 mole) in 60 ml of ethanol-free chloroform was refluxed for 120 hr. The reaction flask was evacuated, and white crystals appeared. The crystals were dried <u>in vacuo</u> for 6 hr. The product was twice crystallized from hexane, mp $136-137^{\circ}$.

<u>Anal</u>. Calcd for $C_{22}H_{38}O_4Cl_2Ge$: C, 51.79; H, 7.52; Cl, 14.23. Found: C, 51.71; H, 7.73; Cl, 14.65.

6. <u>trans</u>-Dichloro(2,2,6,6-tetramethyl-3,5-heptanedionato)germanium(IV)

<u>cis</u>-Dichlorobis(dipivaloylmethanato)germanium(IV) (4.00 g, 0.00780 mole) was dissolved in 20 ml of methylene chloride, and 20 ml of hot hexane was added. After aging four days at room temperature, the solution produced transparent, colorless crystals, which were filtered and dried <u>in vacuo</u> (0.6554 g). Three additional crops of crystals were obtained from the mother liquid by removing <u>ca</u> 10-15 ml of solvent by vacuum distillation, adding a volume of hot hexane equal to the volume of solvent removed by distillation, and allowing the solution to age four days at room

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temperature. The total yield of <u>trans</u> product obtained in this manner was 2.1499 g.

7. <u>Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-</u> germanium(IV) hexachloroantimonate(V)

<u>cis</u>-Dichlorobis (dipivaloylmethanato)germanium (IV) (2.00 g, 0.00390 mole) and antimony (V) chloride (0.45 ml, 0.0039 mole) were mixed in 30 ml of hot glacial acetic acid. The white precipitate which formed was collected by filtration and dried <u>in vacuo</u> for 3 hr. The product was recrystallized from methylene chloride-hexane, mp, 281⁰; lit⁴⁸ 279⁰.

8. An Addition Compound formed with <u>cis</u>-Dichlorobis-(2,2,4,4-tetramethyl-3,5-heptanedionato)germanium(IV) and Antimony(V) Chloride

<u>cis</u>-Dichlorobis(dipivaloylmethanato)germanium(IV) (0.79 g, 0.0015 mole) dissolved in 10 ml of dichloromethane was cooled to -78° in a dry ice-acetone bath for 30 min, and a solution of antimony(V) chloride (0.197 ml, 0.00150 mole) in 10 ml of dichloromethane was added. The mixture was stirred for 10 additional minutes, and then the solvent was vacuum distilled. A light yellow product was obtained, which was dried <u>in vacuo</u> for 12 hr.

<u>Anal</u>. Calcd for $C_{22}H_{38}O_4Cl_7SbGe$: C, 32.65; H, 4.74. Found: C, 32.85; H, 4.95.



9. <u>Attempted Preparation of Dichlorobis(1,1,1-tri-</u> <u>fluoro-2,4-pentanedionato)germanium(IV)</u>

A mixture of germanium(IV) chloride (3.91 ml, 0.00970 mole), trifluoroacetylacetone (10.0 ml, 0.0196 mole) and 40 ml of methylene chloride was heated at reflux temperature. Addition of hexane caused the formation of an intractable brownish yellow oil. Additional solvent combinations such as benzene-hexane, methylene chloride-carbon tetrachloride and neat carbon tetrachloride failed to produce a crystalline product.

10. <u>Attempted Preparation of Dichlorobis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)germanium(IV)</u>

No reaction was observed on heating germanium(IV) chloride and hexafluoroacetylacetone for 20 days. It was hoped that dichlorobis(hexafluoroacetylacetonato)germanium(IV) could be prepared by simple methathesis reaction. The following reaction was attempted.

 $Cu(hfac)_2 + GeCl_4 \xrightarrow{CH_2Cl_2} CuCl_2 + Ge(hfac)_2Cl_2$

Bis(hexafluoroacetylacetonato)copper(II) (3.56 g, 0.00740 mole), which was prepared according to the procedure described by Beldford, Martin and Calvin³⁸, was dissolved in 50 ml of hot dichloromethane. Germanium(IV) chloride (0.85 ml, 0.0074 mole) was added and the mixture was heated at reflux temperature for 50 hr. After the addition of hexane green crystals formed. This product was dried in vacuo.

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its melting point matched the expected values for the copper diketonato complex.

11. Attempted Preparation of Tris(1,1,1,5,5,5-hexa-

fluoro-2,4-pentanedionato)germanium(IV) Iodide(I)

Fay³⁹ has found that the reaction of 1 mole of germanium(IV) iodide with 3 moles of acetylacetone produces the ionic compound [Ge(acac)₃⁺][I⁻] according to:

 $3 \text{Hacac} + \text{GeI}_4 \longrightarrow \text{Ge}(\text{acac})_3 I + 3 \text{HI}$.

In our case, it was hoped to prepare the hexafluoroacetylacetonato analog and then produce the hexachloroantimonate species:

 $\operatorname{Ge}(\operatorname{hfac})_{3}I + \operatorname{SbCl}_{6}^{-} \longrightarrow [\operatorname{Ge}(\operatorname{hfac})_{3}^{+}][\operatorname{SbCl}_{6}^{-}] + I^{-}$

Germanium(IV) iodide (10.18 g, 0.01755 mole) was dissolved in 60 ml of dichloromethane. Hexafluoroacetylacetone (7.54 ml, 0.0527 mole) was added and the mixture was heated at reflux temperature for 120 hr. A product was obtained, dried and recrystallized from methylene chloride-hexane. Its mp and ir spectrum showed it to be GeI₄.

12. <u>Disproportionation of Dichlorobis(2,2,6,6-tetra-</u> <u>methyl-3,5-heptanedionato)germanium(IV) Antimony(V)</u> <u>Chloride Adduct</u>

Dichlorobis (dipivaloylmethanato) germanium (IV) antimony (V) chloride adduct (1.0 g, 0.0012 mole) was dissolved in 20 ml
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of methylene chloride. The solution was gently stirred for 1 hr. A mixture of benzene-hexane was added and a white precipitate formed. This was separated from the mother liquid by filtration. The volume of solvent of the filtrate was reduced to ca 10 ml and a new fraction of benzene-hexane was added. More precipitate formed. It was filtered and dried along with the first collected solid. The solvent was distilled from the filtrate in vacuo to yield a light yellow solid in the reaction flask. This greasy, yellow product was washed several times with hexane-carbon tetrachloride then collected and dried in vacuo for 6 hr. The mp (281⁰) and nmr spectrum of the white solid suggested that this product was tris(dipivaloylmethanato)germanium(IV) hexachloroantimonate(V). The yellow product was identified as tetrachloro(2,2,6,6-tetramethyl-3,5-heptanedionato)antimony (V).

<u>Anal</u>. Calcd for $C_{11}H_{19}O_2Cl_4Sb$: C, 29.56; H, 4.29. Found: C, 29.91; H, 4.22.

D. Antimony Complexes.

1. Antimony(V) Chloride (2,4-pentanedione) adduct²⁰

Acetylacetone (3.5 ml, 0.034 mole) was added to a solution of antimony(V) chloride (4.0 ml, 0.032 mole) in carbon tetrachloride previously cooled to <u>ca</u> -80° in a dry ice-acetone bath. A yellow precipitate formed immediately; it was separated by filtration and dried <u>in vacuo</u> for 3 hr.

The product was recrystallized from cold methylene chloridehexane; mp, 101⁰.

2. <u>Tetrachloro(2,4-pentanedionato)</u> antimony(V)²⁰

Antimony(V) chloride (3.5 ml, 0.034 mole) and acetylacetone (8.0 ml, 0.064 mole) were heated at reflux temperature in <u>ca</u> 40 ml of carbon tetrachloride for 4 hr. Yellow crystals were obtained when the solution was cooled at room temperature. The precipitate was recrystallized from chloroform-hexane; mp, $128-130^{\circ}$, $1it^{20}$ 127° .

3. <u>Antimony(V) Chloride (2,2,6,6-tetramethyl-3,5-</u> heptanedione) Adduct

A solution of dipivaloylmethane (2.50 ml, 0.0136 mole)in dichloromethane $(\underline{ca} \ 10 \text{ ml})$ was cooled in dry ice for 0.5 hr. A solution of antimony(V) chloride (1.74 ml, 0.0136 mole) in 5 ml of dichloromethane was added dropwise. The mixture was stirred for 0.1 hr and hexane was added. A white product began to precipitate. It was filtered and dried <u>in vacuo</u> for 2 hr. The product was recrystallized three times by dissolving in benzene at room temperature and adding hexane; mp, $116-117^{0}$.

<u>Anal</u>. Calcd for $C_{11}H_{20}O_2Cl_5Sb$: C, 27.38; H, 4.18; Cl, 36.75. Found: C, 25.94; H, 4.27; Cl, 37.58.

4. A S adduct (with an mole) in in the n rcom tem After tw temperat is tenta methy1-3 5. As in 10 m bath for ml, 0.00 slowly. removed White c with the Eq mcle) a chlorom

4. <u>Reaction of Antimony(V) Chloride - (2,2,6,6-tetra-</u> <u>methyl-3,5-heptanedione) Adduct and Tetramethylsilane</u>

A solution of dipivaloylmethane-antimony(V) chloride adduct (0.48 g, 0.0010 mole) in dichloromethane was mixed with an equal volume of tetramethylsilane (0.088 g, 0.0010 mole) in the same solvent at room temperature. The change in the nmr spectrum of the mixture as a function of time at room temperature will be presented in the Discussion Section. After two days, the solvent was vacuum distilled at room temperature and a white, solid residue remained. This solid is tentatively identified as methyltrichloro(2,2,6,6-tetramethyl-3,5-heptanedionato)antimony(V).

5. <u>Reaction of Antimony(V) Chloride with Tetramethyl-</u> silane

A solution of tetramethylsilane (1.00 ml, 0.00736 mole)in 10 ml of dichloromethane was cooled in a dry ice-acetone bath for 1 hr. A solution of antimony(V) chloride (0.950 ml, 0.00736 mole) in 10 ml of dichloromethane was added slowly. The mixture was stirred for 1 hr. The solvent was removed from the reaction flask by evacuation to yield a white crystalline solid with mp 74°. The mp is in agreement with the mp of SbCl₃.

Equal volumes of antimony(V) chloride (0.30 g, 0.0010 mole) and tetramethylsilane (0.088 g, 0.0010 mole) in dichloromethane were mixed in a nmr sample tube and the other by-products were identified from their ¹H nmr lines. They were: trimethylchlorosilane and chloromethane.

E. Physical Measurements

1. Infrared Spectra

Infrared spectra in the region $4000-750 \text{ cm}^{-1}$ were recorded with a Perkin-Elmer Model 237 B grating infrared spectrophotometer. Polystyrene film was used to calibrate the instrument. The accuracy of the reported frequencies in this range is estimated to be \pm 5 cm⁻¹. The infrared spectra of the studied compounds were obtained as nujol mulls between KBr plates. Each compound was carefully examined in the region 3800-3000 cm⁻¹ to verify the absence of water and hydroxo-groups. All mulls were prepared in a glove bag purged with dry nitrogen.

2. <u>Nuclear Magnetic Resonance Spectra</u>

Proton nuclear magnetic resonance spectra were obtained with a Varian A-56/60-D high resolution spectrophotometer operated at 60 MHz. For variable temperature work, the probe temperature was controlled to within \pm 0.5° by a Varian temperature controller, Model V-6040. Temperatures were determined by measuring the chemical shift differences (Δv in Hz) for methanol (low temperatures) and 1,2-ethanediol (elevated temperatures) and applying the equations derived by Van Geet⁴⁰. These are: 4 a) For methanol, a quadratic equation fits the data with an error of 0.6^{0} K for the temperature range $220-330^{0}$ K:

T = 435.5 - 1.193 (Δv) - 29.3 ($10^{-2} \Delta v$)²

b) For ethylene glycol, the chemical shift between the CH_2 and the OH groups of glycol fits a straight line with an error of 0.3^{0} K over the range $310-410^{0}$ K:

$$T = 466.0 - 1.694 (\Delta v).$$

At room temperature, these results agree with the calibration charts supplied by Varian Associates within $1^{\circ}K$. The sweep width was calibrated by the sideband method. Relative signal intensities were determined by electronic integration. Small radio frequency fields were employed to avoid saturation effects. It was necessary to resort to low filter band width settings and sweep times where the spectrum amplitude settings were high.

Concentration of the samples varied between 4 and 12% (w/v). Since the compounds reported here are very sensitive to atmospheric moisture in the solid state and in solution, the preparation of the solutions was done in a dry nitrogen-filled glove bag. The compound was weighed into a small glass vial, and the solvent added with a one milliliter syringe. Sometimes, the vial was heated gently to affect dissolution, and the solution was transferred to nmr tube with the syringe. Nmr samples run at room temperature were stoppered with pressure caps. Samples for variable temperature work were frozen in liquid nitrogen, and the tube was sealed with a flame.

III. RESULTS AND DISCUSSION

A. Dihalobis(diketonato)metal(IV) Complexes

1. <u>Preparative Chemistry</u>.- Coordination compounds of titanium(IV) containing β -diketonate ligands have been known several years. The reaction of excess acetylacetone or benzoylacetone and titanium(IV) chloride in glacial acetic acid or chloroform was first studied by Dilthey¹¹ who was able to identify compounds with the empirical formula Ti(dik)₂X₂:

 $TiCl_4 + 2H(acac) \longrightarrow Ti(acac)_2Cl_2 + 2HCl$.

From our experimental work we have found that titanium tetrachloride undergoes an analogous reaction with dibenzoylmethane, trifluoroacetylacetone, hexafluoroacetylacetone, pivaloylacetone and dipivaloylmethane. Morgan and Drew¹³ first reported that germanium tetrachloride and acetylacetone undergo a similar reaction in anhydrous solvents to produce Ge(acac)₂Cl₂ in quantitative yield. By similar techniques we have achieved the preparation of some analogous compounds with pivaloylacetone and dipivaloylmethane. Both germanium and titanium complexes hydrolyse readily in solution when exposed to the atmosphere. Proton

nmr spectra of hydrolyzed products show resonance lines characteristic of the free ligands which increase as decomposition proceeds.

Germanium tetrachloride is considerably less reactive than titanium tetrachloride toward the diketone ligand. For example, the reaction of titanium (IV) chloride and pivaloylacetone in refluxing methylene chloride is complete within two hours. For the germanium analog the reaction under similar conditions requires ca. five days. In addition, the reaction of GeCl₄ and H(dpm) is reversible. For example, the nmr spectrum of a benzene solution containing 9.44 x 10^{-3} M Ge (dpm)₂Cl₂ and 0.182 M anhydrous HCl shows a gradual decrease in the intensity of lines characteristic of the complex and simultaneous increase in the intensity of lines due to the free ligand. After 2 days at room temperature no Ge (dpm) 2Cl2 could be detected in the solution. In addition, Ge (dpm)₂Cl₂ is not observed on heating 5 x 10^{-4} <u>M</u> GeCl₄ and 1 x 10^{-3} <u>M</u> H(dpm) in benzene in a sealed tube at 60° for 6 days. Based on these latter results the equilibrium constant [Ge(dpm)₂Cl₂][HCl]²/ $[GeCl_4][H(dpm)]^2$ is estimated to be less than 10^{-6} at 60^0 . The reaction of TiCl₄ and H(dpm), however, must strongly favor formation of Ti(dpm)₂Cl₂, because no free ligand could be detected in a 0.2 M Ti (dpm)₂Cl₂ solution in benzene satuarated with HCl after 8 days at room temperature. Also, the solution remained bright orange after this time period. The greater thermodynamic stability of titanium β -diketonates

is also reflected in the fact that TiCl₄ and hexafluoroacetylacetone undergo vigorous exothermic reaction in methylene chloride solution at room temperature, whereas no reaction is observed for GeCl₄ and neat hexafluoroacetylacetone after 20 days at 70° . It is known that group IV elements can increase their coordination number beyond four due to the availability of empty d orbitals⁴¹ for both σ and π bonding.⁴⁵ For d²sp³ hybridization, titanium makes use of 3d orbitals, while germanium must use higher-energy 4d orbitals. In addition, Nakamoto⁴⁷ has found that substitution of the methyl groups of acetylacetone by CF_3 groups has influence on bonding through oxygen. The inductive effect of the CF₃ group strengthens the C=C and C=O bonds and weakens the metal-oxygen bonds. The higher hybridization energy of germanium, the low chelating ability of hexafluoroacetylacetone, and the larger mean thermochemical Ge-Cl bond energy could explain the reluctance of GeCl₄ and hexafluoroacetylacetone to undergo reaction.

Several authors have reported the isolation of trishalo-(diketonato) titanium(IV)^{42,43} and trishalo(diketonato) zirconium(IV) complexes⁴⁴ produced by reaction of one mole of free ligand and one mole of the metal tetrahalide in anhydrous solvents. Similar conditions and molar ratios were used in an attempt to prepare $Ge(dpm)Cl_3$, but a product with the same proton nmr chemical shifts of <u>cis</u>-Ge(dpm)₂Cl₂ was isolated.

2. Stereochemistry.- The stereochemistry of the $M(dik)_2Cl_2$ compounds in solution was studied by ¹H nuclear magnetic resonance spectroscopy. Figure 2 shows the possible octahedral configurations for an $M(pvac)_2X_2$ complex. Because the diketonate ligand is unsymmetrical, there are five possible isomers. Three of these have halogen atoms in <u>cis</u> positions, and two have halogens in <u>trans</u> positions. We shall refer to the isomers by three <u>cis</u> or <u>trans</u> prefixes which specify first the relative position of the halogens, then the relative position of the R groups, and finally the relative orientation of the R' groups.

The <u>cis,cis,cis</u> isomer (point group C₁) has no symmetry and, therefore, may give rise to two R, two R' and two ring proton resonances. The other four isomers, cis, cis, trans (point group C₂), cis, trans, cis (C₂), trans, <u>cis</u>, <u>cis</u> (C_{2v}) and <u>trans</u>, trans, trans (C_{2h}) , all possess at least a two fold axis. These isomers, as Figure 2 indicates, should give a single resonance for each type of terminal group. If the diketonate ligands are symmetrical $(\mathbf{R} = \mathbf{R'})$, two octahedral isomers are possible. The three cis possible isomers described for an asymmetric diketonate ligand become equivalent and give only one cis isomer, which possesses a two fold rotation axis. This isomer has two nonequivalent sets of R groups (equatorial and axial) but only one type of ring proton. In the trans isomer (point group D_{2h}) there is a single R group and a single ring proton environment.

Figure 2. Possible isomers for a $M(pvac)_2X_2$ complex. The R and R' indicate the distinguishable terminal group on the diketonate ligand.



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Proton nmr spectra of $Ti(acac)_2X_2$ complexes are known to give single sharp resonance lines for the methyl groups and the ring protons at room temperature. This could give rise to erroneous stereochemical interpretations since the presence of a single methyl line suggests that the trans isomer would be the stable form in solution. However, the possibility of a rapid interchange of the diketonate ligands which averages nonequivalent methyl proton environments cannot be discarded. Fay and Lowry²⁹ have shown that such a differentiation could be made by variable temperature nmr studies. As temperature is lowered, the methyl resonance broadens and then splits into two equally intense lines while the ring proton resonance remains sharp. This indicates that the complexes in solution have the cis configuration. As the temperature increases coalescence of the two methyl lines occurs due to a rapid exchange process which interchanges methyl groups between the axial and equatorial positions of the cis isomer. Titanium complexes with unsymmetrical ligands, such as Ti(bzac)₂Cl₂, show sharp single lines at room temperature for the methyl and ring proton resonances. As it has been shown five isomeric forms are possible. Fay and Sarpone³⁰ have studied this complex at low temperatures and have concluded that the three cis siomeric conformations are the stable ones in solution. Previous work on labile Ti(acac)₂(OR)₂ compounds²⁵ has shown that they also adopt the cis configuration. For Ti(acac)₂(O-But)₂ the two equivalent methyl lines are

visible below 53° , where they then coalesce. Though steric factors would favor the <u>trans</u> isomer, any difference between oxygen and chlorine in π -bonding ability would favor the <u>cis</u> conformation, because more efficient use would be made of the t_{2 α} orbitals on the metal.

Ti(dpm)₂Cl₂ and Ti(pvac)₂Cl₂ show single terminal group and ring proton resonance lines in methylene chloride solution at room temperature. As the temperature is decreased, however, the terminal group lines for both compounds broaden and then split into two or more lines. For $Ti(dpm)_2Cl_2$, two sharp t-butyl lines of equal intensity are observed at -70⁰ (Figure 3). The ring proton line remains sharp. This suggests that Ti(dpm)₂Cl₂ adopts the <u>cis</u> conformation in solution; and that the line broadening is due to a rearrangement process which averages the nonequivalent terminal group environments. As shown in Figure 4. $Ti(pvac)_2Cl_2$ gives rise to four methyl proton lines, three t-butyl proton lines and three ring proton lines at -80° . The presence of 4 methyl proton lines is consistent with the existence of all three isomers in which the chlorine atoms are in a cis position. The presence of only three lines in the -CH= and t-butyl regions may be due to the superposition of two lines with approximately the same chemical shift.

Dichlorobis(dipivaloylmethanato)germanium(IV), as prepared by the previously described method, yields a product that gives rise to two <u>t</u>-butyl resonances of nearly equal intensity and a single ring proton line at room

Figure 3. <u>t</u>-Butyl proton resonance lines of Ti(dpm)₂Cl₂ in dichloromethane, concentration is 10g/100 ml solvent (60 MHz).

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Figure 4. Proton magnetic resonance spectrum of Ti(pvac)₂Cl₂ in dichloromethane at -80° (100 MHz); concentration is 11.7 g/100 ml solvent.

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1080Hz 126.7 Hz 1 218.9 Hz 2305 Hz H 618.5 Hz

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temperture. This is mostly the cis siomer. By careful recrystallization of the cis species, however, we have achieved the separation of the trans compound which shows a single tert-butyl line and has the same chemical shift of the low field line of the cis isomer. Solvents such as 1,4-dibromobutane, deuterochloroform, benzene and dichloromethane were unable to resolve the superimposed t-butyl lines in the cistrans equilibrium mixture. The trans ---> cis isomerization process occurring for this system has been studied and it will be discussed in another section. Figure 5 shows the ¹H nmr spectra of the <u>cis</u> and <u>trans</u> $Ge(dpm)_2Cl_2$ isomers. The nmr spectrum of Ge(pvac)₂Cl₂ in benzene shows six different tert-butyl lines, six methyl resonances and five different ring protons which indicates that all five isomers are in equilibrium. Figure 6 shows the ¹H nmr spectra of the three different regions of Ge(pvac)₂Cl₂ at room temperature in benzene solution. Since time-averaged lines are not observed for the germanium compounds at room temperature, the chelate rings undergo configurational changes more slowly than in the corresponding titanium compounds.

Table II summarizes the chemical shifts of $M(dik)_2X_2$ complexes. The nmr spectrum of $Ge(acac)_2Cl_2$ in deuterochloroform solutions has been studied by Smith and Wilkins.²⁴ Three methyl resonance lines were visible at τ 7.77, 7.89 and 7.96 in the methyl region and only one ring proton signal at τ 4.24. The peaks at τ 7.77 and 7.89 were assigned to the methyl resonances of the <u>cis</u> species. The signal at

Figure 5. Nmr spectra of

- (a) $\underline{\text{trans}}$ -Ge (dpm) $_2$ Cl₂ and
- (b) an equilibrium mixture of <u>cis</u> and <u>trans</u> Ge $(dpm)_2Cl_2$ in benzene at **39⁰**.

Solution (a) is saturated; sample is 5 min old. Solution (b) was equilibrated at room temperature; concentration is 5 g/100 ml. Figure 6. ¹H nmr spectrum of Ge $(pvac)_2Cl_2$ in benzene solution at 39^0 ; concentration is 12 g/100 ml of solvent (60 MHz). The line marked X is due to a trace of free ligand.



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complexes ^a , ^b
M (diketonate) ₂ X ₂
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Table

Compound	Solvent	conc. ^c	-CH=		-CH ₃		-C4H9
Ti (acac) ₂ Cl ₂	CH ₂ C1 ₂	7.0	-5.99		-2.12		
Ge (acac) 2C12	CH ₂ Cl ₂	10	-5.49,	-5.75	-2.01,	-2.07	
Ti (bzbz) ₂ Cl ₂	CH ₂ C1 ₂	4.0	-7.35				
Ti (dpm) ₂ C1 ₂	CH ₂ C1 ₂	10	-6.15				-1.18
Ge (dpm) 2 C1 2	CH2C12	10	-5.94				-1.10, -1.25
Ti (bzac) ₂ Cl ₂	CH2C12	4.0	-6.69		-2.29		
Ge (bzac) ₂ C1 ₂	CDC13	4.0	-6.43		-2.43,	-2.41	
					-2.39,	-2.24	
Ti (pvac)2Cl2	CH2C12	10	-6.06		-2.16		-1.15
Ge (pvac)2C12	benzene	12	-5.45,	-5.39,	-1.64,	-1.66,	-0.964, -0.963,
			-5.38,	-5.37,	-1.62,	-1.59,	-1.12, -1.11,
			-5.35		-1.57,	-1.56	-1.10, -1.09
^a Proton shift	s are in pr	pm (± 0.01	(0) relat	ive to	an inte	rnal ref	erence of

tetramethy lsilane.

^bTemperature is **39⁰.**

^Cconcentration of solutions is given in grams of compound/100 ml of solvent.

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 τ 7.96 was given by the enol form of free acetylacetone. A shoulder on the high field side of the τ 7.77 line was assigned to the keto form of the free ligand. We have found that ¹H nmr spectra of Ge(acac)₂Cl₂ solutions in dichloromethane show four lines in the methyl region at τ 7.99, 7.93, 7.82 and 7.83 and three ring proton resonances at τ 4.51, 4.25 and 4.22 (see Figure 7). The methyl lines at τ 7.93 and 7.82 and the γ -resonance at τ 4.25 are assigned to the cis molecule. The resonances at τ 7.99 and 4.51 are assigned to the methyl protons and the ring proton of the free ligand, respectively. The lines at τ 7.83 and 4.22 are assigned to the trans isomer. The line at τ 7.83 is simply too intense to be due to the keto form of the free ligand. A separation of the isomers may be possible by methods similar to the ones used for the separation of the cis and trans isomers of Ge (dpm) 2Cl2. It should be noted that Osipov and co-workers⁵³ have also assigned a <u>cis</u> configuration to Ge $(acac)_2Cl_2$ and several other Ge $(dik)_2X_2$ complexes based on dipole moment measurements.

Previous studies of Sn $(acac)_{2}X_{2}^{28,52}$ and Sn $(acac)_{2} (C_{6}H_{5})Cl^{24}, ^{51}$ suggest that these molecules exist almost exclusively in the <u>cis</u> form. The report by Kawasaki and Tanaka⁵⁰ that Sn $(acac)_{2}Cl_{2}$ has a <u>trans</u> configuration with localized double bonds in the acetylacetonate rings has been proved to be erroneous.²⁸ <u>Trans</u> configurations have been established only for dialkyl tin (IV) and lead (IV) complexes of the type $R_{2}M(dik)_{2}^{26,49}$. In view of the

Figure 7. Nmr spectra of:

- (a) Acetylacetone in dichloromethane; concentration \underline{ca} 5 g/100 ml (60 MHz).
- (b) Ge $(acac)_2Cl_2$ in dichloromethane; concentration <u>ca</u> 5 g/100 ml (60 MHz).



appreciable equilibrium concentration of <u>trans</u> isomer for $Ge(dpm)_2Cl_2$ and $Ge(acac)_2Cl$ discussed above, it would be interesting to re-investigate, the stereochemistry of the $Sn(acac)_2X_2$ complexes.

B. <u>Tris (β-diketonato) metal (IV)</u> Hexachloroantimonates

1. Preparative Chemistry

Reaction of $M(dik)_2Cl_2$, where M = Ti, Ge and dik = acac, bzbz, dpm or pvac, and antimony(V) chlorides yielded the corresponding $[M(dik)_3]^+$ complexes:

 $3M(dik)_2Cl_2 + 2SbCl_5 \longrightarrow 2[Ti(dik)_3^+][SbCl_6^-] + TiCl_4.$

The reaction of a $M(dik)_2Cl_2$ and a Lewis Acid has been used by numerous earlier workers for preparation of $M(dik)_3^+$ complexes^{11,12,17,54}. The reaction of Ti(hfac)_2Cl_2 or Ti(tfac)_2Cl_2 and SbCl_5 did not yield the desired tractable product. That the reaction does occur, however, was evidenced by the isolation of crystalline TiCl_4 \cdot SbCl_5 \cdot 2(C₂H₅)₂O from the reaction mixture.

The reaction of $Ge(dpm)_2Cl_2$ and $SbCl_5$ was studied in considerable detail in an attempt to understand the role of antimony(V) chloride toward the formation of the tris(diketonato)germanium(IV) hexachloroantimonate complex.

Solutions of antimony pentachloride and dichlorobis-(dipivaloylmethanato)germanium(IV) in dichloromethane were mixed in nmr sample tubes and their spectral changes observed

as a function of time. When a 3:2 molar ratio of Ge(dpm)₂Cl₂ and SbCl₅ were mixed at room temperature in methylene chloride, the t-butyl region of the nmr spectrum, as well as the -CH= region, showed only one resonance line. The two resonance lines were characteristic of $[Ge(dpm)_3]^+$. Low temperature nmr spectra showed the same features found at room temperature, and the intensity of the peaks did not show any change several days after preparation. When the molar ratio between the reactants was one to one, however, the two t-butyl signals of cis-Ge(dpm)₂Cl₂ disappeared immediately and a new signal appeared. The new single resonance decreased in intensity with time, while two other lines at higher fields increased in intensity (see Figure 8). After three hours the spectrum consisted of two t-butyl and two ring proton resonance lines. It was hoped that the compound which showed an initial t-butyl signal when equal molar amounts of antimony (V) chloride and dichlorobis (di pivaloylmethanato)germanium(IV) were mixed could be isolated and consequently identified. Mixing of solutions of the reactants at low temperature $(\underline{ca} - 80^{\circ})$ and consequent distillation of the solvent yielded a product whose carbon and hydrogen analyses indicated a 1:1 adduct, Ge(dpm)₂Cl₂, SbCl₅. The isolated product could adopt any one of the structures shown in Figure 9. The attachment of one antimony pentachloride molecule to one of the chlorine atoms of Ge(dpm)₂Cl₂ could give an octahedral structure with four nonequivalent tert-butyl environments and two different ring

Figure 8. Nmr spectral changes for an equal molar mixture of Ge(dpm)₂Cl₂ and SbCl₅ in dichloromethane at room temperature.

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Figure 9. Possible structures for the compound Ge(dpm)₂Cl₂·SbCl₅.

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proton resonances (structure I) or a structure in which the chelate rings are in <u>trans</u> positions to each other (structure II), which would give rise to a single <u>tert</u>butyl line and a single C-H resonance line. Structures (III) and (IV) show two pentacoordinated ionic species which would give rise to three and two <u>tert</u>-butyl ¹H signals. The nmr spectrum at <u>ca</u> -80° suggests structure (II), although a rapid rearrangement of one of the other isomers would give the same result. Whether or not the adduct is dissociated might be determined by Raman and far infrared absorption studies.

The disproportionation of the isolated $Ge(dpm)_2Cl_2$. SbCl₅ in methylene chloride gives disproportionation products with the same chemical shifts as the two higher field <u>t</u>-butyl resonance lines shown in Figure 8. The nmr spectrum of the disproportion products is shown in Figure 10. The highest field lines in the -CH= and <u>t</u>-butyl regions correspond to the chemical shifts of $[Ge(dpm)_3]^+$. The remaining -CH= and <u>t</u>-butyl lines represent a new compound. The molar ratio of the two products is 3:1, as judged from the relative intensities of the <u>t</u>-butyl lines. Separation of the disproportionation products by fractional crystallization and subsequent elemental analysis indicated that the new compound was SbCl₄(dpm). Based on these results the following sequence of reactions can be suggested for a mixture of Ge(dpm)₂Cl₂ and SbCl₅:

Figure 10: Ring proton and <u>tert</u>-butyl resonance lines (60 MHz) of the products obtained by the disproportionation reaction of $Ge(dpm)_2Cl_2 \cdot SbCl_5$ in methylene chloride solution at 40° .



(1)
$$\operatorname{Ge}(\operatorname{dpm})_2\operatorname{Cl}_2$$
 + $\operatorname{SbCl}_5 \xrightarrow{v. \text{ fast}} \operatorname{Ge}(\operatorname{dpm})_2\operatorname{Cl}_2 \cdot \operatorname{SbCl}_5$

$$(2) 2\operatorname{Ge}(\operatorname{dpm})_{2}\operatorname{Cl}_{2} \cdot \operatorname{SbCl}_{5} \xrightarrow{\operatorname{slow}} [\operatorname{Ge}(\operatorname{dpm})_{3}] [\operatorname{SbCl}_{6}] + \operatorname{SbCl}_{4}(\operatorname{dpm}) + \operatorname{GeCl}_{4}.$$

Failure to observe formation of $SbCl_4(dpm)$ in a 3:2 molar mixture of $Ge(dpm)_2Cl_2$ and $SbCl_5$ suggests that the following reaction is fast:

$$\operatorname{Ge}(\operatorname{dpm})_2\operatorname{Cl}_2 + \operatorname{SbCl}_4(\operatorname{dpm}) \longrightarrow [\operatorname{Ge}(\operatorname{dpm})_3^+] [\operatorname{SbCl}_6].$$

In conjunction with the study of the reaction of $Ge(dpm)_2Cl_2$ and $SbCl_5$, several reactions of $SbCl_5$ and β -diketones were investigated. These will be described in a later section.

2. Stereochemistry

¹H nuclear magnetic resonance was used to study the stereochemistry of the $[Ge(dik)_3]^+$ complexes. Coordination compounds in which the central atom is bound to three symmetrical β -diketonate ligands can exist in only one isomeric form which gives a single ring proton line and a single resonance for the terminal group in the diketone ligand. If the three bidentate ligands are unsymmetrical ($R \neq R'$), as in $[Ge(pvac)_3]^+$, then two geometric isomers may exist. If the distinguishable ends of an unsymmetrical bidentate ligand are represented by R and R' (see Figure 11) the R groups may be in the 1,2,3- or 1,2,6- positions. We shall refer to the isomer with R groups in the 1,2,3-positions as the <u>cis</u> isomer and the isomer with R groups in the
Figure 11. Possible <u>cis</u> and <u>trans</u> isomers of a trischelate complex in which the ligand is bidentate and unsymmetrical.





1,2,6-positions as the <u>trans</u> isomer. The <u>cis</u> isomer has a three fold rotation axis; whereas the <u>trans</u> isomer has no symmetry (group point C_1). In the <u>cis</u> isomer, therefore, all three chelate rings are in identical environments, while in the <u>trans</u> isomer all three chelate rings are in different environments. Thus, in the case of $[Ge(pvac)_3]^+$, one should observe a proton resonance spectrum for the <u>cis</u> isomer which exhibits a single <u>t</u>-butyl, methyl, and ring proton resonance, while the spectrum of the <u>trans</u> isomer should give rise to three <u>t</u>-butyl, methyl, and ring proton lines.

Nuclear magnetic resonance studies of tris chelated ionic complexes has never been reported. We have found that the hexachloroantimonates of $\text{Ti}(\text{bzbz})_3^+$, $\text{Ge}(\text{bzbz})_3^+$, $\text{Ti}(\text{acac})_3^+$, $\text{Ge}(\text{acac})_3^+$, $\text{Ti}(\text{dpm})_3^+$ and $\text{Ge}(\text{dpm})_3^+$ yield the characteristic lines expected from stereochemical considerations, but their resonances are shifted to lower fields, because of the positive charge on the complexes.

As shown in Figure 12 nuclear magnetic resonance spectrum at 100 MHz of $[Ge(pvac)_3]^+$ in methylene chloride shows three <u>t</u>-butyl resonance lines, three methyl lines and two ring proton lines. If a mixture of <u>cis</u> and <u>trans</u> isomers were present, four resonance signals should be visible for each region. Integration of the ring protons gives a ratio of 2.9 to 1.0 which suggests that a mixture of <u>cis</u> and <u>trans</u> isomers exists at room temperature. Failure to observe the expected number of lines in each region is attributed to

Figure 12. ¹H nmr spectrum (100 MHz) of $[Ge(pvac)_3][SbCl_6]$ at room temperature and at -80° . Concentration is 10 g/100 ml of methylene chloride.



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overlapping of lines with nearly the same chemical shifts. It is interesting to note that only one rather broad line is observed in each region at -80° (cf Figure 14). Apparently, the chemical shift differences for the nonequivalent proton environments in the <u>cis</u> and <u>trans</u> isomers decreases with decreasing temperature.

The nmr spectrum at 100 MHz of $[\text{Ti}(pvac)_3]^+$ in methylene chloride solution shows one sharp line in the <u>t</u>-butyl, methyl and ring proton regions. No change in the spectrum is observed at room temperature. In view of the result obtained for $[Ge(pvac)_3]^+$, it would be unreasonable to conclude that only the <u>cis</u> isomer is present. The existence of single lines in each proton region at room temperature may well be due to stereochemical rearrangement processes which average the nonequivalent environments of the <u>cis</u> and <u>trans</u> isomers. At -80° , however, where such rearrangement processes should be slow, the presence of one <u>t</u>-butyl, methyl, and ring proton line is probably due to small chemical shift differences, as was observed for the stereochemically rigid $[Ge(pvac)_3]^+$ at -80° .

Table III summarizes the chemical shifts of the $M(dik)_3^+$ compounds at room temperature.

Table III. Chemical shifts for $[M(dik)_3][SbCl_6]$ compounds at 37 ± 2⁰.^a

Compound	-C ₄ H ₉ ^b	-CH3 ^b	-с-н= ^b
[Ti(acac) ₃] [SbCl ₆]		7.75	3.80
[Ge(acac) ₃] [SbCl ₆]		7.76	4.03
$[\texttt{Ti}(\texttt{dpm})_3]$ [SbCl ₆]	8.78		3.61
$[Ge(dpm)_3]$ [SbCl ₆]	8.78		3.81
[Ti(pvac) ₃] [SbCl ₆]	8.82	7.71	3.72
[Ge(pvac) ₃] [SbCl ₆]	8.80, 8.81	8.54, 8.55, 8.53	3.93, 3.96

^aMeasured at 60.0 MHz. With TMS as internal reference.

^bAll shifts are reported as τ values. Solvent is methylene chloride; concentration is 10 g/100 ml of solvent.

C. <u>Kinetics of Isomerization of trans-Ge(dpm)</u>₂Cl₂

The rate of isomerization of $\underline{\text{trans}}-\text{Ge}(dpm)_2\text{Cl}_2$ was studied in anhydrous benzene. In a typical kinetic run, the $\underline{\text{trans}}$ isomer was dissolved in benzene in an nmr tube to give a solution containing <u>ca</u> 5 g of solute per 100 ml of solvent. The tube was placed in the nmr spectrometer probe at a known temperature. Approximately five minutes was allowed for temperature equilibrium. The rate of change of the molar fraction of the $\underline{\text{trans}}$ and <u>cis</u> isomers was determined by electronic integration of their $\underline{\text{t}}$ -butyl proton resonance signals. Since the resonance line of the $\underline{\text{trans}}$ isomer was superimposed on one of the two, equally intense resonance components of the <u>cis</u> isomer, the molar fraction of <u>cis</u> isomer was determined by doubling the intensity of the non-superimposed cis line.

In order to determine the rate law for the isomerization process, it was necessary to determine the temperature dependence of the equilibrium constant $K_{eq} = [cis]/[trans]$. Mean values of K_{eq} for seven temperatures in the range 28-75° are given in Table IV. The slope and intercept of a log K_{eq} \underline{vs} 1/T plot of all 105 data points gave $\Delta H =$ -0.433 \pm .004 kcal/mole and $\Delta S = +2.349 \pm 0.293$ eu.

The kinetic studies suggested a first order reversible process for the isomerization:

trans-Ge(dpm)₂Cl₂
$$\xrightarrow{k_1}{k_2}$$
 cis-Ge(dpm)₂Cl₂.

Table IV. Temperature dependence of K for Ge(dpm)₂Cl₂ in benzene solution.

Temperature	K _{eq} a		
74.4	6.04 ± .08		
64.0	$6.20 \pm .04$		
60.1	6.33 ± .08		
53.3	6.40 ± .07		
43.4	6.40 ± .07		
37.6	6.59 ± .01		
28.5	6.67 ± .13		

^aAverage values obtained by electronic integration of 15 spectral copies at each temperature are reported. Errors are for one standard deviation. The integrated form of the rate law for such a process is given by

$$\log[f_{trans} - (\frac{1}{K_{eq}}) f_{cis}] = -[k_1 + k_2] t/2.303$$

where f_{trans} and f_{cis} are the instantaneous molar fractions of the respective isomers, and $K_{eq} = k_1/k_2$. Values of k_1 and k_2 at six different temperatures were obtained from the slope of the least squares line of a $\log[f_{trans} - (\frac{1}{K_{eq}}) f_{cis}] \underline{vs}$ time plot. Approximately 36 data points were obtained at each temperature. The plots are shown in Figure 13. Values of k_1 and k_2 for the isomerization reaction are given in Table V. An Arrhenius plot for the forward reaction (see Figure 14) gave $E_a = 30.61 \pm 5.43$ kcal/mole and $\Delta S^* = 23.22 \pm 8.07$ eu. Similar plots for the reverse reaction gave $E_a = 31.05 \pm 5.41$ kcal/mole and $\Delta S^* = 20.88 \pm 8.00$ eu. In each case, the value of ΔS^* was calculated at 25° from the equation

$$\Delta S^* = R \ln A - R [1 + \ln \frac{kT}{h}]$$

where A is the Arrhenius frequency factor.

There are four mechanisms which can be proposed for the isomerization process: (1) dissociation of chloride ion to give a five-coordinated germanium intermediate, (2) complete dissociation of a dpm ligand to give a four-coordinated, (3) rupture of one Ge-O bond to give a five-coordinated germanium intermediate containing a dangling or unidentate dpm ligand, and (4) an intramolecular twisting

Figure 13. Plots of $\log[f_{trans} - (\frac{1}{K_{eq}})f_{cis}] \underline{vs}$ time for the <u>trans</u> \longrightarrow <u>cis</u> isomerization of $Ge(dpm)_2Cl_2$ in benzene at various temperatures. Concentration is <u>ca</u> 5.0 g/100 ml solvent.



MINUTES

\underline{CIS} isomerization of $Ge(dpm)_2CI_2$ in denzene.					
Temperature	$10^{5}k_{1}$, sec ⁻¹	$10^{5}k_{2}$, sec ⁻¹			
16.8	1.37	.199			
21.9	5.07	.747			
26.8	15.6	2.30			
28.1	22.7	3.39			
34.2	33.1	5.02			

56.8

8.68

Table V. Temperature dependence of the forward and reverse first order rate constants for <u>trans</u> cis isomerization of Ge(dpm)₂Cl₂ in benzene.

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37.6

Figure 14. Arrhenius plot for the isomerization of <u>trans</u>-Ge(dpm)₂Cl₂ in benzene.

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mechanism. In dichloromethane, which has a higher dielectric constant than benzene, the isomerization of the <u>trans</u> isomer is complete in less than one minute at room temperature. A more polar solvent should lower the energy required to achieve charge separation in a dissociative process. Thus an intramolecular twisting mechanism is not favored. None of the dissociative processes proposed, however, can be supported based on the present data. Finally, it should be noted that the isomerization of <u>trans-Ge(dpm)₂Cl₂ is also instantaneous in a solution of HCl (.18 <u>M</u>) in benzene. This result may be due to a change in the dielectric constant of the solvent, or it may have specific mechanistic implications.</u>

D. Some reactions of Antimony(V) Chloride

1. <u>Reaction of Antimony(V) Chloride and Tetramethyl-</u> silane.

Tetramethylsilane was selected several years ago as the ideal reference standard for proton nuclear magnetic resonance due to its volatility, non-associative nature and its "chemical unreactivity".⁵⁴ This has been accepted universally, but only a few papers have reported some anomalies of tetramethylsilane when it is used as an internal reference. Laszlo, and co-workers⁵⁵ have reported that tetramethylsilane gives rise to interactions with aromatic solvents such as pyridine, nitrobenzene, benzaldehyde, benzonitrile or aniline due to the formation of weak complexes which produce variations in chemical shifts of the order 0.10-0.15 ppm. Reavill⁵⁶ reports that when tetramethylsilane is used as an internal reference for sulfuric acid solutions it reacts to give two different products by cleavage of the siliconcarbon bond, <u>viz</u>., trimethylsilylsulfate and methane. Cleavage of alkyl silicon compounds by metal halides has been described in the case of tetraethylsilane^{57,58} and tetrabenzylsilane⁵⁹. The most efficient halide is aluminum trichloride (100% reaction yield), but the reaction can also be accomplished with iron trichloride or bismuth trichloride.⁶⁰ Since ethane is formed on hydrolysis of the reaction mixture from the cleavage of tetraethylsilane, the reaction apparently gives rise to ethyl substituted metal halides:

 $(C_2H_5)_4Si + MCl_3 \longrightarrow (C_2H_5)_3SiCl + (C_2H_5)MCl_2$

Reactions of aryl silanes proceed in a similar way.⁶¹ Yakubovich and Motsarev, have shown that aluminum trichloride⁶² and iron trichloride⁶³ break silicon-carbon bonds when they react with diphenyldichlorosilane at 30° . When antimony trichloride is used, the reaction does not occur at temperatures lower than 200° . However, in the case of antimony(V) chloride, it was found⁶⁴ that Si-C rupture occurs at room temperature yielding phenyltrichlorosilane, chlorobenzene and antimony(III) chloride. From these results, it seems possible to assume that the silicon-carbon bond cleavage proceeds according to:

(I)
$$\phi_2 SiCl_2 + SbCl_5 \longrightarrow \phi SiCl_3 + \phi SbCl_4$$

$$(II) \quad \diamond SbCl_4 \qquad \longrightarrow \phi Cl + SbCl_3 \quad .$$

During the course of a study of the reaction of Ge(dpm)₂Cl₂ and SbCl₅ in the presence of tetramethylsilane (TMS), which was intended for use as an internal nmr standard, a reaction between SbCl₅ and TMS was observed. In order to identify the reaction product or products, equal molar amounts of SbCl₅ and TMS were mixed in dichloromethane at room temperature for 1 hour under anhydrous conditions. Vacuum distillation of some of the solvent and subsequent cooling gave a white crystalline compound. The white compound did not give an nmr spectrum and is believed to be SbCl₃. The spectrum of the soluble products gave methyl proton singlets at τ 7.38 and 9.58. The line at τ 9.58 is assigned to (CH₃)₃SiCl and the line at τ 7.38 is assigned to methyl chloride. The methyl proton resonance of pure methyl chloride in dichloromethane occurs at τ 7.00. However, in the presence of SbCl₅ the line is shifted upfield by 0.38 ppm, presumably because of adduct formation.66 Thus the reaction proceeds via ligand exchange between SbCl₅ and TMS and subsequent rapid disproportionation of (CH₃)SbCl₄ to SbCl₃ and methyl chloride:⁶⁷

 $SbCl_5 + (CH_3)_4Si \longrightarrow (CH_3)_3SiCl + (CH_3)SbCl_4$

 $(CH_3)SbCl_4 \xrightarrow{v. fast} CH_3Cl + SbCl_3.$

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Figure 15 shows the nmr spectral changes which occur as a

Figure 15. Nmr spectral changes for an equimolar mixture of SbCl₅ and TMS in dichloromethane at room temperature.

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function of time on mixing equimolar amounts of $SbCl_5$ and TMS in dichloromethane at room temperature.

Mixtures of SbCl₅ and $(CH_3)_2SiCl_2$ or $(CH_3)_3SiCl$ showed no changes in their nmr spectra after several days at room temperature, thus indicating no reaction.

2. Reaction of Antimony(V) Chloride and β-Diketones

It has been known for several years that antimony(V) chloride reacts very easily with β -diketones.²⁰ The products formed depend upon the preparative techniques used. If the reactants are mixed at low temperatures in anhydrous sol-vents or directly, they yield addition compounds of the type SbCl₅·H(dik). If they are mixed at room temperature or above, however, then HCl is evolved and a substitution product of the type SbCl₄(dik) is formed. Very little is known regarding the constitution of the adducts or substitution.

In the course of studying the reaction of $SbCl_5$ and Ge (dpm)₂Cl₂, SbCl₄ (dpm) was obtained as a reaction product as described earlier. It was decided to prepare SbCl₅. H (dpm), SbCl₅.H (acac), and SbCl₄ (acac) by reaction of SbCl₅ and the appropriate diketone. The compounds were characterized by nmr spectroscopy. The chemical shifts of lines appearing in the nmr spectrum of each compound are listed in Table VI along with the chemical shifts of the free diketones.

Compound	-C4H9	-CH ₃ (enol)	С-Н	-ОН
HACAC		-2.01	-5.51	-15.38
SbCl ₅ ·HAcAc		-2.41	-5.92	-14.20
SbCl ₄ (AcAc)		-2.30	-5.99	
H•dpm	-1.16		-5.75	-16.16
SbCl ₅ •Hdpm	-1.44		-6.31	-11.68
$\mathtt{SbCl}_5(\mathtt{dpm})^{\mathtt{b}}$	-1.30		-6.25	

Table VI. Chemical shifts at 37 ± 2^{0} of some free diketone ligands and their addition and substitution products formed with antimony(V) chloride.^a

^aShifts are in ppm relative to an internal reference of TMS; concentration is 10 g/100 ml of dichloromethane.

^bThis compound was formed in the disproportionation of Ge (dpm)₂Cl₂·SbCl₅. Its chemical shifts were measured relative to the known chemical shift of Ge (dpm)₃ and then converted to τ values.

Two possible structures that can be proposed for the SbCl₅·H(dik) adducts:



The appearance of an hydroxyl proton resonance line for both $SbCl_5 \cdot H(acac)$ and $SbCl_5 \cdot H(dpm)$ favors assignment of structure I. However, such a structure predicts two terminal proton $(CH_3 \text{ or } \underline{t}-C_4H_9)$ lines, whereas only one is observed. However, the presence of only one terminal proton line may arise because of a rapid proton-antimony exchange process between the two oxygen atoms which leads to environmental averaging of the terminal groups. It is interesting to note that the hydroxyl proton resonance is shifted upfield by 4.48 ppm for $SbCl_5 \cdot H(dpm)$ and 1.18 ppm for $SbCl_5 \cdot H(acac)$ relative to the -OH resonance of the free diketones. This result is also consistent with structure I.

The structures of the $SbCl_4(dpm)$ and $SbCl_4(acac)$ are presumably based on an octahedron with both oxygen atoms coordinated to antimony. The nmr data are not inconsistent with this assumption. It is interesting to note that mixtures of $\text{SbCl}_5 \cdot \text{H}(\text{dpm})$ and TMS in dichloromethane at room temperature undergo reaction but mixtures of $\text{SbCl}_5 \cdot \text{H}(\text{acac})$ and TMS do not. If the molar ratio is one to one the reaction goes to completion in <u>ca</u> 30 hr. The reaction was followed by nuclear magnetic resonance spectroscopy. As it proceeds, seven resonances are detected at τ 10.00, 9.58, 8.76, 8.56, 7.32, 3.86 and 3.69. The signals at τ 3.69 and 8.56 belong to the adduct. The signal at τ 10.00 corresponds to TMS. The signals at τ 9.58, 8.76, 7.32 and 3.86 increase in intensity as the reaction proceeds. Upon completion of the reaction, the solvent was removed by distillation and a white solid product was recovered. A nmr spectrum of this compound did not show any signal at τ 9.58, which is attributed to

trimethylchlorosilane. The lines at τ 8.76 and 7.32 had a ratio of six to one, respectively. It is suggested that these latter lines are due to methyltrichloro (dipivaloylmethanato)antimony (V). The line at τ 7.32 agrees closely with the τ value of the methyl group of chloromethane. Figure 16 shows the reaction of SbCl₅.Hdpm and TMS as a function of time at room temperature.

Recently, Okawara, Matsura and Nishii⁶⁸ have prepared methyltrichloromono (acetylacetonato) antimony (V), which is a white solid at room temperature. This supports our assignment for the product with signals at τ 8.76, 7.32 and 3.86 as being MeSbCl₃ (dpm), because the dipivaloylmethanato complexes are as easy to prepare as the acetylacetonato complexes. For methyltrichloro (dipivaloylmethanato)antimony (V), two isomeric forms possible. One of them has the chlorine and methyl group in <u>cis</u> positions and the other has them in <u>trans</u> positions. The <u>trans</u> isomer should give rise to only one <u>t</u>-butyl proton line. The <u>cis</u> isomer should give two <u>t</u>-butyl lines. The presence of one <u>t</u>-butyl line in the spectrum of the compound may be due to rapid rearrangement process, rather than the presence of only the <u>trans</u> isomer.

Figure 16. Nmr spectrum of the reaction between SbCl₅ Hdpm and tetramethylsilane in dichloromethane at room temperature as a function of time.



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