STUDIES ON TITANIUM (IV) β-DIKETONATES
AND
INVESTIGATION OF THE TETRACARBONYLCOBALTATE ANION FOR M-M BOND FORMATION

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ABSTRACT

A series of β-diketonato titanium (IV) complexes of the type $F_2Ti(dik)_2$ and $[F_3Ti(dik)]_2$, (dik = benzoylacetonate, dibenzoylacetonate) have been prepared. Infrared evidence is presented for the aimeric nature of $[F_3Ti(bzac)]_2$ and $[F_3Ti(bzbz)]_2$. Tentative assignments of $\nu(Ti-F)_{br}$ (600 cm^{-1} and 598 cm^{-1} respectively for dik = bzac and bzbz) and $\nu(Ti-F)_{ter}$ (637 cm^{-1} in bzac, 667 cm^{-1} and 624 cm^{-1} in bzbz) have been made for the dimers. The low solubility of these complexes in various organic solvents precluded solution infrared spectra.

The structure of $[Cl_3Ti(acac)]_2$ has been determined by single-crystal x-ray diffraction methods using the θ-2θ scan technique with Mo Kα radiation (0.071069 Å). The unit cell data are: space group $P2_1/n$ (No. 14), $Z = 2$, $a = 8.381(5)$ Å, $b = 10.734(5)$ Å, $c = 10.517(6)$ Å,

$\alpha = \gamma = 90.00^\circ$, $\beta = 93.92^\circ$, and V = 994.573 Å^3. The final discrepency indices were R = 0.031 and R_w = 0.029 after full-matrix anisotropic refinement of all non-hydrogen atoms. The O-O "bite" distance of 2.582(4) Å in $[Cl_3Ti(acac)]_2$ is considerably shorter than those reported in other acetylacetonate complexes. This is rationalized in terms of a greater effective nuclear charge at titanium, and supports the notion of significant $p\pi$-$d\pi$ type bonding in the Ti(acac) planar heterochelated ring.

The synthesis of M-M bonded derivatives of cobalt and titanium was attempted through the nucleophilic displacement of chlorine from $(C_5H_5)_2TiCl_2$ by $[Co(CO)_4]^-$. Evidence is presented that this may not be the method for the synthesis of Co-Ti bonded compounds. The compounds prepared were extremely air sensitive and most were pyrophoric. The presence of $(C_5H_5)Co(CO)_2^+$ as well as anomalous hydrocarbon ions in the mass spectrum of the reaction products suggested that decomposition had occurred, possibly of a high molecular weight cluster compound.

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Part I

STUDIES ON TITANIUM (IV) β-DIKETONATES

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I. INTRODUCTION

Titanium (IV) has an extensive stereochemistry. Coordination numbers of four and six are readily associated with its complexes, while five- and eight-coordinate complexes are known,(1,2) and recently a seven-coordinate(3) N,N-dialkyldithiocarbamate complex of titanium (IV) has been reported. Apart from the tetrahalides which appear to be four-coordinate, tetrahedral moieties in the vapour phase (solid titanium tetrafluoride is polymeric while some association has been postulated for pure liquid titanium tetrachloride), a six-coordinate octahedral geometry is the main feature of titanium (IV) stereochemistry. These tetrahalides form a variety of monomeric 1:2 adducts with neutral unidentate oxygen, nitrogen, sulphur and phosphorous containing donor ligands or dimeric bridging structures as 1:1 adducts to achieve six-coordination.

The tetraalkoxides, which are already octahedrally coordinated tetrameric compounds in the solid state, do not show this affinity for adduct formation. They do, however, parallel the tetrahalides in the formation of neutral bis chelate complexes with suitable bidentate donor ligands. Amoung the compounds formed, the β-diketonates have been most studied.(4-9) Invariably, these compounds $X_2Ti(dik)_2$, X = halide or alkoxide, and dik = a β-diketonate anion, have been shown to contain a cis-dihalo or cis-dialkoxy octahedral structure.(4,5,7) From fluorine and proton nuclear magnetic resonance exchange studies, Fay and Serpone,(5) have calculated the rate constants for the interconversion of geometrical isomers. Their results have been confirmed both by Fay and Lowry,(4) and Bradley and Holloway.(7) These workers used solution infrared spectroscopy in conjunction with variable temperature proton magnetic resonance data to arrive at their conclusions. It appears that little remains to be done(8) in the characterization of these compounds and interest is increasing in the less common coordination geometries, particularly in the case of higher coordination numbers.

The maximum theoretical coordination number of a d^0 system is nine(1,2) but as yet no nine-coordinate titanium (IV) complex has been observed. The first isolated eight-coordinate titanium (IV) complex was the 1:2 adduct of titanium tetrachloride with O-phenylenebisdimethylarsine, $TiCl_4 \cdot 2diars$.(10) Subsequent efforts to synthesize eight-coordinate titanium (IV) complexes using a variety of bidentate nitrogen, phosphorous, sulphur, oxygen, or arsenic containing donor ligands with titanium tetrachloride have failed to increase the coordination about the titanium atom beyond six.(15) However, sustained efforts resulted in the complex $TiCl_4$·2dip (dip = O-phenylenebisdimethylphosphine)(16) analogous to the original complex prepared. Eight-coordination has also been confirmed in $Ti(NO_3)_4$(11) via single crystal x-ray diffraction techniques. It became clear that further study of eight-coordination was necessary to establish the properties of both the metal centre and the surrounding ligands that would favour this high coordination number.(1,2) The results indicated that the metal atom should be relatively large to accomodate many ligands and have a relatively large positive charge to satisfy the electroneutrality principle.(17) Kepert(1) and Parish(2) also suggested that eight-coordination should be much more prevalent than the few examples cited in the literature, and that, for the most part, this coordination number should be restricted to the early transition metals.

The syntheses of the tetrakis-N,N-dialkydithiocarbamates became evident(3,12-14) once the versatility of the ligand became known. Thus the reaction between titanium tetrachloride and the anhydrous sodium salt of the appropriate diakyldithiocarbamate in molar ratios of

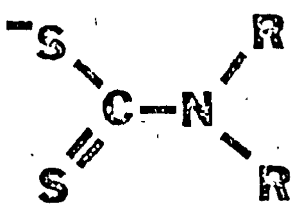
1:2, 1:3, and greater than 1:4 produced respectively the six-, seven-, and eight-coordinate complexes.(3) The reaction

$$TiCl_4 + nNa(S_2CNR_2) \rightarrow Ti(S_2CNR_2)_nCl_{4-n} + nNaCl \quad (1)$$

seems quite general for R = methyl (Me), isopropyl (iPr), and isobutyl (iBu), and n = 2,3 or 4. That these compounds are in fact six-, seven-, and eight-coordinate was ascertained through conductance and infrared evidence.

Because the compounds are non-electrolytes, the higher coordination was deduced. Furthermore, a systematic frequency shift in the infrared for the C-N, C-S, and Ti-Cl bands was observed as coordination increased from six to eight about the titanium atom. The decrease in the C-N frequency, increase in the C-S frequency and decrease in the Ti-Cl frequency was explained in terms of the decreasing strength of the Ti-S bonds as coordination increases and therefore increasing the relative importance of resonance structures 1 and 2 (shown below) and decreasing that of 3. In fact a single crystal x-ray determination of both $Ti(S_2CNMe_2)_3Cl$(3) and $Ti(S_2CNEt_2)_4$(12) have shown the structures to be seven-coordinated pentagonalbypyramidal and eight-coordinate dodecahedral respectively.

The first eight-coordinate titanium dialkyldithiocarbamate, $Ti(S_2CNEt_2)_4$,(12) was prepared by carbon



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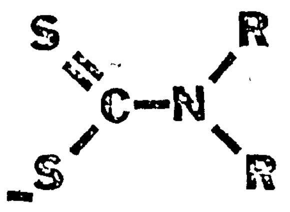

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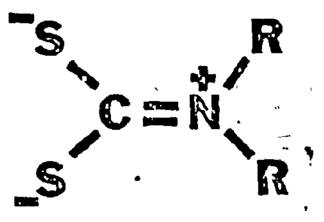

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disulphide insertion into the Ti-N bond of tetrakisdiethylaminotitanium (IV), $Ti(NEt_2)_4$. Since this study, other insertion reactions involving titanium dialkylamines and carbon disulphide, carbonyl sulphide, and carbon dioxide were attempted.(18) The results with these three (CS_2, COS, CO_2) groups are essentially the same as those proposed earlier.(12) The bidentate nature of the carbamate and monothiocarbamate ligands have been verified through infrared analyses.(18) Through ligand exchange reactions, Chisholm and Extine(18) have shown that the product distribution is attained through thermodynamic control. Thus mixing any $TiN_{4-n}L_n$ ($n \leq 4$) and

$TiN_{4-m}L_m$ ($m \leq 4$) in benzene will rapidly yield the expected product distribution.

e.g.

$$2TiNL_3 + TiN_4 \rightarrow 3TiN_2L_2 \qquad (2)$$

$$TiN_2L_2 + TiN_4 \rightleftarrows 2TiN_3L \qquad (3)$$

All compounds of general formula TiN_3L, TiN_2L_2, $TiNL_3$ and TiL_4, were observed where N is the dimethylamino (NMe_2) ligand and L is either dimethyldithiocarbamate, dimethylmonothiocarbamate, or dimethylcarbamate. This immediately implies that the coordination about the titanium atom varied between four and eight and includes both of the elusive species of five- and seven-coordination.

The synthesis of the seven-coordinate species is recent enough to have sparked little controversy. Interest has developed in recent years concerning the nature of five-coordination in titanium (IV).

Five-coordinate titanium (IV) complexes are still rare.(19) Some compounds in which titanium (IV) is found to be five-coordinate include $[TiCl_2(OR)_2]_2$ (where R is phenyl(20) or ethyl(21)) and the polymeric derivative $[TiCl_2NSiMe_3]_n$.(22,23) The reaction between $Ti(OR)_4$, where R is C_2H_5, $n\text{-}C_3H_7$, or $n\text{-}C_4H_9$, with either acetylacetone[a] or ethylacetoacetate (dik) in equimolar

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[a] The nomenclature and abbreviations of the ligands which are mentionned in the text may be found in Table X of the Appendix. The common names of these ligands are used interchangeably with those recommended by IUPAC.

ratios resulted in the species with the stoichiometry (OR$_3$)Ti(dik).(24) Yamamoto and Kambara(24) have postulated five-coordination for titanium (IV) in these compounds from elemental analyses, and mostly from the assignments of infrared frequencies. Subsequently, Mehrotra and coworkers(25-28) observed that titanium tetrachloride reacted with acetylacetone in a 1:1 mole ratio to yield a complex having the stoichiometry Cl$_3$Ti(acac), where acac is the anion of acetylacetone. They also noted that the OR$_3$Ti(dik) complexes underwent the disproportionation reaction:

$$2(OR)_3Ti(dik) \rightleftharpoons (OR)_2Ti(dik)_2 + Ti(OR)_4 \qquad (4)$$

On the basis of elemental analyses, chemical reactions with a variety of alcohols, acetic acid, and methylacetoacetate, and molecular weights, it was concluded that the titanium (IV) species were five-coordinate, although in the case of less bulky R groups, molecular weights were significantly above those required for a monomer.

In order to establish the nature of this apparent five-coordination, Thompson and coworkers(29) undertook the systematic preparation and characterization of several X$_3$Ti(dik) complexes (X = Br, Cl; dik = 3-methylacetylacetonate ($C_6H_9O_2$). The stoichiometry of all complexes was confirmed through elemental analyses. Conductivity data were consistent with a monomeric and non-ionic structure in nitrobenzene; spectral data (IR and NMR) indicated oxygen-chelated enolate complexes. In addition, reactions of 3-methylacetylacetone ($C_6H_{10}O_2$) of the type:

$$TiCl_4 + C_6H_{10}O_2 \rightarrow Cl_3Ti(C_6H_9O_2) + HCl \quad (5)$$

$$TiCl_4 + 2C_6H_{10}O_2 \rightarrow Cl_2Ti(C_6H_9O_2)_2 + 2HCl \quad (6)$$

$$TiCl_4 + Cl_2Ti(C_6H_9O_2)_2 \rightarrow 2Cl_3Ti(C_6H_9O_2) \quad (7)$$

led these workers to believe that there exists in solution a five-coordinate species in equilibrium with a six-coordinate species. However, complicated temperature dependent NMR spectra in nitrobenzene precluded the assignment of stereochemistry.

In contrast, Holloway and Sentek(30) have made the claim that no true five-coordinate complexes of titanium (IV) have been prepared. On the basis of NMR evidence, they have postulated that these apparently five-coordinated $X_3Ti(dik)$ (where X = alkoxide) species are in fact equilibrium mixtures of the well known four- and six-coordinate complexes, TiX_4 and $X_2Ti(dik)_2$ respectively, which are weakly associated in solution according to the reaction:

$$(dik)_2TiX_2 + TiX_4 \rightleftarrows (dik)_2TiX_2TiX_4 \quad (8)$$

Thus an alkoxide bridge exists between the parent TiX_4 and the six-coordinate $X_2Ti(dik)_2$ in their interpretation.

Subsequent studies on the $Cl_3Ti(bzac)$ (bzac = anion of 1-phenyl-1,3-propanedione) by Thompson and coworkers(31) have led them to conclude that there exists in solution an equilibrium between the five- and six-coordinate species of the type described by equation 4. In an NMR study of various $X_3Ti(dik)$ complexes (X = Cl, Br; dik = 1-phenyl-1,3-propanedionate, and 2,2,6,6,-tetramethyl-3,5-heptanedionato), we(32) have confirmed Thompson's results on $Cl_3Ti(bzac)$. Furthermore, Alyea and Merrel(33) have synthesized complexes of the type $Ti(chel)OR_3$, where chel is a uninegative bidentate ligand with an ethane backbone, by reacting the lithium salt of the bidentate ligand with $(OR)_3TiCl$. Their results indicate five-coordination for the titanium (IV) species; the complexes are liquids and so crystallographic structure determinations were precluded.

The preliminary crystallographic studies on the $Cl_3Ti(C_5H_7O_2)$ complex were reported by Serpone and his coworkers.(34) The solid state structure is that of a centrosymetric six-coordinate dimer. It was felt that the full crystal and molecular structure of this apparent five-coordinate titanium (IV) complex was a good basis on which to start infrared spectroscopic investigations. Thus knowing the solid state structure and being able to assign the solid state infrared spectra of this and related compounds, it was reasoned that a handle could be gained in assigning structural changes upon dissolution from infrared analysis. Because titanium-chlorine frequencies for bridging chlorine atoms occur below 300 cm^{-1}, infrared studies on compounds containing Ti-Cl were precluded. Therefore, it was decided to investigate the corresponding fluorides. Again differences between the solid state and solution spectra were believed to indicate structural differences in solution. However, these compounds were soluble to the degree required (10% solution) for infrared analysis in only a very limited number of solvents. In these, a strong solvent band obscured those of interest.

II. EXPERIMENTAL

A. Materials and Techniques

Titanium tetrachloride (Fisher Certified Reagent), titanium tetrafluoride (98%, ROC/RIC), benzoylacetone (1-phenyl-1,3-butanedione) (Aldrich), and Eastman dibenzoylmethane (1,3-diphenyl-1,3-propanedione) were used without further purification. Benzene, hexane, and dichloromethane were dried by continuous reflux over calcium hydride and distilling therefrom when needed. The solvents used for spectroscopic studies were dried by refluxing over molecular sieves (Linde, 4A) and distilling onto a fresh batch of molecular sieves. These solvents were stored over molecular sieves in brown bottles fitted with rubber septa.

All glassware was dried in an oven at 140°C for at least two hours and cooled in a dry nitrogen atmosphere just prior to use.

Syntheses, handling of compounds, and subsequent physical measurements were carried out under anyhdrous conditions in an inert nitrogen atmosphere. The purity of the products isolated was checked by melting point determinations and infrared spectra.

One of two general procedures was followed in the syntheses of complexes.

1. The appropriate β-diketone was refluxed with the desired titanium tetrahalide in either benzene or dichloromethane in a 1:1 molar ratio. After cooling to room temperature hexane was added and the solution was cooled in the freezer. The crystals were filtered, washed with hexane, and dried under vacuum.

2. The mixed halo complexes were prepared from the bis-β-diketonato titanium dihalide and the corresponding tetrahalide by refluxing equimolar amounts of reactants. After cooling to room temperature, hexane was added and the solution was cooled in the freezer. The crystals were filtered, washed with hexane and dried under vacuum.

B. Physical Measurements

Infrared spectra were recorded either on a Perkin Elmer 457 or a 225 grating spectrophotometer as Nujol mulls between KBr windows or as solutions in KBr sealed cells. (0.10mm path length) The solution and mulls were prepared in a glove-bag under anhydrous conditions and the spectra were immediately recorded.

Melting points were taken with a Gallenkamp Melting Point Apparatus, Model MF 370. The capillary tubes were sealed with modeling clay in an anhydrous nitrogen atmosphere. The reported melting points are uncorrected.

C. Syntheses

Difluorobis-(2,4-pentanedionato) titanium (IV): $F_2Ti(acac)_2$

In a glove-bag, TiF_4 (3.15gm, 0.025 mole), a stirring bar, and dry dichloromethane (about 50 ml) were added to a 125 ml Erlenmeyer flask fitted with a gas inlet side-arm. The flask was removed from the glove-bag, nitrogen was admitted through the side-arm, and 2,4-pentanedione (5.25 ml, 0.050 mole) (Hacac) in 10 ml of dichloromethane was added dropwise from a syringe with vigorous stirring. The flask was fitted with a reflux condenser carrying a drying tube and the nitrogen was turned off. The solution was allowed to reflux for four hours. The hydrogen fluoride evolved was occasionally flushed out of the system by admitting dry nitrogen through the side-arm. The solution was reduced to one-half volume by passing a stream of nitrogen through the flask while gently heating with the air gun, and an equal volume of hexane was added. The solution was cooled in the freezer for two hours before the yellow crystals were filtered off on a medium porosity glass fritted funnel. Recrystallisation from dichloromethane/hexane yielded the pure product which was dried in vacuo overnight. An infrared spectrum showed neither bands between 1600 and 1800 cm^{-1} nor at 3300 cm^{-1}. Bands in the 1600-1800 cm^{-1}

region are indicative of the free ligand carbonyl vibrations while those centered at 3300 cm^{-1} are representative of free hydroxyl vibrations. The absence of these bands was the criterion used for sample purity. (see section III A) Yield 4.58 gm, 64%; mp. 164-167° dec; lit[(35)] 165-166°.

Dichlorobis-(2,4-pentanedionato) titanium (IV):
$Cl_2Ti(acac)_2$

To a stirred solution of $TiCl_4$ (3.20 ml, 0.031 mole) in 50 ml dichloromethane was added dropwise from a syringe 6.42 ml (0.062 mole) 2,4-pentanedione under a slow stream of nitrogen. The flask was fitted with a reflux condenser carrying a drying tube and heated to reflux. Hydrogen chloride evolution ceased within the reflux time of three hours. The solution volume was reduced to one-half by passing a stream of nitrogen over the solution surface while heating with an air gun. Hexane (about 15 ml) was added until the solution appeared turbid. Cooling in the freezer for three hours resulted in bright orange crystals of the product. These were filtered through a medium porosity glass fritted funnel, washed twice with hexane, and dried *in vacuo* overnight. Because infrared bands were absent between 1600 and 1800 cm^{-1} and 3300 cm^{-1}, the product was judged pure. (see section III A) Yield 6.4 gm, 65%; mp. 187-188° dec; lit(35) 191-192°.

Di-μ-chlorotetrachlorobis-(2,4-pentanedionato) dititanium (IV): $[Cl_3Ti(acac)]_2$

Acetylacetone (3.20 ml, 0.029 mole) in 10 ml of benzene was added dropwise from a syringe to a stirred solution of titanium tetrachloride (3.00 ml, 0.027 mole) in 50 ml of benzene. Anhydrous conditions were insured by passing a slow stream of nitrogen through the system. The flask was fitted with a reflux condenser carrying a drying tube and the nitrogen was turned off. Hydrogen chloride evolution ceased within the reflux time of three hours. The solution volume was reduced to one-half by passing a stream of nitrogen over the solution surface while heating with an air gun. Hexane (about 15 ml) was then added until the solution became turbid. Cooling in the freezer overnight resulted in red crystals of the product. The crystals were filtered using a medium porosity glass fritted funnel. Recrystallisation from dichloromethane/hexane and washing twice with 10 ml portions of hexane resulted in the pure product. The crystals were dried for 10 hours *in vacuo*. The sample was judged pure because of the absence of bands at 3300 cm^{-1} and free ligand carbonyl vibrations between 1800-1600 cm^{-1}. (see section III A) *Yield* 5.50 gm, 75%; mp. 180-181° dec; lit(36) 180-182° dec.

Tetrachlorodifluorobis-(2,4-pentanedionato) dititanium (IV): $[Cl_2FTi(acac)]_2$

To a 125 ml Erlenmeyer flask fitted with a gas inlet side-arm, $TiF_2(acac)_2$ (4.92 gm, 0.017 mole), a stirring bar, and about 50 ml of dry dichloromethane were added in the glove-bag. Swirling gently, 1.90 ml (0.017 mole) of $TiCl_4$ in 10 ml of dichloromethane was added dropwise from a syringe. The flask was removed from the glove-bag, nitrogen was admitted through the side-arm, and the flask was fitted with a reflux condenser carrying a drying tube. The nitrogen was turned off, and the solution was refluxed with vigorous stirring for three hours. The solution volume was reduced to one-half by passing a stream of nitrogen over the top of the solution while gently heating with an air gun. After three hours in the freezer, the red-brown crystals were filtered from the solution on a medium porosity glass fritted funnel. Washing twice with hexane gave the pure product which was dried *in vacuo* overnight. The product was judged pure because infrared bands at 3300 cm^{-1} and between 1800 and 1600 cm^{-1} were absent. (see section III A) Also the infrared bands for this compound in the 950-500 cm^{-1} range agree well with those reported by Bickley.(36) *Yield* 1.9 gm, 46%; mp. 150-151° dec; lit(36) 148-150° dec.

Di-μ-fluorotetrafluorobis-(2,4-pentanedionato) dititanium (IV): $[F_3Ti(acac)]_2$

Titanium tetrafluoride (5.48 gm, 0.044 mole) was slurried in 50 ml dry benzene. Under a slow stream of nitrogen 4.55 ml (0.044 mole) of 2,4-pentanedione was added from a syringe. The solution turned yellow and some hydrogen fluoride was evolved. The flask was fitted with a reflux condenser carrying a molecular sieves (Linde, 4 A) drying tube and the nitrogen was turned off. The solution was allowed to reflux for about three hours (until hydrogen fluoride evolution was at a minimum), occasionally purging the evolved hydrogen fluoride with dry nitrogen. The solution volume was reduced to about 20 ml under vacuum with gentle heating. Addition of an equal volume of hexane produced an intractable red oil. Attempts to crystallise the oil by quick freezing in liquid nitrogen or changing the solvent system failed. (Similar results were obtained by D. G. Bickley.(36))

Difluorobis-(1-phenyl-1,3-butanedionato) titanium (IV): $F_2Ti(bzac)_2$(37)

Titanium tetrafluoride (2.88 gm, 0.023 mole) was slurried in dry dichloromethane (20 ml) under anhydrous nitrogen in the glove-bag. The flask was removed, nitrogen was admitted through the side-arm, and 1-phenyl-1,3-butanedione (Hbzac) (7.54 gm, 0.046 mole) dissolved in 25 ml of dichloromethane was slowly added from a syringe with vigorous stirring. The solution immediately turned yellow, then orange. The flask was fitted with a reflux condenser carrying a drying tube, the nitrogen was turned off, and the solution was refluxed for two hours. Evolved hydrogen fluoride was frequently flushed from the flask using nitrogen. The solution was reduced to one-half volume by passing a stream of nitrogen over the surface of the solution while gently heating with an air gun. Crystallisation occured overnight while cooling in the freezer. The solution was filtered on a medium porosity glass fritted funnel and washed twice with dry pentane. Drying six hours _in vacuo_ resulted in a yellow powder. The infrared spectrum showed the absence of bands due to free carbonyl groups (1800-1600 cm^{-1}) and also those due to the hydrolysis products (3300 cm^{-1}). For this reason, the product was judged pure. _Yield_ 4.0 gm, 42%; mp. 195-197° dec; lit(37) 196-198.5° dec.

Di-μ-fluorotetrafluorobis-(1-phenyl-1,3-butanedionato) dititanium (IV): $[F_3Ti(bzac)]_2$

To a slurry of titanium tetrafluoride (2.60 gm, 0.021 mole), in a dry dichloromethane (about 40 ml), was added under a stream of dry nitrogen 1-phenyl-1,3-butanedione (Hbzac) (3.40 gm, 0.021 mole) dissolved in 10 ml of dichloromethane. The solution turned red upon addition of the ligand. The flask was fitted with a reflux condenser carrying a drying tube. The solution was refluxed for two hours during which time evolved hydrogen fluoride was frequently flushed out of the system using dry nitrogen. The solution volume was reduced to one-half by passing a stream of nitrogen over the surface of the solution while gently heating with an air gun. Cooling overnight in the freezer resulted in a red oil which was crystallised by freezing in liquid nitrogen and evacuating the flask. Recrystallisation from dichloromethane/pentane and drying overnight under vacuum gave red crystals. The product purity was verified by the absence of infrared bands at 3300 cm^{-1} and between 1800 and 1600 cm^{-1}. Infrared bands in the 600 cm^{-1} region that are not in the $F_2Ti(acac)_2$ sample show it to be an authentic sample. (see section III A) Yield 5.0 gm, 90%; scinters 175-180°, mp. 193-196° dec.

Difluorobis-(1,3-diphenyl-1,3-propanedionato) titanium (IV): $F_2Ti(bzbz)_2$ (37)

Titanium tetrafluoride (0.95 gm, 0.008 mole) was slurried in dry dichloromethane (50 ml) under a dry nitrogen atmosphere in the glove-bag. The flask was removed, nitrogen was admitted through the side-arm, and 3.44 g (0.015 mole) of 1,3-diphenyl-1,3-propanedione (Hbzbz) was added slowly as the solid, with vigorous stirring. The reactant sticking to the neck of the flask was washed in with 10 ml dichloromethane. Upon addition of Hbzbz, the solution immediately turned red. The flask was then fitted with a reflux condenser carrying a drying tube and the nitrogen was turned off. The reactants were refluxed during two hours during which time evolved hydrogen fluoride was flushed out of the system with dry nitrogen. The solution volume was then reduced to one-third and crystallisation was allowed to occur overnight in the freezer. (Addition of hexane causes oil formation which is difficult to crystallise). The yellow-orange crystals were washed twice with cold hexane and dried overnight in vacuo. The product was considered pure because of the absence of bands at 3300 cm^{-1} and in the 1800-1600 cm^{-1} region. Also, infrared band positions in the 950-500 cm^{-1} region agree with those reported by Serpone.(37) (see section III A) Yield 2.46 gm, 60%; mp. 192-194° dec; lit(37) 204.5-206°.

Di-μ-fluorotetrafluorobis-(1,3-diphenyl-1,3-propanedionato) dititanium (IV): $[F_3Ti(bzbz)]_2$

Solid 1,3-diphenyl-1,3-propanedione (2.33 gm, 0.010 mole) was added under a stream of nitrogen to a slurry of titanium tetrafluoride (1.29 gm, 0.010 mole) in 35 ml of dichloromethane. The solution immediately turned red. The flask was fitted with a reflux condenser carrying a drying tube. The solution was refluxed for two hours, the evolved hydrogen fluoride being frequently flushed out of the flask with nitrogen, and the solution volume was reduced to one-half by passing a stream of nitrogen over the solution surface while gently heating with an air gun. Cooling in the freezer overnight resulted in bright red crystals. (Addition of hexane to the product solution results in a red oil which is difficult to crystallise). The crystals were washed twice with cold, dry pentane and dried in vacuo overnight. The sample was judged pure on the basis of the absence of infrared bands at 3300 cm^{-1} and in the 1800-1600 cm^{-1} region. The compound was considered authentic because of the presence of infrared bands in the 600 cm^{-1} region that were absent in the $F_2Ti(bzbz)_2$ complex. Yield 2.29 gm, 70%; mp. 163-165° dec.

D. Crystallography(38-40)

1. Unit Cell and Space Group Determination

A suitable crystal of the apparent five-coordinate $Cl_3Ti(acac)$ complex was chosen and sealed in a capillary under anhydrous conditions in a glove-bag to protect it from atmospheric moisture.

Weissenberg and precession photographs taken with Mo Kα radiation were used to determine the space group and to check the crystal for defects other than a normal mosaic structure. Accurate cell dimensions were obtained on a fully automated Picker FACS-1 diffractometer. Values of 2θ, ω, χ, and ϕ obtained for twelve Bragg reflections centered at both positive and negative 2θ values, and appropriately averaged, were used in the least-squares refinement of the unit cell parameters and the crystal orientation matrix. The programs employed for this procedure were those supplied by the Picker Nuclear Company.

2. Data Collection

An assymetric unit of intensity data was collected on the diffractometer within angular limits chosen to include all reasonably strong reflections. The background was estimated from a measured curve. Instrument stability was monitored by measuring the intensity of a standard reflection after every thirty cycles and by determining the intensity of the reciprocal axis reflections with both positive and negative indices before and after data collection. The intensity data which had been collected (i.e. indices (hkl), background counts on either side of the peak (B_1 and B_2), scan time, counting time, peak count, attenuator number, relfection number, setting angles, 2θ, χ, and ϕ) and stored on paper tape were transferred to magnetic tape to be used as input for data reduction.

3. Data Reduction

The Concordia Univeristy CDC 6400 computer was used for all computations. A locally written program, PREP, was employed to perform the data reduction. The values of the reflection intensities, (I), were computed as:

$$I = N - B(t_s/t_b) \qquad (8)$$

and

$$\sigma(I) = |N + B(t_s/t_b)^2 + (0.02N)^2|^{\frac{1}{2}} \qquad (9)$$

where N is the total counts accumulated during the scan period t_s, and B is the total count accumulated during the total background counting time t_b (i.e. $B = B_1 + B_2$). The reflection was considered absent for negative values of I. Data for which I was less than $3\sigma(I)$ were considered invalid and were rejected along with any systematically absent reflections that were collected.

Ideally, the structure factor modulus $|F_{hkl}|$ used in the calculation of electron density maps from which the atom positions may be determined, is proportional to the square root of the reflection intensities. However, corrections were made on the intensities for polarization by the monochromator crystal and sample crystal and Lorentz effects through a combined term $(Lp)^{-1}$ such that

$$(Lp)^{-1} = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s) \qquad (10)$$

where θ_s and θ_m are the diffraction angles at the sample crystal and the monochromator crystal respectively.

Structure factors were calculated from the equation

$$|F_{rel}| = (I/Lp)^{\frac{1}{2}} \qquad (11)$$

Standard deviations on the structures factors were calculated as

$$\sigma(F) = \sigma(I)/2I^{\frac{1}{2}}(Lp)^{\frac{1}{2}} \qquad (12)$$

The polarization term arises because of the nature of the x-ray beam and the manner in which its reflection efficiency varies with the reflection angle. The electric vectors associated with the photons of the x-ray beam can point in any direction normal to the direction of propogation (i.e. they are unpolarized). Each of these vectors may be divided into components in two directions, one parallel to the plane of the reflecting surface ($I_{||}$) and other perpendicular to it ($I_{\perp}$). Because of random orientations, the sums of these two components will be equal. Reflection of waves having their electric vector parallel to the reflecting plane is determined only by the electron density in the plane. However, waves having their electric vector perpendicular to the reflecting plane are reflected to an extent which is determined both by electron density and a function of 2θ (i.e. $\cos^2 2\theta$) and vanishes at $2\theta = 90^\circ$. Because the initial energy is equally divided between the two vectors, no more than one-half of the intensity will be lost to this effect. Thus, the polarization factor, p, is given by equation 13.

$$p = \frac{1 + \cos^2 2\theta}{2} \qquad (13)$$

It thus becomes obvious that the beam leaving the monochromator crystal will be partially polarized because of the greater reflection efficiency of the parallel ($I_{||}$) component. This partial polarization must be taken into account since it will affect subsequent reflections from the sample crystal.

The Lorentz factor is an expression for the time a plane of a rotating crystal spends in the reflecting position. This is the length of time the lattice point is in contact with the sphere of reflection, and is dependent on the distance of the reciporcal lattice point from the origin. At large Bragg angles (θ) the reciprocal lattice point passes almost tangentially through the sphere of reflection and L is large. Again, L is large at low Bragg angles as the reciprocal lattice point is near the origin of the reciprocal lattice and the time taken in cutting the sphere of reflection is large. Thus, it is seen that L is a minimum at $\theta = 45^\circ$. The expression for L depends upon the diffraction gemoetry used during the collection of intensity data. For the equi-inclination Weissenberg technique, the Lorentz factor is given by equation 14, where μ is the equi-inclination setting angle.

$$L = \frac{\sin\theta}{\sin 2\theta(\sin^2\theta - \sin^2\mu)^{\frac{1}{2}}} \qquad (14)$$

For the particular case where the axis of rotation is perpendicular to the plane containing the incident and reflected beams, the value of L reduces to

$$L = 1/\sin 2\theta \qquad (15)$$

It is this expression (equation 15) which is applicable to zero-level Weissenberg photographs, the zero-layer reflections of rotation and oscillation photographs, for zero-level reflections of equation 14, and to diffractometer data obtained by the usual 2θ or ω scans.

The program PREP also calculates scattering factors, f_o, for each atom and each reflection, from tables supplied on cards. Wilson statistics were applied (i.e. a plot of $\sin^2\theta/\lambda^2$ versus $\ln(I_{rel}/\Sigma f^2_{oj})$ to predict an absolute scale factor and an approximate overall isotropic thermal parameter. Thus the output of PREP on tape are the indices (hkl), the observed structure factors, F_{obs}, with their standard deviations, $\sigma(F_{obs})$, and a list of scattering factors for each element in the compound.

4. Fourier

A Patterson Synthesis was then calculated using the program FORDAP.(41) The program expands the data set to a triclinic and uses the squares of the observed structure factors from PREP as the coeffecients in the Fourier summation.

The summation (equation 16) was calculated for a grid of points spaced at about 0.3 Å intervals in the three dimensions uvw. (e.g. for an assymetric unit 9 x 9 x 9 Å some 30 x 30 x 30 = 27,000 values of P_{uvw} would be calculated) For convenience in the computer printout, the values of P_{uvw} are scaled so that the largest is 999.

$$P_{uvw} = 1/v\, \Sigma_h \Sigma_k \Sigma_l |F_{obs}|^2 \cos 2\pi(hu + kv + lw) \qquad (16)$$

Every pair of atoms in the unit cell produces a peak on the vector map. Thus N atoms produce N^2 peaks. Of these peaks, N corresponds to the vector between each atom and itself. These occur at the origin of the vector map. Thus the largest peak corresponds to vectors between all atoms related by a unit cell translation along the axes a and/or b and/or c. Each of the N^2-N non-origin peaks on a vector map corresponding to two atoms in the unit cell of atomic numbers Z_1 and Z_2, have $Z_1 Z_2$ electrons contained in its volume. The volume of the vector peak is related to the electron density of the atoms it represents. Thus maxima on the vector map which represent heavy atom-heavy atom (titanium-titanium in this case) vectors appear as much larger peaks than any other. (e.g. The titanium atoms at (1) x, y, z, (2) -x, -y, -z, and (3) 1-x, ½+y, ½-z have peaks corresponding to vectors 1-1, 1-2, 1-3, and 2-3, or 0, 0, 0, 2x, 2y, 2z, 2x-1, -½, 2z+½, 1, -2y-½, -½, respectively. Thus for the vector 1-2, $u = 2x$, $v = 2y$, and $w = 2z$.)

The data were sharpened by correcting the scattering power of the atom for thermal motion and for its dependence on $(\sin\theta)/\lambda$. Thus a sharpened Patterson is calculated with the F_{obs} "modified" to simulate what would be observed if the crystal were composed of point scatters at rest.

As explained above, large peaks on the Patterson map correspond to interatomic vectors between the heavy atoms. The positions of these peaks on the Patterson map, u, v, w, are related to the positions of the titanium atom in the unit cell, x, y, z,. Once the heavy atom has been located, the assumption is made that it dominates the diffraction pattern, and the phase angle for each diffraction beam for the whole structure is approximated by that for the heavy atoms. The first approximation to the electron density was phased with the titanium atom alone.

For each reflection, F_{cal} is actually a complex number dependent both on the phase δ and the scattering factors of the individual atoms. Thus

$$F_{cal} = A + iC \qquad (17)$$

where

$$A = \Sigma_j f_j \exp(-B \sin^2\theta/\lambda^2) \cos 2\pi(hx_j + ky_j + lz_j) \qquad (18)$$

$$C = \Sigma_j f_j \exp(-B \sin^2\theta/\lambda^2) \sin 2\pi(hx_j + ky_j + lz_j) \qquad (19)$$

and

$$B = 8\pi^2\bar{\mu}^2 \qquad (20)$$

where $\bar{\mu}^2$ is the mean-square amplitude of atomic vibration.

The simplification, C = 0, can be made for a centrosymetric case, as in this compound, and the simplified equation becomes

$$F_{cal} = A_{cal} \qquad (21)$$

These structure factor calculations with the requisite full-matrix least-squares refinement of the atomic parameters were performed by SFLS-5.(42) However, since the first summation was performed only for the titanium atoms, $|F_{cal}|$ was initially only very approximately equal to F_{obs}. A Fourier synthesis, again using FORDAP and employing the equation

$$\rho_{xyz} = 1/v\ \Sigma_h\Sigma_k\Sigma_l\ s|F_{cal}||F_{obs}|\cos 2\pi(hx + ky + lz) \qquad (22)$$

where $s|F_{cal}|$ is the sign of F_{cal} and ρ is the electron density revealed all of the non-hydrogen atom positions which were then added to the list of titanium atom positions in the structure factor calculations. The positions and isotropic thermal parameters of all of the atoms found were refined until no significant changes occurred. Anisotropic structure factors were then calculated for all atoms not related by the inversion symmetry via

$$F_{hkl} = 2\Sigma_j f_j \cos 2\pi(hx_j + ky_j + lz_j)\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})) \qquad (23)$$

where β_{11}, β_{22}...are the anisotropic thermal parameters. The atomic positions (x_i, y_i, z_i) and thermal parameters were refined again until no significant change occurred in the function

$$D = \sum_{hkl} w(|F_{obs}| - |F_{cal}|)^2 \qquad (24)$$

where $w = |\sigma(F_{obs})|^{-2}$ and F_{cal} is the structure factor based on the model of equation 23.

The synthesis of a difference Fourier, using another function of FORDAP,

$$\Delta\rho_{xyz} = 1/v\ \Sigma_h\Sigma_k\Sigma_l\ (F_{obs} - F_{cal})\cos 2\pi(hx + ky + lz), \qquad (25)$$

was used to locate the positions of the hydrogen atoms. Note here that the difference Fourier, as the Fourier synthesis discussed above, uses the signs of F_{cal} and the magnitude of F_{obs} for the observed structure factors and subtracts from these a calculated synthesis using both the signs and magnitude of F_{cal}. After five cycles of isotropic refinement, the difference Fourier synthesis showed the usual peaks attributable to anisotropic motion of the atoms included in the model, and also peaks at positions expected for all of the hydrogen atoms. However, very diffuse peaks were observed for the methyl hydrogen atoms so that these were refined as rigid bodies in the final structure.

The refined positions of the carbon atoms of the methyl groups and those of the carbonyl carbon atoms were used together with the clearest hydrogen atom peaks of each methyl group to define idealized positions for all three methyl hydrogen atoms of each group via the program RBANG. Thus, the hydrogen atoms were positioned 1.6 Å apart at the corners of an equilateral triangle, and placed symetrically 0.98 Å from their carbon atom. Through a format conversion, using RIGID, the two sets of hydrogen atoms were then included in the least-squares refinement as rigid groups, each with a single group isotropic thermal parameter. The program NUCLS4 was used for the refinement since it can refine certain parts of a molecule as if they were rigid bodies. The least-squares is essentially the same as in SFLS-5 but the program is limited to isotropic thermal parameters for the group. The hydrogen attached to the C3 carbon atom (Figure III) was also allowed to refine isotropically. Again the function minimized was as in equation 24. Also calculated were the residual index R and the weighted discrepency index R_w by equations 26 and 27 respectively.

$$R = \frac{\Sigma||F_{obs}| - |F_{cal}||}{\Sigma|F_{obs}|} \qquad (26)$$

$$R_w = \left|\frac{\Sigma w(|F_{obs}| - |F_{cal}|)^2}{\Sigma w|F_{obs}|^2}\right|^{\frac{1}{2}} \qquad (27)$$

The "goodness of fit" was defined as:

$$\sigma pi = \left|\frac{\Sigma w(|F_{obs}| - |F_{cal}|)^2}{(n - m)}\right|^{\frac{1}{2}} \qquad (28)$$

where n and m are the numbers of observations and parameters varied respectively. The "goodness of fit", or the error in an observation of unit weight, reduced to 1.25 after three cycles. The final values of R and R_w may be found in Table III.

Geometric calculations from the determined positional parameters and the analysis of the thermal elipsoids$^{(44)}$ were performed by UTILITY. The program converted the fractional coordinates to orthogonalized coordinates and computed distances, angles, and the estimated standard deviations (esds) thereon for all intramolecular contacts less than a specified value. Thus the output list contained all of the bond angles and distances bracketed by an uncertainty. The program was also used to compute intramolecular contacts, and the best plane through a group of weighted atoms.

The program ORTEP(45) interprets the cards from NUCLS4 and generates a series of instructions which are applied by the Hewlett Packard 2114A computer to a Complot x-y recorder. The options in ORTEP allow for the drawing of the molecule in either "ball and stick" form or the plotting of the thermal elipsoids associated with each atom in the molecule. The molecular bonds in the latter case are drawn to perspective. The stereoscopic view of the molecular packing was accomplished by rotating the packing diagram the required number of degrees to the left and the right and plotting one beside the other.

III. RESULTS AND DISCUSSION

A. Infrared Spectra

In this study, we have concentrated mainly on the acetylacetonato, benzoylacetonato, and dibenzoylacetonato complexes. Because these compounds hydrolysed after prolonged exposure of the mulls to atmospheric moisture, good spectra were exceedingly difficult to obtain. Thus total spectra were recorded only to verify the purity of the samples. The criteria used(24) was the absence of carbonyl vibrations above 1600 cm^{-1} and the absence of hydroxyl vibrations in the 3300 cm^{-1} and 2700 cm^{-1} region of the spectrum. From an infrared investigation of several ketones, Rasmussen and coworkers(48) have assigned the carbonyl vibrations in the free β-diketone ligand at 1639 cm^{-1} for the keto-form. Because of very strong hydrogen bonding in the enol form, the hydroxyl vibration has shifted from 3300 cm^{-1} for free ν(OH) to 2700 cm^{-1} for hydrogen bonded ν(OH). Upon coordination to a metal, the free ligand carbonyl vibration frequencies are shifted to below 1600 cm^{-1} and the ν(OH) vibration at 2700 cm^{-1} disappears.(49) In this way it was ascertained that all of the diketone oxygens were complexed to the titanium and the samples were free of hydrolysis products. Owing to the presence of phenyl groups, spectra of complexes containing the bzac (1-phenyl-1,3-butanedionate) or bzbz (1,3-diphenyl-1,3-propanedionate) ligands were complicated and implications concerning the nature of the titanium-fluorine frequencies were less straight forward than in the acac (2,4-pentanedionate) complexes.

The spectra of $[F_3Ti(bzac)]_2$ and $[F_3Ti(bzbz)]_2$ from 950-500 cm^{-1} have been reproduced in Figures I-II while the infrared frequencies and possible assignments for the Ti-F and Ti-O bands have been reported in Tables I and II. A spectral study of $F_2Ti(bzac)_2$ and $F_2Ti(bzbz)_2$ is available(37) and the values reported in this study agree closely. The $[F_3Ti(bzac)]_2$ and $[F_3Ti(bzbz)]_2$ complexes have not yet been reported and were required to assign the bridging titanium-fluorine frequencies $\nu(Ti-F)_{br}$. This study parallels preliminary investigations performed earlier on a series of $[XY_2Ti(acac)]_2$ (X,Y = F,Cl) complexes.(46)

Ideally, to avoid the complications of the numerous bands found in the bzac and bzbz compounds, the same information concerning the positions of $\nu(Ti-F)_{br}$ should be available from the series of compounds $F_2Ti(acac)_2$, $[FCl_2Ti(acac)]_2$, $Cl_2Ti(acac)_2$, $[Cl_3Ti(acac)]_2$ and $[F_3Ti(acac)]_2$. These compounds have been synthesized; unfortunately the $[F_3Ti(acac)]_2$ complex is an intractable

Table I - Infrared Frequencies (cm^{-1}) for Solid $F_2Ti(bzac)_2$ and $[F_3Ti(bzac)]_2$ in Nujol.[a]

$F_2Ti(bzac)_2$[b]	$[F_3Ti(bzac)]_2$	Possible Mode
970 s (967 ms)	977 vw	
934 vw (931 vw)	943 ms	
852 ms (849 m)	851 vw	
828 ms (822 m)	832 w	
796 s (791 s)	795 ms	
-	780 ms	
-	735 ms	
718 s (711 s)	711 s	
700 sh (693 sh)	700 s	
689 s (683 s)	680 ms	
625 vs (620 s)	637 s	$(Ti-F)_{ter}$
619 vs (613 s)	-	$(Ti-F)_{ter}$
610 sh (608 sh)	-	
-	600 s	$(Ti-F)_{br}$
578 ms (573 s)	-	
557 m (551 mw)	560 m	
447 ms (442 ms)	465 ms	(Ti-O)

[a] Key: sh, shoulder; s, strong; v, very; br, broad; m, medium; w, weak. [b] Values in brackets are from reference 37.

Table II - Infrared Frequencies (cm^{-1}) for Solid $F_2Ti(bzbz)_2$ and $[F_3Ti(bzbz)]_2$ in Nujol.[a]

$F_2Ti(bzbz)_2$[b]	$[F_3Ti(bzbz)]_2$	Possible Mode
980 vw (978 w)	977 vw	
948 m (945 ms)	941 m	
- (940 ms)	-	
930 vw (928 m)	-	
845 vw (854 w)	850 w	
826 w (820 m)	833 w	
820 w (816 m)	-	
805 vw (799 w)	-	
790 m (794 sh)	792 m	
- (784 ms)	-	
776 ms (768 s)	778 ms	
770 ms (763 s)	-	
732 s (727 s)	-	
722 m (716 ms)	725 s	

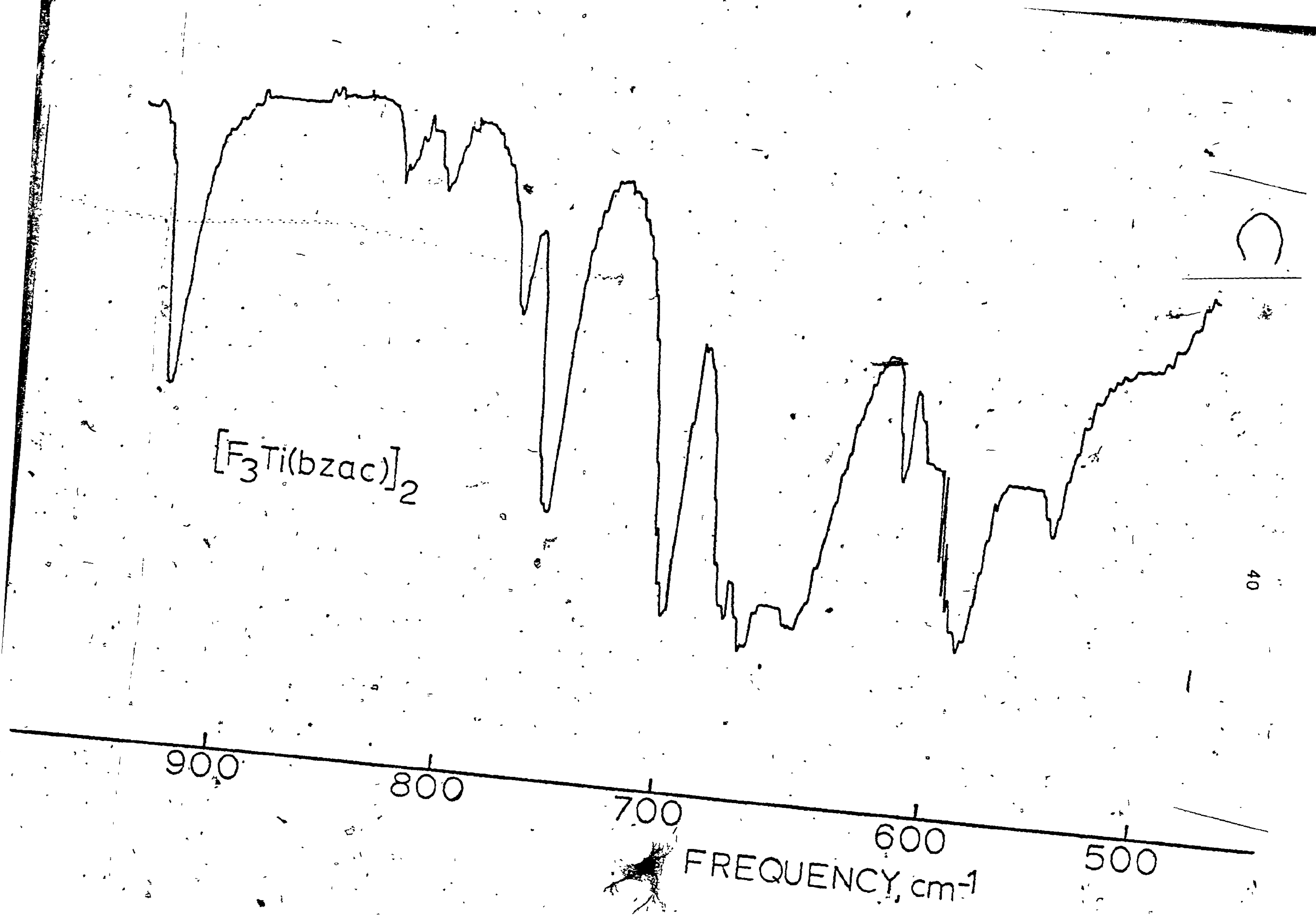
Table II - cont'd

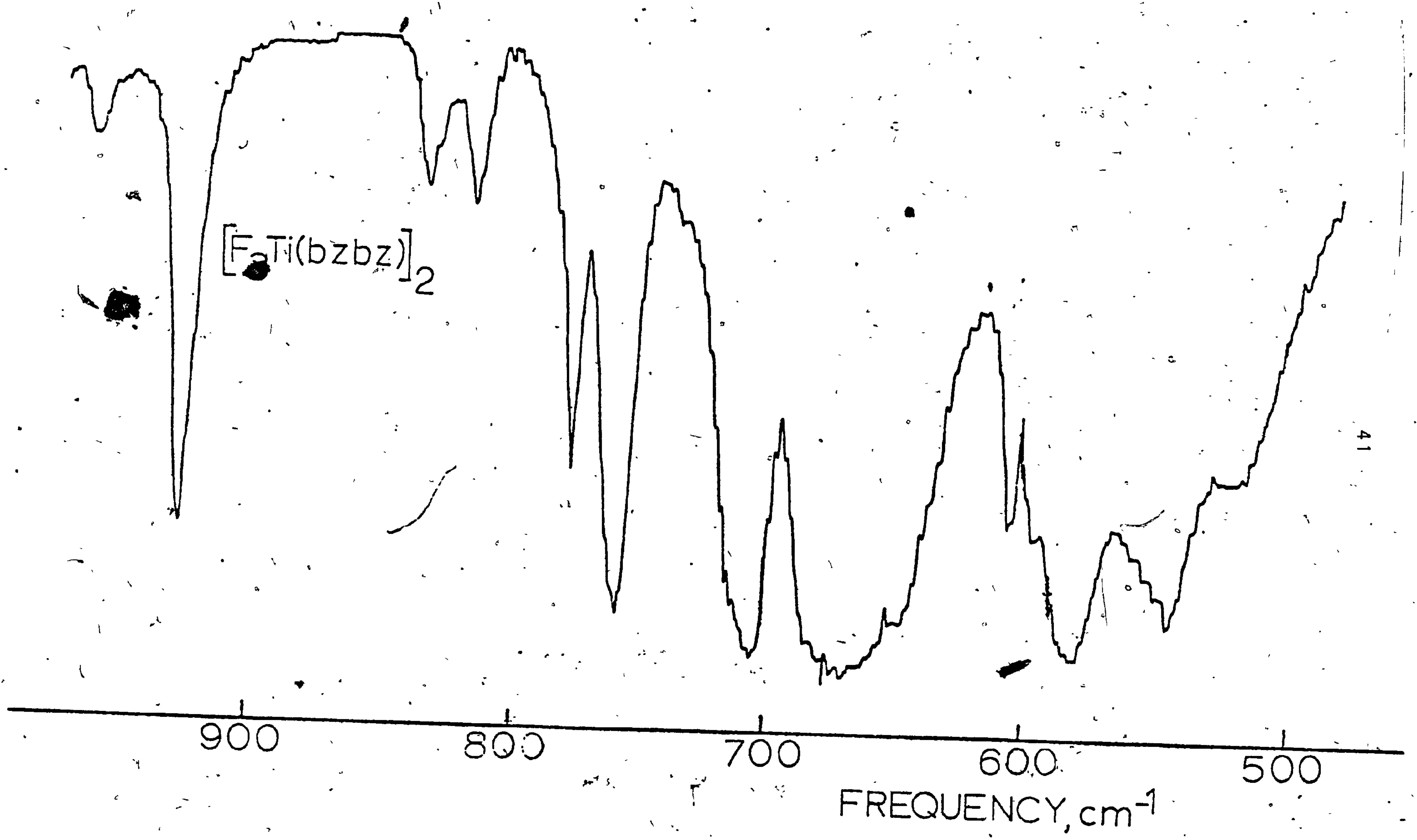
$F_2Ti(bzbz)_2$[b]	$[F_3Ti(bzbz)]_2$	Possible Mode
718 m (711 s)	-	
696 ms (701 m)	-	
682 m (689 s)	690 vs	
648 s (642 s)	667 vs	$(Ti-F)_{ter}$
636 vs (637 s)	-	$(Ti-F)_{ter}$
625 s (629 s)	624 s	$(Ti-F)_{ter}$
619 s (620 s)	-	
- (614 s)	-	
- -	598 s	$(Ti-F)_{br}$
590 m (586 m)	-	
574 m (570 s)	558 ms	
546 m (542 ms)	-	
468 w (462 m)	463 w	(Ti-O)

[a] Key: sh, shoulder; s, strong; v, very; br, broad; m, medium; w, weak. [b] Bracketed values are from reference 37.

1. Figure I - Infrared Spectra of Solid $[F_3Ti(bzac)]_2$ in the 950 - 500 cm^{-1} Region in Nujol.

2. Figure II - Infrared Spectra of Solid $|F_3Ti(bzbz)|_2$ in the 950 - 500 cm^{-1} Region in Nujol.


$[F_3Ti(bzac)]_2$
900
800
700
600
500
FREQUENCY, cm-1


$[F_2Ti(bzbz)]_2$
900
800
700
600
500
FREQUENCY, cm^{-1}

oil, and because of rapid hydrolysis of neat samples, infrared frequencies are impossible to assign with certainty. The infrared frequencies associated with the four remaining samples agree with those reported earlier$^{(35,46)}$ and are summarized in Table III.

An intense absorption band centered at about 625 cm^{-1} in the parent $F_2Ti(dik)_2$ complexes has been assigned to a terminal Ti-F stretching frequency.$^{(35,37,46)}$ If a five-coordinate complex is formed on reaction of $F_2Ti(dik)_2$ with TiF_4 or $TiCl_4$, the $\nu(Ti\text{-}F)_{ter}$ band in the $X_3Ti(dik)$ complex should shift to a higher frequency.$^{(47)}$ However, in the case where the Ti-F moiety forms a bridging unit in a dimeric structure as in $[F_3Ti(bzac)]_2$ or $[F_3Ti(bzbz)]_2$ the $\nu(Ti\text{-}F)_{ter}$ band should be accompanied by a $\nu(Ti\text{-}F)_{br}$ band at a lower frequency. In $[FCl_2Ti(acac)]_2$, where no $\nu(Ti\text{-}F)_{ter}$ band exists, this band in the parent complex should be replaced by a $\nu(Ti\text{-}F)_{br}$ band at a lower frequency.$^{(47)}$

In agreement with infrared spectra reported earlier$^{(35,46)}$ the spectrum of $F_2Ti(acac)_2$ reveals two $\nu(Ti\text{-}F)_{ter}$ bands at 632 and 615 cm^{-1}. In agreement with the results of Bickley,$^{(46)}$ the assignment is based on the absence of these bands in the spectra of $Cl_2Ti(acac)_2$, "$Cl_3Ti(acac$" and "$FCl_2Ti(acac)$". Furthermore, since no additional bands appear in the higher frequency region of the "$FCl_2Ti(acac)$" spectrum that might be assigned to a $\nu(Ti\text{-}F)_{ter}$ band, as would be expected from the formation

Table III - Infrared Frequencies (cm^{-1}) for Solid Ti(acac)$_2$X$_2$ and [X$_3$Ti(acac)]$_2$ Complexes in Nujol.[a]

Ti(acac)$_2$F$_2$	[FCl$_2$Ti(acac)]$_2$	Ti(acac)$_2$Cl$_2$[b]	[Cl$_3$Ti(acac)]$_2$	Possible Mode
948 (m)	949 (m)	949 (m)	950 (m)	(C - CH$_3$)
935 (ms)	926 (ms)	931 (ms)	924 (ms)	
806 (ms)	799 (ms)	802 (ms)	799 (ms)	(C - H)
-	676 (s)	678 (sh)	676 (s)	
669 (s)	-	665 (s)	-	(Ti - O)
655 (s)	641 (w)	-	-	
-	-	-	640 (w)	
632 (vs)	-	-	-	(Ti - F)$_{ter}$
615 (vs)	-	-	-	(Ti - F)$_{ter}$
544 (m)	539 (m)	537 (m)	540 (m)	
465 (s,br)	484 (s,br)	467 (s,br)	484 (s,br)	(Ti - O)
-	-	-	413 (m)	

[a] Key: sh, shoulder; s, strong; v, very; br, broad; m, medium; w, weak. [b] Band positions agree with those reported by Lowry(35) and Bickley.(46)

of a five-coordinate complex, the Ti-F stretching frequency must have been shifted to a lower frequency and must result from the formation of a bridging unit in a dimeric structure.

There are two $\nu(\mathrm{Ti\text{-}F})_{\mathrm{ter}}$ bands in the spectrum of $F_2Ti(bzac)_2$ at 625 and 619 cm^{-1} while three such bands at 648, 636, and 625 cm^{-1}, have been assigned(37) ~~as~~ $\nu(\mathrm{Ti\text{-}F})_{\mathrm{ter}}$ in the spectrum of $F_2Ti(bzbz)_2$. Agreement with reported positions is not as good in the latter compounds(37) as in the former.(46) However, agreement with reported results is especially good for the acac complexes.(35,46) In the spectra of the apparent five-coordinate complexes, one new band (600 cm^{-1} for "$F_3Ti(bzac)$", 598 cm^{-1} for "$F_3Ti(bzbz)$") appears at a lower frequency from the $\nu(\mathrm{Ti\text{-}F})_{\mathrm{ter}}$ band in the parent complex. These bands could thus be assigned to $\nu(\mathrm{Ti\text{-}F})_{\mathrm{br}}$ in the dimeric structures $[F_3Ti(bzac)]_2$ and $[F_3Ti(bzbz)]_2$. Furthermore, it was suggested(46) that the band at 603 cm^{-1} in the spectrum of "$FCl_2Ti(bzac)$" could posibly be due to the $\nu(\mathrm{Ti\text{-}F})_{\mathrm{br}}$ vibration; however, insufficient data precluded a definite assignment.

The $\nu(\mathrm{Ti\text{-}F})_{\mathrm{ter}}$ bands in the spectrum of the parent $F_2Ti(bzac)$ at 625 and 619 cm^{-1} have been replaced by a single $\nu(\mathrm{Ti\text{-}F})_{\mathrm{ter}}$ band at 637 cm^{-1} in the spectrum of the bridged complex. Curiously, the $\nu(\mathrm{Ti\text{-}F})_{\mathrm{ter}}$ band at 625 cm^{-1} in the spectrum of the $F_2Ti(bzbz)_2$ complex remained unchanged in the spectrum of dimer, while the remaining two $\nu(Ti-F)_{ter}$ bands (648 and 636 cm^{-1}) in the parent complex have been replaced by a single $\nu(Ti-F)_{ter}$ band at 667 cm^{-1} in the spectrum of $[F_3Ti(bzbz)]_2$. It is interesting to note that there is an increase of about 10-20 cm^{-1} in the $\nu(Ti-F)_{ter}$ stretching frequency in the six-coordinate bridged complex with respect to the unbridged parent complex. Although no such shifts have been reported for titanium fluorides, this shift was the basis for postulating a five-coordinate solid state structure for "$Cl_3Ti(dik)$" (dik = acac, bzac) complexes.(31)

A recent article(50) has appeared on the synthesis and characterization of perfluorotitanate (IV) salts. The authors report Raman active bands at 601 and 599 cm^{-1} $\nu(A_{1g})$ for the NF_4^+ and Cs^+ salts respectively of $TiF_6{}^{2-}$. Infrared active bands belonging to this ion (point group O_h) are reported at 563 and 562 cm^{-1} $\nu_3(T_{1u})$ again for the NF_4^+ and Cs^+ salts. These results support the assignment of $\nu(Ti-F)_{ter}$ as the band at about 625 cm^{-1}. It is also tempting to postulate at least some Ti-F character in the band appearing at about 560 cm^{-1}, however, these bands are also present in the spectra of the chlorides(37) and bromides(37) and therefore little can be said about them.

Vibrational spectra have also been interpreted for a variety of perfluoro compounds.(50) Of particular importance to this discussion are $CsTi_2F_9$ and $Cs_2Ti_2F_{10}$. Infrared active bands in the former appear at 725, 650, 530, and 446 cm^{-1}, while in the latter, which bears a greater structural resemblance to the bridged dimers in this study than the former, bands appear at 730-600, 468, and 441 cm^{-1}. Thus it may be seen that the problem of assigning a band as $\nu(Ti-F)_{br}$ or as $\nu(Ti-O)$, for example, is quite complex. In fact, because of the possible overlap of different bands, the possibility of degenerate vibrations, and the possibility of infrared inactive bands becoming active (or vice-versa) on changing the symmetry (i.e. forming a bridged dimeric compound), it is even difficult to postulate whether a certain band in the region of interest is mainly, or for that matter, has any $\nu(Ti-F)_{br}$ component in it.

No earlier reports of the values of $\nu(Ti-F)_{br}$ in titanium (IV) complexes are available. However, a band at 470 cm^{-1} has been assigned to $\nu(Ti-F)_{br}$ in $[(h^5 - C_5H_5)TiF_2]_2$.(51) Monocyclopentadienyl-titanium (III) halides, $(h^5 - C_5H_5TiX_2)$, are at least dimeric and probably polymeric in the solid state.(52) It is well known that an increase in the oxidation state of the metal increases the frequency of metal-ligand vibrations.(47) Thus it would not be inconceivable to find $\nu(Ti-F)_{br}$ in the fluorine bridged dimers in this study above 500 cm^{-1}.

The crystal structure of the $Ti_2Cl_{10}^{2-}$ anion(53) shows a good structural resemblance to the bridged dimers in this study.(34) The infrared spectra of the anion has been determined,(54,55) and from the assignment of $\nu(Ti-Cl)_{ter}$ and $\nu(Ti-Cl)_{br}$, (for more than one bridging or terminal mode), the ratio $\nu(Ti-Cl)_{br}/\nu(Ti-Cl)_{ter}$ can be calculated as 0.61 to 0.74. A similar ratio calculated for the bromides gives 0.55 to 0.69. Extrapolation of this ratio to the fluorides should give the range 0.66 to 0.79. Applying this ratio to obtain a range of frequencies in which $\nu(Ti-F)_{br}$ may be located yields 420-500 cm^{-1}, assuming the extrapolations holds for the fluorides.

A vibrational analysis of both the $Ti_2F_{10}^{2-}$ (50) and $Ti_2Cl_{10}^{2-}$ (53-55) anions were based on the vibrational analysis of Nb_2Cl_{10}.(56-58) Since the infrared active modes for the bridging chlorides are reported as b_{2u} and b_{3u}, it is not unreasonable to assume the same modes as bridging in the $Ti_2F_{10}^{2-}$ anion. These modes are reported as 441 and 468 cm^{-1} in the fluoride.(50) However, bands in this region appear at essentially the same frequencies in the spectra of both six-coordinate parent compound $F_2Ti(dik)_2$ and the bridged dimer $[F_3Ti(dik)]_2$. Furthermore, these bands have previously been assigned as $\nu(Ti-O)$.

Tentative assignments as ν(Ti-F)$_{br}$ for the $[F_3Ti(dik)]_2$ complexes may be made in the 590 cm^{-1} region of the infrared spectrum. Again, the sole reason for this assignment is the absence of these bands in the parent complex. The absence of a band around 590 cm^{-1} in the $[FCl_2Ti(acac)]_2$ complex is not explainable with certainty at present. Two possible explanations are that the band is shifted as a result of the nature of the ligands (i.e. bzac vs acac, F vs Cl) or that the band becomes inactive because of a difference in symmetry. In either case, more work is required to clarify the situation with respect to the position of ν(Ti-F)$_{br}$ in the bridged dimer, as well as to establish the positions of ν(Ti-X) (X = F,Cl) in the five-coordinate species.

B. The Crystal and Molecular Structure of $[Cl_3Ti(acac)]_2$

The crystal and intensity collection data are summarized in Table IV while Table V contains the final positional and thermal parameters for the non-hydrogen atoms. The positional parameters as well as the isotropic thermal parameters for the hydrogen atoms are collected in Table VI. The crystallographic analysis demonstrates that the apparent five-coordinate $Cl_3Ti(acac)$ complex exists as the cyclic dimer, di-μ-chlorotetrachlorobis (2,4-pentanedionato) dititanium (IV), with two chlorine atoms bridging the two titanium atoms. The molecular structure and atom numbering scheme are illustrated in Figure III; Figure IV depicts a stereographic view of the molecular packing. Selected bond distances and bond angles are collected in Table VII; structure factor amplitudes are presented in Table VIII. Close intermolecular contacts are ruled out on the basis of Van der Wall's radii.(57)

Figure III shows that the two $Cl_2Ti(acac)$ fragments of the dimer are joined by Cl(3) and Cl(3'). As required by symmetry, the Ti_2Cl_2 ring unit is planar. The titanium-titanium and chlorine-chlorine intramolecular distances are 3.772(1) Å and 3.267(2) Å respectively, while the bond angle at titanium is 81.77(4)°, and at chlorine is 98.23(4)°. The bond angles between adjacent donor atoms range from 81.77(4)° to 97.43(5)°, while bond angles defined by the trans bonds are 166.50(9)° (Cl_3-Ti-O1), 168.18(9)° (Cl1-Ti-O2), and 173.17(5)° (Cl2-Ti-Cl3') giving rise to a distorted octahedral geometry at the titanium atom. Such an octahedral distortion at the titanium atom appears common in several other chlorine- as well as oxygen-bridged titanium IV complexes. For example, bond angles between adjacent donor atoms range from 79.28(5)° to 100.23(7)° in $[TiCl_4 \cdot CH_3COOC_2H_5]_2$(60) and 78.5(3)° to 98.2(4)° in $[TiCl_4 \cdot OPCl_3]_2$.(61) The corresponding bond angles

Table IV - Summary of Crystal and Intensity Collection Data for $[Cl_3Ti(acac)]_2$

A. Crystal parameters at 18° with Mo Kα = 0.71069 Å	
a	8.8308 Å
b	10.7339 Å
c	10.5171 Å
α	90.00°
β	93.92°
γ	90.00°
V	944.573 $Å^3$
Space Group	$P2_1/n$ (No. 14)
Mole. Wt.	506.74 g/mol
ρ_{cal}	1.69 g cm^{-3}
ρ_{exp}	1.78 g cm^{-3}
μ	16.4485 cm^{-1}
Crystal dimension	0.2 x 0.2 x 0.2 mm
Estimated Transmission factors	t_{min} = 72% ; t_{max} = 80%

Table IV - cont'd

Radiation	Mo Kα
Monochromator	graphite $2\theta_{002} = 12.1^{\circ}$
Crystal to detector distance	25 mm
Detector	Scintillation detector and pulse height analyzer set for 100% of Mo Kα peak.
Attenuators	Ni foil used for intensities > 10^4 Hz
Take off angle	3.0°
Detector aperture	4 x 4 mm square
Scan type	coupled $\theta - 2\theta$, 1°min^{-1}
Scan length	$\Delta(2\theta)$ = (base width + 0.692 tanθ) starting base width/2 below peak.
Rotation axis	a
Reflections measure	±h, +k, +l
Maximum and minimum 2θ	45.0°, 4.0°
Scan base width	1.3°
Standard reflection	002
Variation of standards	±3%
Number of reflections collected	1301
Number of reflections with $I > 3\sigma(I)$	1092
Weighted R	0.029 } includes hydrogens
R	0.031

Table V – Final Positional and Thermal Parameters for the Non-hydrogen Atoms with Estimated Standard Deviations

Atom	x	y	z
Ti	0.015037(79)	0.158716(65)	-0.075155(78)
Cl 1	0.23428(12)	0.20111(10)	0.05297(12)
Cl 2	0.10494(13)	0.22968(11)	-0.25460(12)
Cl 3	0.09706(11)	-0.05218(9)	-0.11851(10)
O1	-0.09334(28)	0.30481(23)	-0.30481(23)
O2	-0.19475(28)	0.10963(24)	-0.15463(26)
C1	-0.26563(53)	0.47522(43)	0.04499(41)
C3	-0.35937(52)	0.27170(44)	-0.09714(46)
C4	-0.33491(45)	0.15574(39)	-0.15070(39)
C5	-0.47032(54)	0.07992(46)	-0.20844(52)

Table V - cont'd

Atom	β_{11}	β_{22}	β_{33}
Ti	0.00841(11)	0.00528(7)	0.00958(7)
Cl 1	0.0095(2)	0.0065(1)	0.0114(1)
Cl 2	0.0152(2)	0.0100(1)	0.0098(1)
Cl 3	0.0104(2)	0.0052(1)	0.0079(1)
O1	0.0090(4)	0.0051(3)	0.0108(4)
O2	0.0077(4)	0.0070(3)	0.0090(4)
C1	0.0147(9)	0.0062(5)	0.0143(7)
C2	0.0107(7)	0.0061(4)	0.0081(5)
C3	0.0082(7)	0.0093(6)	0.0111(6)
C4	0.0101(7)	0.0079(5)	0.0060(5)
C5	0.0100(7)	0.0111(6)	0.0128(7)

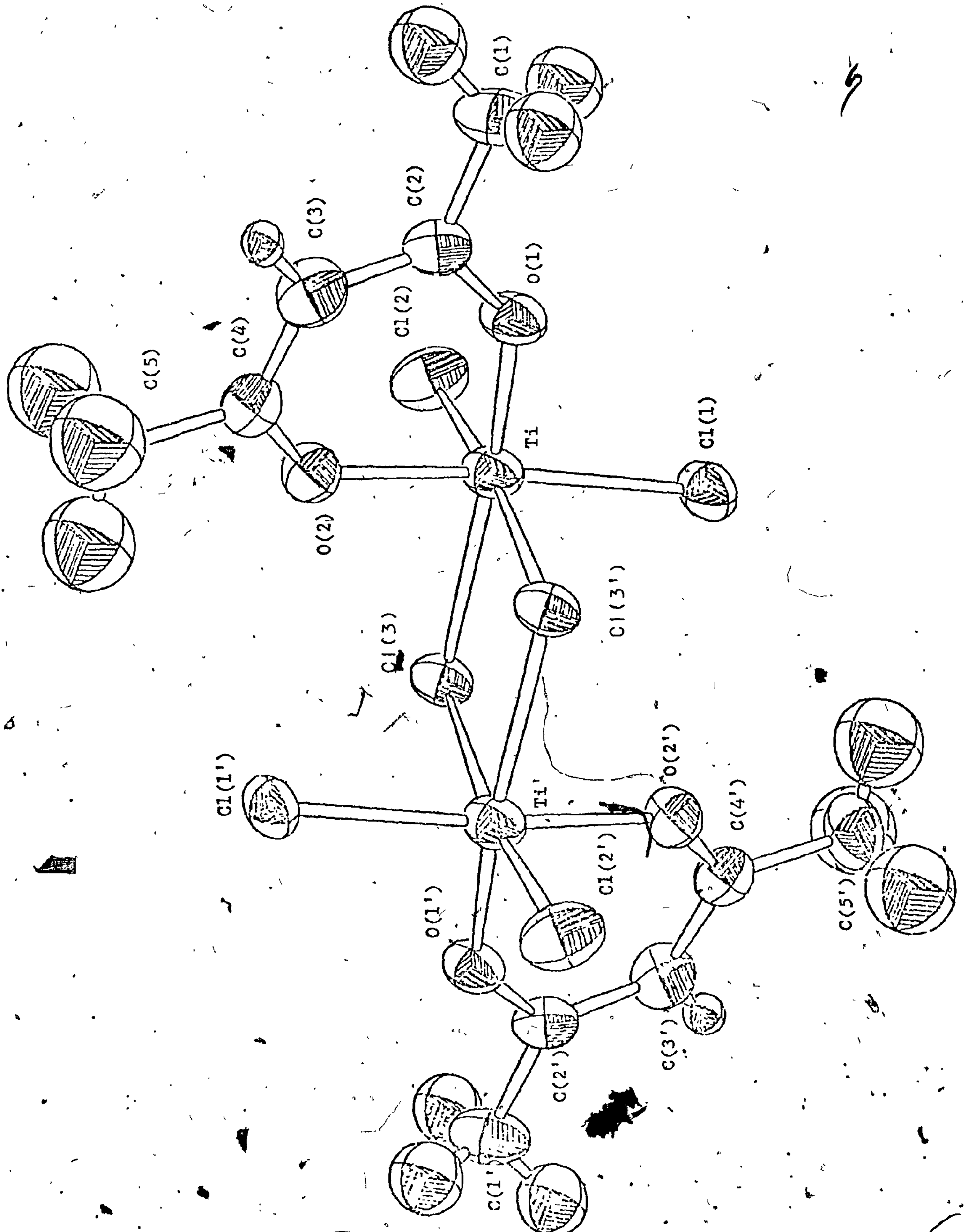
Table V - cont'd

Atom	β_{12}	β_{13}	β_{23}
Tl	0.00058(7)	0.00040(8)	-0.00001(7)
Cl 1	-0.0007(1)	-0.0016(1)	-0.0010(1)
Cl 2	0.0018(1)	0.0029(1)	0.0030(1)
Cl 3	0.0012(1)	0.0023(1)	-0.0008(1)
O1	0.0014(3)	0.0006(3)	-0.0008(3)
O2	0.0009(3)	-0.0003(3)	-0.0007(3)
C1	0.0031(5)	0.0035(6)	0.0001(5)
C2	0.0011(5)	0.0022(5)	0.0010(4)
C3	0.0032(5)	0.0007(6)	-0.0009(5)
C4	0.0000(5)	0.0009(4)	0.0010(4)
C5	-0.0005(6)	-0.0018(6)	-0.0018(6)

Table VI - Hydrogen Atom Positional and Isotropic Thermal Parameters

Atom	x	y	z	B
H31	-0.4501(47)	0.3007(40)	0.1068(41)	1.7(1.1)
H11	-0.1625(37)	0.5245(45)	-0.0036(43)	4.9(1.0)
H12	-0.3395(45)	0.5190(48)	-0.0559(37)	4.9(1.0)
H13	-0.2984(52)	0.4701(46)	0.0837(37)	4.9(1.0)
H51	-0.4947(73)	0.1164(47)	-0.2824(50)	7.4(1.0)
H52	-0.4510(61)	-0.0115(40)	-0.2166(54)	7.4(1.0)
H53	-0.5693(62)	0.0838(48)	-0.1490(45)	7.4(1.0)

Figure III - The Molecular Structure of di-μ-chlorotetrachlorobis (2,4-pentanedionato) dititanium (IV), $[Cl_3Ti(acac)]_2$, illustrating the atom number scheme.


C(1)
C(2)
C(3)
O(1)
Cl(2)
C(4)
C(5)
Ti
Cl(1)
O(2)
Cl(3')
Cl(3)
O(2')
Cl(1')
Ti'
C(4')
Cl(2')
O(1')
C(5')
C(3')
C(2')
C(1')

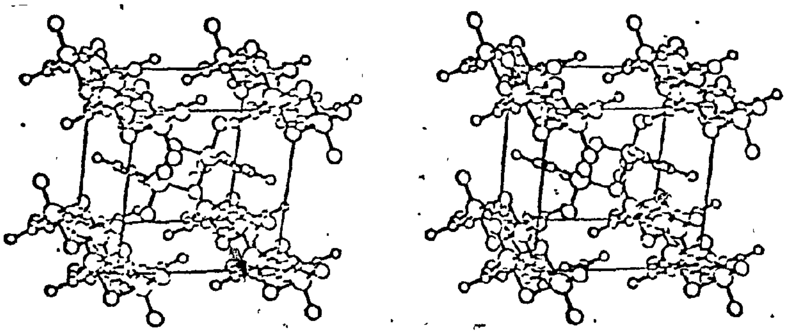


Figure IV - Stereographic View of the Molecular Packing for $[Cl_3Tl(acac)]_2$.

Table VII - Intramolecular Bond Distances (Å) and Bond Angles (deg) and esd's

Bond Distances	
Ti - Cl1	2.250(1)
Ti - Cl2	2.214(1)
Ti - Cl3	2.418(1)
Ti - O1	1.888(3)
Ti - O2	1.966(3)
Ti - Cl3'	2.569(1)
O1 - C2	1.307(5)
O2 - C4	1.278(4)
C1 - C2	1.488(6)
C1 - H11	1.01(4)
C1 - H12	0.95(4)
C1 - H13	0.94(4)
C2 - C3	1.360(6)
C3 - C4	1.387(6)
C3 - H31	0.82(4)
C4 - C5	1.492(6)
C5 - H51	0.88(5)
C5 - H52	1.00(4)
C5 - H53	1.07(5)

Table VII - cont'd

Bond Angles			
Cl1 - Ti - Cl2	97.43(5)	C2 - C1 - H13	107.3(3.0)
Cl1 - Ti - Cl3	94.08(4)	H11 - C1 - H12	104.0(3.7)
Cl1 - Ti - Cl3'	86.74(4)	H11 - C1 - H13	112.0(3.8)
Cl1 - Ti - O1	93.99(9)	H12 - C1 - H13	112.2(3.6)
Cl1 - Ti - O2	168.18(9)	O1 - C2 - C1	115.0(4)
Cl2 - Ti - Cl3	92.50(5)	O1 - C2 - C3	120.8([illegible])
Cl2 - Ti - Cl3'	173.17(5)	C1 - C2 - C3	124.2(4)
Cl2 - Ti - O1	97.16(9)	C2 - C3 - C4	124.2(4)
Cl2 - Ti - O2	94.38(9)	C3 - C4 - C5	121.7(4)
Cl3 - Ti - Cl3'	81.77(4)	C2 - C3 - H31	118.4(3.0)
Cl3 - Ti - O1	166.50(8)	C4 - C4 - H31	116.8(3.0)
Cl3 - Ti - O2	85.78(8)	O2 - C4 - C3	121.5(4)
O1 - Ti - O2	84.10(11)	O2 - C4 - C5	116.8(4)
O1 - Ti - Cl3'	87.91(9)	C4 - C5 - H51	103.9(3.7)
O2 - Ti - Cl3'	81.54(8)	C4 - C5 - H52	116.6(3.0)
Ti - Cl3 - Ti'	98.23(4)	C4 - C5 - H53	109.8(2.7)
Ti - O1 - C2	135.59(25)	H51 - C5 - H52	112.9(4.7)
Ti - O2 - C4	132.82(26)	H51 - C5 - H53	110.8(4.7)
C2 - C1 - H11	110.1(2.6)	H52 - C5 - H53	103.0(4.1)
O2 - C1 - H12	111.3(2.9)		

across the trans bonds are 166.28(5)° to 169.77(10)° for the former ethylacetate dimer,(60) and 165.0(4)° to 173.0(6)° in the latter compound.(61) Similar distortions have also been reported for the oxygen-bridged titanium IV dimer, $[TiCl(acac)_2]_2O \cdot CHCl_3$(62) and $[TiO(acac)_2]_2$.(63)

Deviations from the least-squares plane for the 2,4-pentanedionate group (acac) are listed in Table IX. The bond lengths in the planar chelated (acac) ligand are: O1-C2, 1.307(5) Å; C2-C3, 1.360 Å; C3-C4, 1.387 Å; and O2-C4, 1.278(4) Å. Lingafelter(64) has reported the mean values for the corresponding bond distances for a variety of metal acetylacetonates of varying geometry and oxidation state of the metal ion as d(O-C) = 1.28 Å and $d(C-C_i)$ = 1.40 Å. Note then that O1-C2 is appreciably longer and C2-C3 is significantly shorter than the corresponding values reported by Lingafelter. The titanium-donor atom bond distances are of more value to us. For example, the Ti-O1 bond distance of 1.888(3) Å and the Ti-O2 bond distance of 1.996(3) Å are much shorter than the corresponding Ti-O bond distances of 1.97 and 2.06 Å respectively in $[TiO(acac)_2]_2$(63) or of 1.985(5) Å in bis(2,4-pentanedionato)-bis(2,6-diisopropylphenoxo) titanium (IV).(65) Interestingly, the Ti-O1 bond is trans to the longer (and therefore weaker) Ti-Cl3 bond (2.418(1) Å) and the Ti-O2 bond is trans to the shorter (and stronger) titanium-chlorine terminal bond Ti-Cl1 (2.250(1) Å). Furthermore, the titanium-terminal chlorine bond lengths show some differences which are outside experimental error. The longer Ti-Cl1 (2.250(1) Å) bond is opposite the Ti-O2 bond while the shorter Ti-Cl2 (2.214(1) Å) bond is trans to the bridge Ti-Cl3. There are two possible explanations for these variations in bond lengths. The chlorine-donor atoms have a smaller trans influence than the oxygen-donor atoms O1 and O2. This explanation is in accord with the trans effect postulated to explain the variations in the lengths of the three Ti-O bonds in the $[TiO(acac)_2]_2$ dimer.(63) Second, titanium (IV) is a d^0 system. It thus has available relatively contracted vacant 3d orbitals that are potential π-acceptors. Furthermore, the presence of such electronegative substituents as chlorine should increase the effective nuclear charge at titanium resulting in further contraction of the 3d orbitals. Such a contraction reduces the energy difference between the empty titanium 3d orbitals and the 2p orbitals containing the oxygen lone pairs and thereby enhancing pπ-dπ bonding. The idea of π-type bonding in titanium diketonates is not new. It has been suggested the $Ti(acac)_3^+$ cation(5) as being partially responsible for the low-field shifts in the proton nuclear magnetic resonance spectra, and in a variety of titanium (IV) diketonates

Table VIII - Structure Factor Amplitudes
for $[Cl_3Ti(acac)]_2$

```
 K   L FOBS FCAL

     H =  -8

-5  -1   57   60
-5   0   77   70
-4  -2  131 -133
-4  -1  154 -151
-4   0   52   47
-3  -3  263 -265
-3  -2   52   35
-3  -1  212 -217
-3   0  205 -213
-2  -4  153 -163
-2  -3  130  130
-2  -2  215 -223
-2  -1  133  -97
-2   0  155 -160
-1  -4  174  174
-1  -3   50   21
-1  -2   55  -50
-1  -1   54   50
-1   0   33  -93
 0  -4  131  136
 0  -2  233  259
 0   0  292  265

     H =  -7

-7   0  174  163
-6  -3   78   61
-6  -2  141  146
-6  -1  249  257
-6   0   56   57
-5  -2   94   93
-4  -4  153 -153
-4  -2  161 -161
-4  -1  151 -177
-4   0  135 -179
-3  -5   85   78
-3  -4  107 -109
-3  -2  253 -257
-3  -1   84  -84
-3   0  139 -139
-2  -5  155  151
-2  -4  327  329
-2  -3  192 -198
-2  -2  123  115
-1  -5  183  187
-1  -4  123  122
-1  -3  137  132
-1  -2   49  -46
 0  -5  178  186
 0  -3  331  307
 0  -1  235 -236

     H =  -6

-8  -2   84   93
-8  -1   75   69
-8   0  147  156
-7  -4  131  138

 K   L FOBS FCAL

-7  -3  103  113
-7  -2  119  126
-7  -1  335  337
-7   0  245 -252
-6  -5   55   51
-6  -3  222  233
-6  -2   95   89
-6  -1   88  -92
-6   0  159 [illegible]
-5  -6  176 -175
-5  -5  104  -95
-5  -4  154  -24
-5  -1   47  -46
-5   0   65   64
-4  -5  235 -240
-4  -4  112 -110
-4  -3  135 -132
-4  -2   97 -101
-4  -1  135  141
-4   0  314 -322
-3  -7   93   87
-3  -5  113  113
-3  -4   63  -75
-3  -3   41  -36
-3  -2  227  228
-3  -1  227 -230
-3   0  106 -115
-2  -7  164  166
-2  -6   54   59
-2  -5  133  192
-2  -4  244  249
-2  -3  321  319
-2  -2   62  -70
-2  -1   75   73
-2   0   38   20
-1  -7   50  -40
-1  -6   85   79
-1  -5  143  149
-1  -4  223  217
-1  -2   86   78
-1  -1   39   17
-1   0   98  -97
 0  -6   60   67
 0  -4  169 -165
 0  -2  141 -151
 0   0  105 [illegible]

     H =  -5

-9  -2  111 -106
-9  -1  105  108
-8  -4  216  230
-8  -2  131  135
-8  -1  113  105
-8   0  125 -126
-7  -6   60  -47
-7  -5   98   93
-7  -4   45   55
-7  -3   44   50
-7  -2   73   81

 K   L FOBS FCAL

-7  -1   65   54
-7   0  230  221
-6  -6   78  -74
-6  -5  130 -125
-6  -4  121 -130
-6  -2   83  -78
-6  -1  229  222
-6   0   56  -61
-5  -7   46  -45
-5  -6   79  -31
-5  -5  272 -274
-5  -4   81  -84
-5  -2  158  159
-5   0   92   92
-4  -7   67  -50
-4  -6  264 -240
-4  -5   40   54
-4  -4   77  -60
-4  -2  216  218
-4  -1  274 -270
-4   0  332  327
-3  -8  105  105
-3  -7  136 -136
-3  -6  159  156
-3  -5   61   71
-3  -4  170  169
-3  -3  152  149
-3  -2  365 -364
-3  -1  479 -470
-3   0  443 -439
-2  -7  161  153
-2  -5  255  263
-2  -4  155  153
-2  -3  111  130
-2  -2  119  123
-2  -1  267 -258
-2   0  313 -314
-1  -8  130 -122
-1  -7   75   65
-1  -6   47  -59
-1  -4  117  112
-1  -3  302  295
-1  -2  220  224
-1  -1  319 -322
-1   0   55   40
 0  -7  348 -339
 0  -5  252 -254
 0  -3  139  135
 0  -1  161  163

     H =  -4

-10 -2  105 -105
-10 -1   54  -67
-10  0   56   53
-9  -4  146  149
-9  -3  159 -163
-9   0   54  -50
-8  -6  122  112
-8  -5  157  163

 K   L FOBS FCAL

-8  -4  127 -138
-8  -3   59   59
-8  -2   55  -63
-8  -1  126  132
-7  -5  174 -188
-7  -3   93  -99
-7  -2  112  115
-7  -1  135 -148
-7   0  103  104
-6  -7   71  -67
-6  -6  195 -180
-6  -5  209 -294
-6  -4  101  103
-6  -3   64  -31
-6  -2  111  116
-6  -1   61   57
-6   0  424  427
-5  -7  115 -111
-5  -6  197 -193
-5  -5  113  125
-5  -4  394 -396
-5  -3  103  101
-5  -2   88   75
-5  -1  281  278
-5   0  185  180
-4  -9  163  161
-4  -6  105  195
-4  -5  147 -146
-4  -2   41  -24
-4  -1  295  289
-4   0  408 -409
-3  -9   63   61
-3  -8  105  106
-3  -7  145  141
-3  -6   50  -53
-3  -4  171  169
-3  -3  226 -223
-3  -2  240  242
-3  -1  629 -656
-2  -9   79  -67
-2  -8  128  126
-2  -7   76  -64
-2  -5   53  -45
-2  -4  162  166
-2  -3  225  227
-2  -2  219 -222
-2  -1   82   88
-2   0   87  -80
-1  -9   87  -83
-1  -8  146 -136
-1  -7  234 -234
-1  -4   68  -46
-1  -3  247  246
-1  -2  313  313
-1  -1  326  325
 0  -8  391 -390
 0  -6  119 -128
 0  -4  143  144
 0  -2  877  805
 0   0  219  219

 K   L FOBS FCAL

     H =  -3

-10 -3   62  -60
-10 -1  236 -231
-9  -5   62  -63
-9  -2  159 -155
-9  -1  144 -145
-9   0  254 -252
-8  -4  133  139
-8  -3  305 -303
-8  -2  142  131
-8  -1   41  -25
-8   0  116  124
-7  -5  162 -151
-7  -4  235 -223
-7  -3   53   65
-7  -2   80  -64
-7  -1  342  340
-7   0  370  355
-6  -4  240 -255
-6  -3   86   89
-6  -2  214  221
-6  -1  157  177
-6   0  232  232
-5  -9  120  103
-5  -6  167  159
-5  -5  346 -349
-5  -4  182  190
-5  -3  254 -257
-5  -2  108  102
-5  -1   57   32
-5   0   85   83
-4  -9  111  114
-4  -8  206  208
-4  -6  176 -190
-4  -5  218  210
-4  -4  236 -241
-4  -3  266 -272
-4  -2  375 -346
-4  -1   50  -26
-4   0  334  330
-3  -9  135  135
-3  -5   62  -55
-3  -4   93  -93
-3  -3  271 -274
-3  -2  310 -329
-3  -1  220 -212
-3   0  394 -403
-2 -10   83  -73
-2  -8   57  -55
-2  -6   53   43
-2  -5  257 -259
-2  -4  336  307
-2  -3  327  335
-2  -2  439  442
-2  -1  331 -357
-2   0  144  148
-1  -9  112 -114
-1  -8   85  -33
-1  -7   51  -56

 K   L FOBS FCAL

-1  -6  254 -252
-1  -5  137  141
-1  -4  136  143
-1  -3  652  663
-1  -2  596  607
-1  -1  426  421
-1   0   69  -55
 0  -9   61   62
 0  -7  320 -336
 0  -3  401  398
 0  -1  859  895

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-11 -1  174 -177
-10 -3   91  -95
-10 -2  325 -331
-10  0  282 -257
-9  -6   64  -67
-9  -5  222  225
-9  -4   97 -101
-9  -3  252 -251
-9  -1  355 -350
-9   0   62  -71
-8  -6   94   92
-8  -5   57   46
-8  -4   98   98
-8  -3  225  228
-8  -2   48  -67
-7  -8  136  110
-7  -7   73  -59
-7  -5   95 -100
-7  -4  214  214
-7  -3  307  306
-7  -2  123  137
-7  -1  206  207
-7   0  137  130
-6  -9  142  143
-6  -8   45  -51
-6  -7   71  101
-6  -6  120 -121
-6  -5   51  -70
-6  -4  158 -164
-6  -3  191 -192
-6  -2  100  107
-6  -1  131  132
-6   0   92   94
-5  -9   98  106
-5  -8  139  148
-5  -7   84   88
-5  -6   76   85
-5  -4  626 -613
-5  -3  229 -229
-5  -2   58  -89
-5  -1   53   56
-5   0   52   61
-4  -9   46   52
-4  -8  115  114
-4  -7   84   97
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  K   L FOBS FCAL

 -4  -6   66   69
 -4  -5  434 -433
 -4  -4   53  -46
 -4  -3  550 -551
 -4  -2  195 -205
 -4  -1  176  192
 -4   0  217 -223
 -3 -10   59  -62
 -3  -8   71   67
 -3  -7  120  135
 -3  -6  119 -103
 -3  -5   55   -9
 -3  -4  237 -279
 -3  -3   92   97
 -3  -2  459 -463
 -3   0  643  645
 -2  -8   40  -45
 -2  -7  107  114
 -2  -6   41   30
 -2  -5  404  400
 -2  -3  142  162
 -2  -2  194  195
 -2  -1  198  201
 -2   0   52   50
 -1  -9  103  102
 -1  -8  102 -105
 -1  -7  244 -239
 -1  -6  525  523
 -1  -5  115 -117
 -1  -4  371  371
 -1  -3  275  271
 -1  -2  705  722
 -1  -1  690  691
 -1   0  426 -429
  0 -10  123  138
  0  -8  101 -109
  0  -6  627 -617
  0  -4   82  -84
  0  -2  120  127
  0   0   95   93

        H =   -1

-11  -3  122 -118
-11  -2   47  -55
-11  -1   95  -94
-11   0  159 -170
-10  -5   83   86
-10  -4  114 -118
-10  -3   62  -66
-10  -1  278 -275
-10   0   92  -71
 -9  -6   89   82
 -9  -4  123  131
 -9  -3   72   73
 -9  -2  333 -335
 -9  -1  227  221
 -9   0  159 -169
 -8  -6   73   83
 -8  -5  333  332

  K   L FOBS FCAL

 -8  -4  174  174
 -8  -2   62   77
 -8  -1  174 -175
 -8   0  155  147
 -7  -8  147 -145
 -7  -7  153  165
 -7  -6  153  162
 -7  -5  154  157
 -7  -4  143  139
 -7  -3  172  172
 -7  -2  207  201
 -7  -1   73  -67
 -6  -9  125 -127
 -6  -8  101  104
 -6  -7  195 -193
 -6  -5  201 -201
 -6  -4  279 -276
 -6  -3  110  104
 -6  -2  411 -401
 -6  -1  154  157
 -6   0  361 -371
 -5  -9  241  239
 -5  -7   39   50
 -5  -6  298 -298
 -5  -5  145 -147
 -5  -4  120 -118
 -5  -3  641 -649
 -5  -2  154 -156
 -5  -1  124 -123
 -5   0  154  155
 -4  -9  143  141
 -4  -8  122  125
 -4  -7   91  105
 -4  -6   35  -35
 -4  -5   64   60
 -4  -4  217 -217
 -4  -3  210 -213
 -4  -2  200 -201
 -4  -1   49   51
 -4   0  766  757
 -3  -9  153 -158
 -3  -8  211  215
 -3  -7  207  205
 -3  -6  202  205
 -3  -5  117 -117
 -3  -3  129  130
 -3  -2  220  213
 -3  -1   71  -68
 -3   0  341 -344
 -2 -10  150 -139
 -2  -9  117  115
 -2  -7  256  260
 -2  -6  230  244
 -2  -5   33  -37
 -2  -4   35  -45
 -2  -3  333 -333
 -2  -2  346 -339
 -2  -1   29  -21
 -2   0  175 -175
 -1 -11  113 -114

  K   L FOBS FCAL

 -1 -10   68   73
 -1  -9   69   79
 -1  -7  101  113
 -1  -6  203 -207
 -1  -5  491  498
 -1  -4  207 -203
 -1  -3  257 -251
 -1  -2  276  252
 -1  -1  442  451
 -1   0  546  545
  0 -11   79   58
  0  -9   41  -45
  0  -7  500 -405
  0  -5  525 -513
  0  -3  426 -413
  0  -1  739  750

        H =    0

-11  -2  130 -132
-11  -1   52  -47
-10  -4  160  157
-10  -3  127 -135
-10   0  177 -155
 -9  -7   80   67
 -9  -6   92   96
 -9  -5  201  200
 -9  -4  150  151
 -9  -3   92   93
 -9  -2  125  124
 -9  -1  234 -235
 -8  -7   95   93
 -8  -5  142  143
 -8  -4  126  120
 -8  -3  363  365
 -8  -2  230 -228
 -8   0  252 -251
 -7  -7   94  -57
 -7  -5  120  124
 -7  -4  122  128
 -7  -2  116 -120
 -7  -1   35   -9
 -6  -8  240 -230
 -6  -7   40  -54
 -6  -4   40  -54
 -6  -3  592 -595
 -6  -2  521  515
 -6  -1  255 -252
 -6   0  220  221
 -5  -9  131 -127
 -5  -7  137 -130
 -5  -6   66   67
 -5  -5  100 -112
 -5  -4  335 -333
 -5  -3  153  155
 -5  -2  649 -648
 -4  -8  221  219
 -4  -7  371  365
 -4  -6   81  -79
 -4  -5  167  169

  K   L FOBS FCAL

 -4  -4  325  330
 -4  -3   31  -50
 -4  -2  123 -141
 -4  -1  247 -252
 -4   0   79   65
 -3 -10   69  -85
 -3  -9  211  212
 -3  -8   79   81
 -3  -7  217  209
 -3  -6  205  206
 -3  -5  140  150
 -3  -4   81  -79
 -3  -3  132 -135
 -3  -1  509 -518
 -2 -11  164 -156
 -2 -10  174  161
 -2  -9  130 -126
 -2  -8  151  144
 -2  -7   48  -43
 -2  -6  381  375
 -2  -5   46  -52
 -2  -4  434 -423
 -2  -3  103 -105
 -2  -2  112 -114
 -2  -1  420  423
 -2   0  751 -759
 -1 -10  119 -115
 -1  -7   42  -46
 -1  -5  373 -373
 -1  -4  141  153
 -1  -3  526 -525
 -1  -2  515  528
 -1  -1  545  545
  0 -10  149 -154
  0  -6  455 -459
  0  -2  554  558

        H =    1

-11  -3   67  -63
-11  -2  110  110
-11   0  164 -170
-10  -5  208  206
-10  -3  198  193
-10  -2   54  -45
-10  -1   45  -43
-10   0   71   71
 -9  -6   97  102
 -9  -5  102  101
 -9  -4  230  240
 -9  -1   79  -90
 -9   0  136 -139
 -8  -8  125 -125
 -8  -7   86  -92
 -8  -6  233  237
 -8  -5   84  -83
 -8  -4  183  184
 -8  -2  146  145
 -8  -1  159 -156
 -8   0  143 -147

  K   L FOBS FCAL

 -7  -8  200 -197
 -7  -6  207 -213
 -7  -5  127  135
 -7  -4  111 -124
 -7  -3  146  146
 -7  -2  210  213
 -7  -1   83  -30
 -7   0   34   35
 -6  -7  232 -230
 -6  -4   74   34
 -6  -3  131  123
 -6  -2  182 -154
 -6  -1  411  406
 -6   0  374  371
 -5  -7   42   50
 -5  -5  112  105
 -5  -4  220  209
 -5  -3  606 -593
 -5  -2  134 -133
 -5  -1  302 -202
 -5   0  139  126
 -4 -10  103  101
 -4  -9   55  -59
 -4  -8  130  154
 -4  -7  213  215
 -4  -6  324  317
 -4  -5  220  210
 -4  -4  195 -197
 -4  -3  107  131
 -4  -2  691 -695
 -4  -1  537 -530
 -4   0  773 -757
 -3  -9   55  -58
 -3  -8  140  145
 -3  -7   95  107
 -3  -6  376  373
 -3  -5   51  -41
 -3  -3  315  305
 -3  -2  345 -349
 -3  -1  851 -842
 -3   0  340 -344
 -2 -11  100 -100
 -2 -10  223 -214
 -2  -9  130  105
 -2  -8  195 -201
 -2  -6  106 -100
 -2  -5  153 -152
 -2  -4  700  695
 -2  -3  986 -953
 -2  -2  518  523
 -2  -1  159 -154
 -2   0  175  175
 -1 -11  123 -127
 -1  -9  100  -94
 -1  -8  114  118
 -1  -7  218 -212
 -1  -6  141 -139
 -1  -5  452  458
 -1  -4  521 -519
 -1  -3  334  344

  K   L FOBS FCAL

 -1  -2  228  228
 -1  -1  279  271
 -1   0  555  546
  0  -7  309  308
  0  -5  310 -311
  0  -3  762  735
  0  -1  950  951

        H =    2

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-10  -5   50  -36
-10  -4  127  124
-10  -3   62  -57
-10  -2   68   70
-10  -1   89  -34
-10   0  272 -267
 -9  -5   80  -91
 -9  -3  243  250
 -9  -1  196 -180
 -9   0   67   71
 -8  -7   50  -56
 -8  -5  158 -191
 -8  -5   77   74
 -8  -3  137  145
 -8  -2  155  156
 -7  -8  132 -136
 -7  -7  284 -278
 -7  -5  157  192
 -7  -4  170  158
 -7  -3  134  128
 -7  -2  245  239
 -7  -1  492  488
 -7   0  185 -190
 -6  -9   95  -69
 -6  -8  139 -140
 -6  -7   51   68
 -6  -6  141 -140
 -6  -5  205  207
 -6  -4   55  -84
 -6  -3  137  138
 -6  -2  142  149
 -6   0   97   94
 -5  -8  117  121
 -5  -7   84   82
 -5  -5  113 -103
 -5  -4  112   99
 -5  -2  426 -427
 -5  -1  251 -256
 -5   0   52  -61
 -4 -10   61  -45
 -4  -8  114  121
 -4  -7   98 -101
 -4  -6  257  261
 -4  -5  144 -135
 -4  -3  512 -509
 -4  -2  402 -402
 -4  -1  742 -733
 -4   0  227 -223
 -3  -9   48   64
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 K   L FOBS FCAL

-3  -8  304 -319
-3  -7  297  289
-3  -6  239  239
-3  -5  423  424
-3  -3  145 -152
-3  -2   35   55
-3  -1   72   53
-3   0  674 -645
-2 -11   51  -16
-2 -10  155 -151
-2  -9  236 -254
-2  -6   34   29
-2  -5  631  623
-2  -4  163 -152
-2  -3  527  623
-2  -2  175 -172
-2  -1  224  225
-2   0   59   52
-1 -11   47  -35
-1 -10  179 -197
-1  -6   34  -31
-1  -5   67  -73
-1  -4  752  754
-1  -3  113 -109
-1  -2   27  -27
-1  -1   55   55
-1   0  413  427
 0 -10   84   75
 0  -8  123  127
 0  -6  122 -171
 0  -2  772 -759
 0   0   34   78

      H =   3

-10  -4   53  -57
-10  -2  175 -197
-10  -1   75  -79
-9  -3  214  212
-9  -2   41   53
-9  -1  233  241
-9   0  246 -252
-8  -5   53  -55
-8  -4   67   94
-8  -3  236  237
-8  -2  293 -262
-8  -1   55   81
-8   0  113 -124
-7  -7   55  -84
-7  -6  157 -157
-7  -5  111 [illegible]
-7  -4   97 [illegible]
-7  -3  233  234
-7  -2  258  253
-7  -1   74   73
-7   0  225 -225
-6  -7  217 -219
-6  -5  142 -157
-6  -4  125  154
-6  -3  212 -212
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```
 K   L FOBS FCAL

-6  -2  172 -162
-6  -1  355  369
-6   0  232 -232
-5  -8   95  -93
-5  -6   92 -109
-5  -4  329 -332
-5  -2  149 -145
-5  -1  433 -467
-5   0   55   87
-4  -8  222 -210
-4  -7  222  276
-4  -5   55  -70
-4  -4   74  -78
-4  -3  127  133
-4  -2  143 -159
-4  -1  322 -317
-4   0  325 -330
-3 -10  123 -131
-3  -9   72  -50
-3  -8  145  149
-3  -7  151 -177
-3  -6  337  345
-3  -5  237  238
-3  -4  373  378
-3  -3  152  178
-3  -2  143 -143
-3  -1  155  156
-3   0  425 -423
-2 -10   57  -55
-2  -8   75  -93
-2  -7   95   94
-2  -6   55   74
-2  -5  554  560
-2  -4  676  671
-2  -3  125  -97
-2  -2  145  163
-2   0  149 -145
-1 -10   72  -71
-1  -9  122 -179
-1  -8   73  -35
-1  -7   45   35
-1  -6   51   53
-1  -5   94   97
-1  -4  155 -162
-1  -3  467  476
-1  -2  272 -243
-1  -1  237 -275
-1   0   71  -55
 0  -9  162 -171
 0  -5  470 -457
 0  -3  135 -130
 0  -1  429 -454

      H =   4

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-9  -4  193  207
-9  -2  137  192
-9   0   54   60
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 K   L FOBS FCAL

-9  -5  144  149
-9  -4   61  -53
-9  -3  251  253
-9  -2   97   93
-9  -1  137  179
-8   0   43  -59
-7  -7   92  -92
-7  -6  133 -134
-7  -5  269 -265
-7  -4   99  106
-7  -3   63  -73
-7  -2  173  173
-7  -1  107  115
-7   0  179 -154
-6  -7   46  -47
-6  -6  322 -322
-6  -5  125 -134
-6  -4  117 -116
-6  -3  175  153
-6  -2  135  155
-6  -1  155 -154
-6   0  433  427
-5  -7  124 -131
-5  -6  124 -127
-5  -5  245 -253
-5  -4   87  -93
-5  -3   63   59
-5  -2  246 -244
-5  -1  247  245
-5   0  177 -193
-4  -9   65   70
-4  -7   41  -55
-4  -6  275  292
-4  -5  125  129
-4  -4   35   18
-4  -3   57  -61
-4  -2  172  143
-4  -1   75   72
-4   0  412 -429
-3  -8  147 -151
-3  -7  222  221
-3  -6   75   83
-3  -5  400  401
-3  -4  237  209
-3  -3   40  -27
-3  -2  461  447
-3  -1  545 -535
-2 -10  111 -105
-2  -9  161 -163
-2  -8  157  155
-2  -7  173 -174
-2  -6  142  145
-2  -5   42   42
-2  -4  433  474
-2  -3  278  305
-2  -2  464 -473
-2  -1  243  242
-2   0   30  -67
-1 -10   45  -59
-1  -9  125 -127
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```
 K   L FOBS FCAL

-1  -8  143 -143
-1  -7  129 -147
-1  -6  145 -152
-1  -4   96   87
-1  -3   75  -71
-1  -2  127 -121
-1  -1  243 -229
 0  -8  357 -357
 0  -4   74  -75
 0  -2  229  199
 0   0  218  219

      H =   5

-9  -3   72   65
-9  -2  117  120
-8  -5   93  -97
-8  -4  152  145
-8  -3  131 -133
-8  -2  127  123
-8  -1   72   83
-8   0  139  125
-7  -5  254 -254
-7  -4  197 -203
-7  -3   43   54
-7  -2  221 -225
-7  -1  154  155
-7   0  217  226
-6  -7   93 -103
-6  -6   34  -83
-6  -5  155 -147
-6  -3   45   35
-6  -2  143  145
-6  -1  122  113
-5  -8   45  -61
-5  -5  255 -251
-5  -4  101  103
-5  -3   76   93
-5  -2  321  317
-5  -1  154 -157
-5   0   95   92
-4  -8  143  144
-4  -6  122 -126
-4  -5  127  128
-4  -4   57  -70
-4  -3   74   74
-4  -2   71  -75
-4  -1  133 -133
-4   0  337 -327
-3  -9  111  117
-3  -8   63   57
-3  -7   87  -96
-3  -6  123  123
-3  -5   83   91
-3  -4  282  275
-3  -3   58   57
-3  -2  212 -207
-3  -1  135  165
-3   0  443 -439
-2  -9  133 -129
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 K   L FOBS FCAL

-2  -8  167 -153
-2  -6  112 -113
-2  -4  148  152
-2  -3   70   54
-2  -2  536  531
-2  -1 [illegible] -273
-2   0  325 [illegible]
-1  -9  227 -227
-1  -8  125 -135
-1  -7  123  -99
-1  -5  300 -333
-1  -4   71   62
-1  -3  373  355
-1  -2   83   93
-1  -1  229  226
-1   0   45   40
 0  -9   97 -109
 0  -7  157 -151
 0  -5  135  133
 0  -3   34  -14
 0  -1  141  135

      H =   6

-8  -3   84   59
-8  -2   31   73
-8  -1  174  172
-8   0  152  155
-7  -5  254 -256
-7  -4   41   53
-7  -3   92  -94
-7  -2  173  165
-7  -1  161  170
-7   0  259  252
-6  -6  105 -105
-6  -5   63  -71
-6  -4  127 -152
-6  -3   57   62
-6  -2  132 -135
-6  -1   84   83
-6   0  155  147
-5  -6   55   55
-5  -5  112  123
-5  -4  133 -135
-5   0   65  -64
-4  -7   65  -92
-4  -6   97   93
-4  -5  199 -194
-4  -4  129  112
-4  -3  277 -275
-4  -2   62   57
-4  -1  133 -173
-4   0  331 -372
-3  -8   93   98
-3  -6  243 -243
-3  -5  119  122
-3  -3  221  221
-3  -1  226 -229
-3   0  214  215
-2  -3   79  -71
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 K   L FOBS FCAL

-2  -7   97  -95
-2  -6   51  -92
-2  -4  254  251
-2  -3  417  422
-2  -2   37    5
-2  -1  439  435
-2   0   33   27
-1  -8  137 -193
-1  -7  115 -127
-1  -4   95   94
-1  -3  135  115
-1  -2  575  576
-1  -1  115  121
-1   0  135   97
 0  -8  125 -112
 0  -6  125 -111
 0  -4  133 -173
 0  -2   67   57
 0   0  132 -184

      H =   7

-7  -1  139  185
-7   0  124  161
-6  -4  171 -174
-6  -3   99 -103
-6   0   54  -57
-5  -5  129 -132
-5  -4  179 -171
-5  -3  175 -194
-5  -2  122 -124
-4  -6  145 -144
-4  -5  217  216
-4  -4  171 -171
-4  -3   65  -51
-4  -2   63  -73
-4   0  175  179
-3  -7   51  -68
-3  -6  105   89
-3  -5  117 -127
-3  -4  191  187
-3  -3   77   72
-3  -1  123  121
-3   0  145 -139
-2  -7   64   52
-2  -4   87   97
-2  -3  379  399
-2  -2  217  211
-2  -1   34   45
-2   0   45  -47
-1  -7   52  -52
-1  -6  179 -179
-1  -5   52   32
-1  -4   45  -49
-1  -3  192  202
-1  -2  175  172
-1  -1  116  107
 0  -7  319 -313
 0  -5  236 -235
 0  -3  132 -199
```

```
 K   L FOBS FCAL

 0  -1  125  114

      H =   8

-5  -2  114 -105
-5  -1  123  116
```

```
 K   L FOBS FCAL

-5   0   73  -70
-4  -4   57   35
-4  -2   73   89
-4   0   42   47
-3  -1  115  129
-3  -2   75  -77
```

```
 K   L FOBS FCAL

-3   0  212  213
-2  -5   48  -71
-2  -4   98  100
-2  -3   90  -93
-2  -2  167  172
-2  -1   58   67
```

```
 K   L FOBS FCAL

-2   0  157 -160
-1  -5  135 -137
-1  -4   75  -72
-1  -3   54   45
-1  -2  135  126
-1  -1   54   63
```

```
 K   L FOBS FCAL

-1   0  139   93
 0  -4   65  -90
 0   0  234  265
```

```
 K   L FOBS FCAL

      H =   9

 0  -1  237  278
```

Table IX - Deviations from the Least-Squares Plane for the Acetylacetonate Group

Atom	Deviation (Å)
Ti	0.042
O1	-0.002
O2	-0.067
C2	-0.042
C3	0.041
C4	0.028

with regard to spectral shifts in the charge transfer band.(37) Finally, it is interesting to note that the titanium-terminal chlorine bond distances (2.21-2.25 Å) in the present six-coordinate dimer are comparable in length to those of the six-coordinate adducts $[TiCl_4 \cdot POCl_3]_2$(61) (2.20-2.24 Å) and $[TiCl_4 \cdot O_3C_{10}H_{12}]_2$ (2.23-2.25 Å) or the five-coordinate $[TiCl_2 \cdot NSiMe_3]_2$.(22,23) The terminal chlorine-titanium bond lengths found in the $Ti_2Cl_{10}^{2-}$ (53) anion (2.25-2.29 Å) and $[TiCl(C_5H_7O_2)_2]_2O \cdot CHCl_3$(62) (2.30-2.32 Å) represent a better estimate of such bond lengths found in six-coordinate titanium (IV) complexes. The difference of 0.15 Å in the titanium-bridge chlorine distances is larger than the 0.07 Å found in $[TiCl_2 \cdot NSiMe_3]_2$(22,23) and seems significant when compared to similar differences of 0.03 Å in the $Ti_2Cl_{10}^{2-}$ anion(53) or 0.01 Å in $[TiCl_4 \cdot O_3C_{10}H_{12}]_2$.(66)

The O1-O2 distance, the bite of the acac ligand, in $[Cl_3Ti(acac)]_2$ is considerably shorter (2.582(4) Å) than that found in other acetylacetonate systems. It has been pointed out(64) that in first row transition metal acetylacetonates, the only effect in varying the metal ions is a variation in the O-O distance, and that such a variation is clearly not due to difference in the metal radii. Rather the O-O bite distance is shortened by an increased oxidation state of the metal (e.g. Co(II) 2.96 Å, Mn(III) 2.81 Å, Zr(IV) 2.67 Å). Thus, the O-O bite in the bis(diisopropylphenoxo)bis(2,4-pentanedionato) titanium (IV) complex is 2.66 Å,(67) nearly the same as that of $Zr(acac)_4$. That the O-O bite is comparatively short in the present Ti (IV) compound suggests an increased effective nuclear charge at titanium and supports the notion of significant pπ-dπ bonding in the Ti(acac) heterochelated rings.

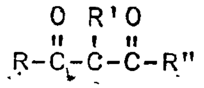
C. Solution Structure

It has been shown(31) from molecular weight, conductivity, and nmr spectral data that $Cl_3Ti(bzac)$ exists as a five-coordinate monomer in solution. A more complete nmr spectral investigation in nitrobenzene of $[Cl_3Ti(bzac)]_2$ and $[Cl_3Ti(dpm)]_2$(68) has revealed that $[X_3Ti(dik)]_2$ complexes break up in solution to yield $X_3Ti(dik)$ which subsequently disproportionates into the well-known six-coordinate $X_2Ti(dik)_2$ and TiX_4. Thus it appears that $[Cl_3Ti(acac)]_2$ as well as $[F_3Ti(bzac)]_2$ and $[F_3Ti(bzbz)]_2$ undergo cleavage to give a true five-coordinate species. This cleavage occurs in $[TiCl_2 \cdot NSiMe_3]_2$(22,23) for which the solution species appear to have discrete $(Ti-N)_2$ rings based on four-coordinate titanium. These species react with pyridine to form the bis-pyridine adduct. Also, $Cl_3Ti(bzac)(py)$ is formed when a solution of $Cl_3Ti(bzac)$ is treated with pyridine.(31) In contrast, dissolution of the oxygen-bridged $[TiOCl(acac)]_2$ in pyridine results in no bis-pyridine formation.$^{(67)}$ The dimer $[TiO(acac)_2]_2$$^{(70)}$ also appears to be stable towards cleavage and pyridine adduct formation. This suggests that probably only monomeric, coordinatively unsaturated titanium (IV) complexes undergo adduct formation with pyridine. From inspection of the two titanium-bridge chlorine bond distances (Table VII), Ti-Cl3 and Ti-Cl3', it seems reasonable the cleavage occurs at the longer (and weaker) Ti-Cl3' bond and at the symmetry related Ti'-Cl3 bond. Disproportionation followed by intermolecular ligand exchange or preceded by intramolecular ligand exchange may lead to observed six- and four-coordinate compounds.

Solution infrared spectra would have been useful; unfortunately they are not available for reasons discussed earlier. In the solid state spectrum of $F_2Ti(dik)_2$, the titanium-fluorine $\nu(Ti-F)_{ter}$ frequencies occur around 625 cm^{-1}. These bands are slightly shifted to higher frequencies in $[F_3Ti(dik)]_2$. In solution the $\nu(Ti-F)_{ter}$ for $F_2Ti(dik)_2$ should remain unchanged whereas the $\nu(Ti-F)_{ter}$ for $[X_3Ti(dik)]_2$ band should shift to higher frequencies in $F_3Ti(dik)$. The $\nu(Ti-F)_{br}$ band at 600 cm^{-1} should also vanish. The expected shifts to higher frequencies of $\nu(Ti-F)_{ter}$ would have confirmed the five-coordinate nature of both $F_3Ti(bzac)$ and $F_3Ti(bzbz)$ in solution and would have provided evidence for the five-coordinate nature of $\mathrm{FCl_2Ti(acac)}$ in solution.

IV. APPENDIX

Table X - Nomenclature and Abbreviations for β-diketonate Ligands



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{R'}{|}}{C}-\overset{\overset{O}{\|}}{C}-R''$$

Abbreviations	Ligand	R	R'	R"
dik	any β-diketonate			
py	pyridine			
acac	acetylacetonate (2,4-pentanedionate)	CH_3	H	CH_3
bzac	benzoylacetonate (1-phenyl-4,3-pentanedionate)	CH_3	H	C_6H_5
bzbz	dibenzoylmethanate (1,3-diphenyl-1,3-propanedionate)	C_6H_5	H	C_6H_5
dpm	dipivaloylmethanate (2,2,6,6-tetramethyl-3,5-heptanedionate)	$t-C_4H_9$	H	$t-C_4H_9$
3-Me-acac	3-methylacetylacetonate (3-methyl-2,4-pentanedionate)	CH_3	CH_3	CH_3
etac	ethylacetoacetate (butane acid, 3-oxo-ethyl ester)	CH_3	H	OC_2H_3

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(43) NUCLS4 is a rigid-body, least-squares program rewritten for X-Ray Crystallography by R. J. Doedens and J. A. Ibers from the original ORFLS by W. B. Busing and H. A. Levy.

(44) UTILITY was written by P. H. Bird.

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Part II

INVESTIGATION OF THE TETRACARBONYLCOBALTATE ANION FOR M-M BOND FORMATION

Arpad F. Somogyvari

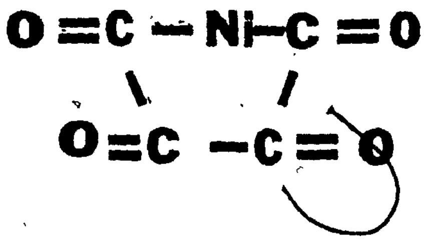
I. INTRODUCTION

The purpose of this part of the thesis is to report on our endeavours in synthetic organometallic chemistry. The project chosen involved the synthesis of cobalt-metal bonded compounds (where metal = Ti to Ni). Since no heterometal-metal bonded complexes of titanium had been reported in the literature, when the project was started, it was decided that our efforts be directed in that direction.

The INTRODUCTION has been divided into three sections: Section A gives a brief historical background to the topic and brings the reader to the present day state of the art. Section B is an outline of the relevant features of organometallic chemistry required in the synthesis of metal-metal bonded compounds. Section C reports on the properties and some useful reactions of the starting material, octacarbonyl dicobalt.

A. Historical

The first metal carbonyl, tetracarbonyl nickel, was discovered by C. Langer in 1890(1) during the study of the transformation of carbon monoxide to carbon dioxide and carbon, catalysed by metallic nickel. The next member of this new class of compounds, pentacarbonyl iron, was reported by Monde(2) and Berthelot(3) a year later. At that time, these carbonyl complexes were regarded as anomalous organic compounds with structures 1 and 2 below



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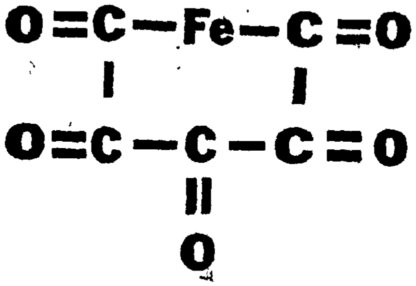


2

This is not surprising in view of the fact that carbon monoxide was recognized as a ligand only twenty years earlier in the synthesis and characterisation of $Pt(CO)_2Cl_2$(4,5) and that little was known about the nature of chemical bonds. For the next few decades progress in discovering these new types of compounds was slow; however, a bimetallic metal carbonyl, notably octacarbonyl dicobalt, was discovered.

It was not until the early 1940's that chemists began to consider these metal carbonyls as neutral coordination compounds with the metal in the zero oxidation state.(6) The field of metal carbonyl chemistry began to grow rapidly a decade later. It was during this time that Hieber and his students made many of their significant contributions which led to the development of transition-metal carbonyl chemistry.(7) This was also the decade in which ferrocene(8,9) and dibenzenechromium(10) were synthesized.

Prior to the late 1950's only a few compounds containing metal-metal bonds were known; these had been accidentally synthesized and aroused very little interest.(11) Deliberate study of these compounds began in the early 1960's and by the middle of the decade these complexes moved from the realm of "scarce" to the present idea of "rather commonplace".

B. General Considerations

Although the organometallic chemistry of transition-metal carbonyl compounds is a relatively new field of endeavour for the chemist, interest has been keen in the past twenty-five years and several excellent reviews may be found.(12-17) The features which distinguish this highly specialized topic and which are responsible for the unique chemistry, are the presence of partially filled orbitals on the metal and the ability of carbon monoxide to stabilize the low oxidation states in these metals.

The stability of the bond between a metal and carbon monoxide was attributed in valence bond terms, by Pauling,(18) to resonance between single and double metal-

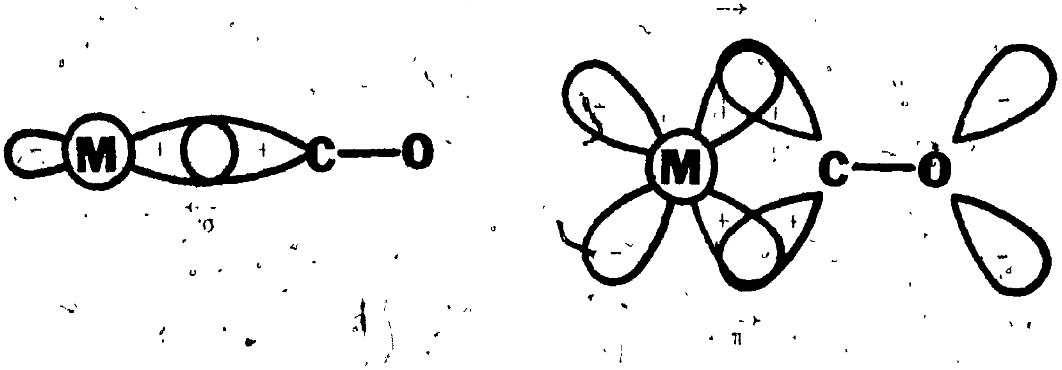


Figure 1 - The Synergic Effect of CO

carbon bonds as illustrated below

$$M - C \equiv O \leftrightarrow M = C = O \qquad (1)$$

However, chemists now prefer to talk in terms of molecular orbital theory. Thus bonds with little transfer of negative charge from the donor atom of the ligand to the metal can be accounted for by invoking a π-back donation from the metal into a suitably empty orbital of the ligand.(19) This process is illustrated in Figure 1.

Thus a weak dative sigma bond is formed by the donation of the carbon monoxide lone pair of electrons to the metal. The excess electron density on the metal is removed by back-donation into the empty π* molecular orbital of carbon monoxide. This has the effect of increasing the strength of the sigma bond. A stronger sigma bond allows more extensive π-bonding. This effect is termed "synergic". However, there is no direct experimental proof of back-donation; only indirect evidence is yet available. Such evidence may be manifested as a shorter metal-ligand interatomic distance than is generally expected for a single bond(20) or as very low bond moments, as expected for nearly apolar bonds of the synergic type.(21)

A consequence of the presence of electrons in the antibonding orbitals of carbon monoxide is the lowering of the C-O bond order. This is conveniently demonstrated by noting that the free ν(CO) occurs at 2143 cm^{-1} (22) while that bonded to a metal may be observed in the 2000 cm^{-1} region of the infrared spectrum.(22,23) Furthermore, as the carbonyl groups are replaced with ligands which are stronger σ-donors and weaker π-acceptors ν(CO) decreases. Thus, on substituting a phosphine for a carbonyl ligand, there is an increased flow of charge to the metal. Since the removal of electron density from the metal via the empty 3d orbitals of the phosphines is less efficient than that of carbon monoxide, the increased electron density at the metal must be removed by additional charge transfer to the antibonding CO π* orbitals. This leads to a reduction of the CO bond order and a consequent decrease in ν(CO).(15)

Metal-metal interaction has been postulated for every element in the transition block except the scandium triad. The occurrence of metal-metal (abbreviated M-M) bonded compounds is restricted mainly to coordination compounds and to organometallic compounds.(25) This type of bonding appears to occur readily, even in higher oxidation states, for the early transition metals, whereas M-M bonding appears to be restricted to the lower oxidation states for the latter transition elements. A maximum in M-M bonding appears to be reached in the middle of the transition series with the second and third row elements showing a greater propensity for such bonding than the first row elements.(24)

The main criteria for M-M bond formation are threefold.(25)

1. The metal centers must contain relatively expansive d orbitals to allow good overlap with each other.
2. These orbitals must contain electrons which can be used for M-M bonding.
3. Unfavorable steric effects must be absent; metals closely surrounded by bulky ligands militate against the close approach of the metals.

It is generally observed that there are two classes of compounds for which M-M bonding may be considered. These two are: (a) inorganic compounds in which the metal is essentially attached to σ-donors in which the atomization energy is the most important factor in determining M-M bonding, and (b) organometallic compounds in which unfavorable non-bonding electron repulsions are decreased by delocalization of these electrons into ligand orbitals via dπ-pπ bonding. The formation of M-M bonds is primarily governed by the number of electrons which are available for bonding.(25)

The metal oxides and halides are of the type "a" above. The main factor which must be considered for M-M bond formation in these compounds is the thermochemical cycle. If oxygen or halogen bond formation cannot compensate for the metal vaporisation, the stability can be gained only through M-M bond formation.(26,27)

Of greater import to this thesis are the carbonyl and carbonyl type complexes of type "b" above. For M-M bonding to occur in these compounds, the metal atom generally has an odd number of electrons. Metal carbonyls containing an even number of electrons can form M-M bonds if the gain attained by sharing electrons in the formation of the M-M bond is compensated by the loss of one donor carbonyl group. The ligands are thus seen to be rather important. Good ligands will stabilize the low oxidation states of the metal and reduce non-bonding (and sometimes antibonding) electronic repulsions by delocalizing these electrons into the ligand oribtals.(25)

A metal-metal bond may be recognized by the close approach of two metals in the absence of bridging groups or by the closer approach of the metal atoms than seems necessary from the bridging geometry.(24,29) Another criterion that is quite often invoked is diamagnetism. However, care must be taken in deducing M-M bonding on the basis of diamagnetism or reduction of paramagnetism. This becomes apparent(24) when one considers that

(a) for a system with an even number of electrons in the metal, paring may result from some stereochemical requirement and not M-M bonding.

(b) for metals with orbitally degenerate ground states, the magnetic properties may be modified by spin-orbit coupling.

(c) magnetic interactions between metal ions may occur through the participation of bridging groups (i.e. antiferromagnetism is an extreme case).

Crystallographic data is therefore absolutely necessary before experiment and theory can be compared. However, the method gives limited (but vital) information on M-M bonds, and one must resort to other methods (e.g. shape of potential energy curve and dissociation energy) to obtain these data.(29)

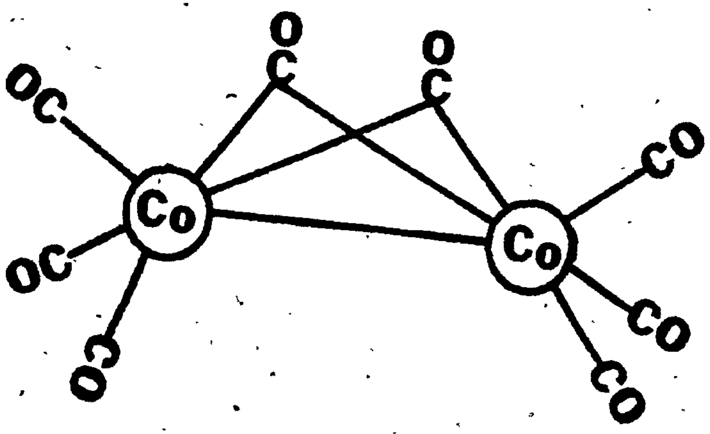
C. Properties and Reactions of $Co_2(CO)_8$

There exists a large number of M-M bonded derivatives of cobalt based on the simple carbonyls. The best known of these $Co_2(CO)_8$, is an orange, air-sensitive solid which slowly decomposes at room temperature.(30) The results of crystallographic analysis have revealed the structure as di-μ-carbonylhexacarbonyl dicobalt.(31)

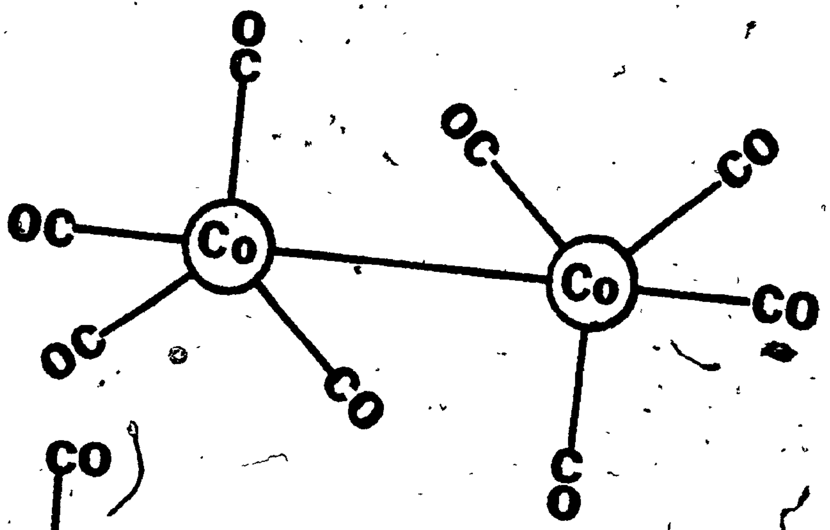
The x-ray crystal structure of $Co_2(CO)_8$ shows the cobalt atoms to be bonded via two bridging carbonyl groups. The diamagnetism of the molecule and the closeness of the cobalt atoms (Co-Co = 2.52 Å) indicates the presence of a Co-Co bond. However, in solution a temperature dependent equilibrium exists between a low temperature or bridged form, and a high temperature or unbridged form.(32,33) Furthermore, rapid exchange between all carbon monoxide groups has been verified by Basolo and Wojcicki.(34) Recent spectroscopic investigations have presented results consistent with a third isomer of yet unknown stereochemistry.(35,36) The infrared spectra may be interpreted in terms of a structure with D_{2d} symmetry having no bridging carbonyl groups. All three isomers (Figure II) are reported to interconvert rapidly.(36)

There are several excellent methods of preparing anionic metal carbonyl derivatives.(37) The most useful of these is the reduction of the metal carbonyls with an alkali metal or amalgam in the presence of a basic solvent(37-42) although a direct reaction with some metals

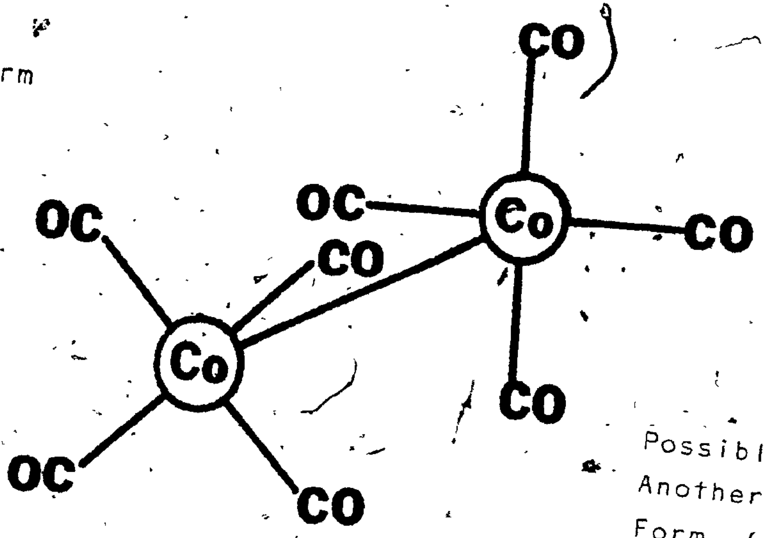
Figure II - The Molecular Structures of the Three Isomers of $Co_2(CO)_8$



Low Temperature Form
(ref. 31)



High Temperature Form
(ref. 32)



Possible Third Isomer
Another High Temperature
Form (ref. 35)

is often successful.(43) Also, dicobalt octacarbonyl is very sensitive to base. Some very weak bases such as acetonitrile or tetrahydrofuran which are often considered inert, will bring about the disproportionation reaction in equation 2.(44-46) However, phosphines,(47) phosphites,(48) and isonitriles(50) react differently.

$$3\,Co_2(CO)_8 + 12\ \text{base} \rightarrow 2[Co(\text{base})_6][Co(CO)_4]_2 + 8\,CO \qquad (2)$$

The phosphites always react to give a substitution product(50) (equation 3) whereas the substitution product is only obtained at elevated temperatures with the phosphines.(51) At low temperatures, the phosphines react with dicobalt octacarbonyl (equation 4) to yield a cobalt I salt,(49) similar to the reaction of the isonitriles (equation 5).

$$Co_2(CO)_8 + 2P(OR)_3 \rightarrow [Co(CO)_3P(OR)_3]_2 + 2\,CO \qquad (3)$$

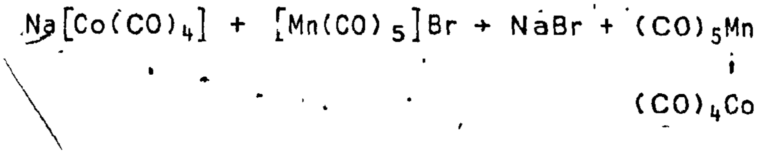
$$Co_2(CO)_8 + 2PR_3 \rightarrow [Co(CO)_3(PR_3)_2][Co(CO)_4] + CO \qquad (4)$$

$$Co_2(CO)_8 + 5RNC \rightarrow [Co(RNC)_5][Co(CO)_4] + 4\,CO \qquad (5)$$

(R = an alkyl group)

Reactions 2 and 4 also illustrate some of the useful methods of preparing cationic metal carbonyls of cobalt.(54)

Heterometallic compounds of cobalt containing metal-metal bonds are now known.(53-56) The most useful procedure in synthesizing M-M' bonded derivatives is alkali halide displacement.(54-58) This method, and a variation of it, has been used to prepare $(CO)_5Mn - Co(CO)_4$,(52,55,56) $(CO_5Re - Co(CO)_4$,(54,55) and $(CO)_5Mn - Cr(CO)_4CC_6H_5$,(57) and is illustrated in equation 6.



$$Na[Co(CO)_4] + [Mn(CO)_5]Br \rightarrow NaBr + \begin{array}{c}(CO)_5Mn\\ |\\ (CO)_4Co\end{array} \qquad (6)$$

Reactions of this type are generally performed in tetrahydrofuran as solvent and the products are purified by column chromatography.(57,58)

II. EXPERIMENTAL

A. Materials and Techniques

The chemical reactions reported in this thesis were carried out in an Erlenmeyer flask with a side-arm under an atmosphere of pre-dried nitrogen gas. When appropriate, a water-cooled reflux condenser was in turn connected by an air-tight link to an oil bubbler, otherwise the side-arm was connected to the bubbler. The reaction mixture was stirred using a magnetic stirrer in combination with a hotplate.

The chemicals used in these reactions were obtained from the manufacturers listed in Table I and, for the most part, were used without further purification. The solvents were dried over calcium hydride for several days and distilled just prior to use. Using a gas dispersion tube (ASTM 40-60 medium porosity frit), nitrogen was bubbled through the solution during one-half hour to ensure the removal of all dissolved oxygen. Water was first boiled before saturating with nitrogen.

B. Physical Measurements

1. Melting Points

Melting points were determined on a Gallenkamp

Table I - Source of Chemicals and Solvents

Chemicals

Dicobalt octacarbonyl (98%)	Alfa Inorganics
Bis(cyclopentadienyldicarbonyl iron)	Alfa Inorganics
Titanium tetrachloride (99.9%)	Alfa Inorganics
Thallium (I) nitrate	Alfa Inorganics
Thallium metal (4-20 mesh, 99.999%)	Alfa Inorganics
Vanadium tetrachloride (90%)	Apache Chemicals
Sodium hydroxide (pellets, reagent)	Canlab
Triphenylphosphine (99%)	Aldrich Chemicals
Triphenylphosphite (97%)	Aldrich Chemicals
Dicyclopentadiene	Eastman Kodak

Solvents

Toluene (certified)	Fisher
Benzene (certified)	Fisher
Tetrahydrofuran (certified)	Fisher
Chloroform (N.F.)	Fisher
Diethyl ether (practical)	Fisher
Pentane (technical)	Anachemia
Methanol (reagent)	Anachemia
Dimethylsulphoxide (spectrometric)	Aldrich
Dimethylsulphoxide d_6 (99.9%)	Aldrich

Miscellaneous

Calcium Hydride (purified)	Fisher
Molecular Sieves (type 4A)	Fisher

melting point apparatus, model MF-370. A sample of the compound was crushed to a powder and packed into a capillary tube under an atmosphere of dry nitrogen in the glove bag and sealed with modeling clay. The melting points were not corrected and they represent the most consistent of several determinations.

2. Infrared Spectra

Infrared spectra were routinely recorded on a Perkin-Elmer grating double beam spectrophotometer, model number 457. Peak frequencies are believed accurate to ±3 cm^{-1}. Some spectra were recorded on a Perkin-Elmer grating double beam spectrophotometer model number 225. For this instrument, peak frequencies can be reported to ±1 cm^{-1}. Spectra from both instruments were calibrated using a polystyrene film at 2850.7, 1601.4, 906.7, and 698.9 cm^{-1}.

The cells used for solution spectroscopy were either 1.0 mm matched sodium chloride cells (Beckman) or 1.0 mm matched potassium bromide cells (Beckman). Nujol mulls were prepared in the glove-bag and the spectra were recorded as films between potassium bromide windows (Wilks) in a demountable infrared cell.

3. Nuclear Magnetic Resonance

The proton magnetic resonance spectra were recorded on a Varian A60-A high resolution spectrometer operating at 60 MHz. The sweep width of the A60-A spectrometer was calibrated against a standard sample of chloroform-tetramethylsilane in carbon tetrachloride. The chemical shifts quoted are those relative to tetramethylsilane used as an internal reference.

4. Mass Spectrometry

Mass spectra were recorded using a Hitachi Perkin-Elmer double-focusing mass spectrometer, model number RMU-6E.

C. Syntheses

Dichlorobis-π-cyclopentadienyltitanium (IV): $(C_5H_5)_2TiCl_2$ (59)

Dicyclopentandiene was cracked by slowly dripping it from an addition funnel onto hot (200° C) mineral oil in a 250 ml 3-neck round bottom flask and collecting the vapours coming off between 40-42° from an air cooled reflux condenser.

Sodium sand (10.00 gm, 0.434 mole) was partially dissolved in 60 ml dry, oxygen-free tetrahydrofuran in a 500 ml 3-neck round bottom flask. The solution was stirred using a stirring motor and was slowly but continuously flushed with nitrogen. The freshly cracked cyclopentadiene (32.08 gm, 0.480 mole) was added dropwise from a pressure-equalizing dropping funnel. The reaction mixture is pink or red in color when the addition is complete. The reaction was considered complete when no more sodium was visible in the bottom of the flask.

To 250 ml of dry tetrahydrofuran in a one litre 3-neck round bottom flask was added (41.42 gm, 0.218 mole) titanium tetrachloride with vigorous stirring using a stirring motor. The flask was kept at 0° C and was continuously flushed with nitrogen. (CAUTION: the reaction is extremely violent at first.) The reaction was over as the last drops of titanium tetrachloride were added producing the yellow $TiCl_4 \cdot 2thf$ adduct.

A cold solution (about 0°) of $TiCl_4 \cdot 2thf$ in thf was added slowly to the cooled pink solution of $(C_5H_5)Na$ with stirring, caution being taken to maintain the inert atmosphere. The color of the reaction mixture continually changed to deeper red as the addition of the tetrahydrofuranate continued. When the addition was complete, a bright red slurry resulted. This was stirred at room temperature for one-half hour and placed in the freezer overnight. The air stable product was vacuum-filtered through a large Buchner funnel and washed with three, 50 ml portions of distilled water to remove the sodium chloride formed. Finally, the sample was washed with two, 20 ml portions of cold methanol and dried under vacuum for six hours. Yield 28.65 gm, 53%; mp. 265-267°, lit(59), 289-291°; δ 6.57 ppm, (in $CDCl_3$), lit(60), 6.55 ppm; IR(cm^{-1} as nujol mull) 3110 s, 1440 s, 1370 w, 1137 vw, 1035 m, 1023 s, 880 m, 829 vs; lit(60) 3118 s, 1445 s, 1375 w, 1131 vw, 1020 m, 1014 s, 868 m, 820 vs.

Dichlorobis-π-cyclopentadienylvanadium (IV): $(C_5H_5)_2VCl_2$(59)

As in the previous synthesis, sodium cyclopentadienide was prepared by the reaction between sodium sand (15.00 gm, 0.652 mole) and freshly cracked cyclopentadiene (44.00 gm, 0.667 mole) in 100 ml of dry, nitrogen-saturated tetrahydrofuran under a nitrogen atmosphere.

Again, as in the synthesis of $(C_5H_5)_2TiCl_2$, the tetrahydrofuranate, $Cl_4V \cdot 2thf$, was prepared by adding dropwise from a pressure equalizing dropping funnel (128.00 gm, 0.667 mole) of vanadium tetrachloride to cold (0°C), well stirred tetrahydrofuran (50 ml) in a one litre, three-neck round bottom flask under an atmosphere of dry nitrogen. (CAUTION: the reaction is extremely violent at first).

This tetrahydrofuranate solution was added to the sodium cyclopentadienide from a pressure equalizing dropping funnel. The reactants were stirred using a stirring motor and continuously flushed with a slow stream of nitrogen passing through the one litre, three-neck round bottom flask. Care was taken not to mix the reactants too quickly because solids will block the addition funnel. When the addition was complete, the contents of the flask were stirred at room temperature for four hours. The green precipitate was vacuum-filtered.

An additional crop of pale green product was obtained by removing the solvent from the filtrate. The two crops were mixed and dried in air on the filter. The desired product was obtained by repeated extraction with boiling chloroform saturated with HCl. Recrystallization from chloroform saturated with HCl gave pale green crystals. These were washed with three, 20 ml portions of cold diethyl ether and vacuum-dried for six hours. Yield 48.37 gm, 29%; mp. 245-248° dec, lit(53) 250 dec.

Sodium Tetracarbonylcobaltate: $Na[Co(CO)_4]$(61)

Into 65 ml of nitrogen saturated tetrahydrofuran in a 125 ml Erlenmeyer flask, fitted with a gas inlet sidearm, was added an excess of NaOH (crushed under a nitrogen atmosphere) and a stirring bar. Under a stream of nitrogen, $Co_2(CO)_8$ (2.64 gm, 0.0077 mole) was added with vigorous stirring. The solution immediately turned dark brown. The solution was stirred at room temperature for one hour. During this time, the color of the solution was successively deep violet, wine red, and finally, at completion of the reaction, a pale yellow. The solution was filtered from the excess NaOH and a blue precipitate using a medium porosity glass fritted funnel. The contents of the frit were washed with a 15 ml portion of tetrahydrofuran and the filtrates were combined. The solvent was removed from the pale yellow solution leaving a white residue. The residue was vacuum-dried for six hours. <u>Yield</u> 2.40 gm, 89%; ν(CO), (cm^{-1} in nujol) 1880, lit$^{(62,63)}$ 1886.

<u>Thallium Tetracarbonylcobaltate</u>: $Tl[Co(CO)_4]^{(43,64)}$

Either one of the two methods was used to prepare this compound:

<u>Method 1</u>

Into 20 ml of toluene (benzene, or tetrahydrofuran were also used) was added $Co_2(CO)_8$ (2.00 gm, 0.0029 mole), a stirring bar, and excess thallium metal from which all oxides were removed. This procedure was carried out under an inert nitrogen atmosphere in the glove-bag. The solution was red in color when removed from the glove-bag. Stirring at room temperature during 18 hours yielded a red-brown solution (literature$^{(43,64)}$ reports yellow-brown solution after about two hours). The solution was then syringed onto 80 ml of pentane yielding a brown solution. Cooling the solution in the freezer for one hour resulted in a bright yellow product. The precipitate was filtered onto a fine porosity glass fritted funnel, washed with three, 10 ml portions of pentane, and dried under vacuum for six hours. <u>Yield</u> 1.66 gm, 76%; mp. 138-144° dec., lit$^{(53)}$ 120-130° lit$^{(65)}$ 140-142°.

<u>Method 2</u>

Onto a solution of $TlNO_3$ (2.13 gm, 0.0080 mole) in 20 ml of distilled water was added a solution of

Na[Co(CO)$_4$] prepared in situ by the reaction between NaOH and Co$_2$(CO)$_8$ (2.42 gm, 0.0071 mole) in 15 ml tetrahydrofuran. The Na[Co(CO)$_4$] solution was added by filtering it from the excess NaOH through a medium porosity glass fritted funnel. The tetrahydrofuran was removed under vacuum precipitating a bright yellow product. The mixture was filtered on a fine porosity glass fritted funnel. The precipitate was washed with two 10 ml portions of cold water and dried under vacuum overnight. Yield 2.14 gm, 81%; mp. 140-146° dec.

Bis(tricarbonyltriphenylphosphitecobalt):
$[P(OC_6H_5)_3Co(CO)_3]_2$ (48)

To a 150 ml of dry, nitrogen saturated benzene in a 250 ml Erlenmeyer flask, fitted with a gas inlet sidearm, was added Co$_2$(CO)$_8$ (1.31 gm, 0.0038 mole) and a stirring bar under an inert nitrogen atmosphere. Triphenylphosphite (2.00 ml, 2.38 gm, 0.0076 mole) was added to the stirred solution dropwise from a syringe under a constant stream of nitrogen. When all of the triphenylphosphite was added, a reflux condenser attached to an oil bubbler, was fitted to the flask. The solution was stirred at room temperature for one and a half hours under a slow stream of nitrogen. The solution was then refluxed for a half hour and cooled in the freezer for six hours. The crystals were then filtered on a medium porosity glass fritted funnel and dried under vacuum for six hours. Yield 2.43 gm, 70%; mp. 147-148° dec, lit(48) 150°.

Bis(tricarbonyltriphenylphosphinecobalt): $[P(C_6H_5)_3Co(CO)_3]_2$(48,66)

To 75 ml of dry, nitrogen saturated benzene in a 250 ml Erlenmeyer flask fitted with a gas inlet side-arm was added $Co_2(CO)_8$ (1.75 gm, 0.0051 mole) and a stirring bar under a slow stream of nitrogen. Triphenylphosphine (2.68 gm, 0.0102 mole) was dissolved in 50 ml of benzene and added slowly to the stirred solution from a syringe. The flask was fitted with a reflux condenser attached to an oil bubbler. The solution was stirred at room temperature under a slow stream of nitrogen for one hour resulting in yellow-brown crystals. The solution was then refluxed for one hour resulting in red-brown crystals in a deep red solution. The solution was placed in the freezer overnight. The crystals were filtered on a medium porosity glass fritted funnel and dried under vacuum for six hours. Yield 4.12 gm, 99.7%; begins to decompose 190-195° and then melts at 208-211°.

Thallium tricarbonyl triphenylphosphitecobaltate: $Tl[(CO)_3CoP(OC_6H_5)_3]$(65)

A solution of $Tl[Co(CO)_4]$ prepared in situ by the reaction between $Co_2(CO)_8$ (1.38 gm, 0.0040 mole) and thallium metal (1.76 gm, 0.0076 mole) in 25 ml toluene, was syringed onto triphenylphosphite (1.07 ml, 0.0060 mole) under an inert nitrogen atmosphere. The solution immediately turned dark red. The solution was removed from the glove-bag and stirred at room temperature (18-20°) for one and one half hours. The solution was filtered through a fine porosity glass fritted funnel, concentrated to one half its volume, and then heptane (35 ml) was added. Cooling in the freezer for six hours resulted in orange crystals. These were filtered, washed twice with pentane, and dried in vacuo for three hours. Yield 2.30 gm, 58%; mp. 117-118° dec, lit(65) 118-122°; ν(CO) (cm^{-1} as nujol mull) 2040 m, 2012 s, 1970 s, 1907 vs, and 1895 vs; lit(60) ν(CO) (cm^{-1} in nitromethane) 2009 w, 1970 m, 1907 vs, 1881 s; The sample probably contains some $Tl[(CO_3CoP(OC_6H_5)_3]_3$ impurity, viz., ν(CO) 2046 cm^{-1} lit(65) 2046 cm^{-1}.

Trimethyltincyclopentadienyldicarbonyliron: $(CH_3)_3Sn\text{-}Fe(C_5H_5)(CO)_2$(68)

The salt $Na[(C_5H_5)Fe(CO)_2]$ was prepared in situ by the reaction between a five-fold excess of five percent sodium amalgam and $[(C_5H_5)Fe(CO)_2]_2$ (1.22 gm, 0.0034 mole) in 20 ml tetrahydrofuran. The solution was stirred at room temperature until the violet color of $[(C_5H_5)Fe(CO)_2]_2$ gave way to the orange color of its sodium salt (usually three hours). This orange solution was syringed onto a solution of $(CH_3)_3SnCl$ in 10 ml of tetrahydrofuran and was stirred at room temperature for seven hours. The solvent was then removed under vacuum with gentle heating, leaving a brown residue. The product was extracted from the residue with three 10 ml portions (until only a slight coloration remains in hexane) of hexane. The solvent was again removed under vacuum leaving a viscous red liquid. The product was purified by vacuum distillation. Yield 1.00 gm, 43%; $\nu(CO)$ (cm^{-1} in hexane) 1977 vs, 1930 vs, (cm^{-1} in DMSO) 1963 vs, 1910 vs; $\delta(C_5H_5)$4.67 ppm, lit$^{(68)}$, 4.68 ppm, $\delta(CH_3)$0.33 ppm, lit$^{(68)}$, 0.32 ppm (in $CDCl_3$).

D. Reactions

Reaction Between $(C_5H_5)_2TiCl_2$ and $Tl[Co(CO)_4]$

Under an inert nitrogen atmosphere, $Tl[Co(CO)_4]$ (0.90 gm, 0.0024 mole) dissolved in 20 ml of tetrahydrofuran was syringed onto solid $(C_5H_5)_2TiCl_2$ (0.62 gm, 0.0025 mole). After stirring at room temperature for ten minutes, the solution developed a deep red color, a gas was evolved, and large white crystals deposited. Stirring at room temperature was continued for 20 hours. The solution was then filtered, the solvent was removed under vacuum, and the solids were carefully dried at reduced pressure. A yellow compound was sublimed into an Erlenmeyer flask cooled in liquid nitrogen from the product of the reaction. Upon warming to room temperature, the yellow solid became a viscous red liquid. $\nu(CO)$ (cm^{-1}, neat) 2062, 2052, 1992, 1987; lit(67) ν(CO) (cm^{-1}) 2028, 1967 for $C_5H_5Co(CO)_2$: mass spectra gave evidence for $C_5H_5Co(CO)_2$. (see discussion)

Reaction Between $Tl[Co(CO)_3P(OC_6H_5)_3]$ and $(C_5H_5)_2TiCl_2$

To solid $(C_5H_5)_2TiCl_2$ (0.40 gm, 0.0016 mole) was added $Tl[(CO)_3CoP(OC_5H_6)_3]$ (1.00 gm, 0.0016 mole) in 20 ml of tetrahydrofuran under an inert nitrogen atmosphere. After standing for one hour at room temperature, a white film formed on the sides of the flask, and the formation of a precipitate was observed. The solution was filtered and concentrated to one half of its original volume under vacuum. Addition of heptane (20 ml) and cooling for two hours in the freezer resulted in red crystals. These were filtered and dried under vacuum. mp. 120-130° dec, ν(CO) (cm^{-1}) 1995 s br, 1955 s br.

The solvent was removed from the solution under vacuum resulting in a gummy dark solid. Volatile materials were removed by heating to 95° under vacuum and collecting them in a liquid nitrogen trap. The residue was a dark red powder. mp. 124-129° dec; ν(CO) (cm^{-1}) 1995 s br, 1950 s br.

Reaction Between $Na[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$

To a mixture of $Na[Co(CO)_4]$ (0.60 gm, 0.0031 mole) and $(C_5H_5)_2TiCl_2$ (0.38 gm, 0.0015 mole) was added 15 ml of diethyl ether under an inert nitrogen atmosphere.

The solution immediately turned brown, and a gas was evolved (probably CO). The reaction mixture was stirred at room temperature for 18 hours. During this time the solution turned deep red and deposited a brown precipitate. The precipitate was filtered, washed twice with 10 ml portions of diethyl ether and dried under vacuum. The volatile materials were removed by heating the dried sample to 80° under vacuum. The product was then extracted from the residue with 20 ml of dichloromethane, the solvent was vacuum-removed, and the sample was subsequently dried in vacuo for six hours. The product slowly decomposes without melting; $\nu(CO)$ (cm^{-1}) 2080 m, 2040 s, 2020 s; $\delta(C_5H_5)$ 6.33 ppm (in tetrahydrofuran); for mass spectrum see discussion.

Reaction Between $Na[Co(CO)_3P(OC_6H_5)_3]^{(70)}$ and $(C_5H_5)_2TiCl_2$

Onto solid $(C_5H_5)_2TiCl_2$ (0.15 gm, 0.0006 mole) was syringed a solution of $Na[Co(CO)_3P(OC_6H_5)_3]$ which was prepared in situ by the reaction between a ten-fold excess of 4% Na(Hg) and $[Co(CO)_3P(OC_6H_5)_3]_2$ (0.59 gm, 0.0006 mole) in 20 ml of tetrahydrofuran. The solution was stirred at room temperature for two hours. The solution was filtered through a fine porosity glass fritted funnel. The solvent was then removed under vacuum resulting in a red oil. An infrared spectrum of the oil showed essentially the same bands as those for

$[Co(CO)_3P(OC_6H_5)_3]_2$ except for an extra band at 1266 cm^{-1}, ν(CO) (cm^{-1}, neat) 1965 vs,br.

Reaction Between $Na[Co(CO)_3P(C_6H_5)_3]^{(70)}$ and $(C_5H_5)_2TiCl_2$

$Na[Co(CO)_3P(C_6H_5)_3]$ was prepared in situ by the reaction between $[Co(CO)_3P(C_6H_5)_3]_2$ (0.90 gm, 0.0010 mole) and a ten-fold excess 5% Na(Hg) in 20 ml of tetrahydrofuran. This solution was syringed onto solid $(C_5H_5)_2TiCl_2$ (0.27 gm, 0.0011 mole). The solution was stirred at room temperature for twenty hours. The solids were filtered off and the solution was concentrated under vacuum until turbidity. Bright orange crystals deposited upon cooling in the freezer for four hours. The crystals were filtered and dried in vacuo for four hours. mp. 190° dec; ν(CO) (cm^{-1}) 1940 w; $\delta(C_5H_5)$ 6.33 ppm (in tetrahydrofuran).

To the solution was added three times its volume of pentane. The red solution immediately turned orange, depositing brown/green crystals. The solution was cooled in the freezer for six hours; the crystals were filtered and dried in vacuo for four hours. mp. 170-175° dec; ν(CO) (cm^{-1}) 2000 w, 1941 s; $\delta(C_5H_5)$ 6.60 ppm, 6.35 ppm (in tetrahydrofuran) c.f. $\delta(C_5H_5)$ for $(C_5H_5)_2TiCl_2$, 6.57 ppm (in $CDCl_3$).

Reaction Between $Na[Co(CO)_4]$ and $(C_5H_5)_2VCl_2$

To a slurry of $Na[Co(CO)_4]$ (1.49 gm, 0.0077 mole) in 20 ml dichloromethane, a solution of $(C_5H_5)_2VCl_2$ (1.00 gm, 0.0040 mole) was added under a stream of nitrogen. The resulting brown solution was stirred at room temperature for three hours. The solution was filtered through a fine porosity glass fritted funnel, the solvent was removed under vacuum, and the residue was dried in vacuo for four hours. The dried sample was then stirred in 30 ml of diethy ether for fifteen minutes and filtered through a fine porosity glass fritted funnel. The golden brown product was dried in vacuo. mp. scinters at 111-115°, 168-170° dec; ν(CO) (cm^{-1} in nujol) 2062 m, 2053 s, 2040 sh, 1995 s, 1878 vs,br; for mass spectrum see discussion.

Reaction Between $(CH_3)_3Sn-Fe(C_5H_5)(CO)_2$ and $TiCl_4$(69)

Titanium tetrachloride (0.13 gm, 0.0007 mole) was added dropwise from a syringe to deuterated dimethylsulfoxide (DMSO-d_6) (2.48 gm, 0.0295 mole) under a dry nitrogen atmosphere. The solution was constantly swirled to prevent the formation of solids.

To $(CH_3)_3SnFe(C_5H_5)(CO)_2$ (2.11 gm, 0.0003 mole) in an nmr tube was added 1.24 gm of the above $TiCl_4$/DMSO-d_6 solution (5.24% w/w $TiCl_4$ = 0.0003 mole $TiCl_4$). The color of the solution changed from orange to deep red and some solid material precipitated. This was dissolved by the addition of more DMSO-d_6 solvent. An nmr spectrum was immediately recorded showing the chemical shifts expected for $(CH_3)_3SnCl$. An infrared spectrum was then taken of the contents of the nmr tube using 0.025 mm IRTRAN II cells. $\delta(CH_3)$ 0.58 ppm, lit(69) 0.55 ppm; $\delta(C_5H_5)$ 5.26 ppm, lit(60) 5.31 ppm; $\nu(CO)$ (cm^{-1}) 2044 s, 1981 s.

III. RESULTS AND DISCUSSION

A. Syntheses

The syntheses of the starting materials, where the absence of moisture and/or oxygen was required only to the degree afforded through glove-bag techniques, were reproduced by the literature methods. However, the syntheses of compounds, where the rigorous absence of oxygen was necessary and the cited reference suggested vacuum line techniques, were reproduced with considerable difficulty since a vacuum line was not available. This is particularly noteworthy in the case of the thallium compounds. The best yield of $Tl[Co(CO)_4]$ obtained in these syntheses was about 76% after a reaction time of 18 hours, whereas a 95% yield was obtained after two hours by Schussler, Robinson, and Edgell.(43) These complexes, once isolated, showed considerably less stability than suggested in the literature,(43) and decomposition rapidly occurred (10 seconds in air) even when sealed into a nitrogen filled vial in the dark (about 2 days).

B. Reactions and Attempted Characterizations

Nucleophilic substitution of a halide group in a metal halide has been successfully employed for a number of different metals(71-73) in the synthesis of M-M bonded derivatives. Thus the method chosen for M-M bond synthesis was the reaction between $Na[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$ or $(C_5H_5)_2VCl_2$. The thallium salt, $Tl[Co(CO)_4]$, was reported$^{(43,64,65)}$ to have some desirable properties (e.g. good stability, ionic in polar solvents, covalent in non-polar solvents) from a synthetic point of view, and some reactions were attempted using this salt.

However, as it will become evident, the reactions of $Na[Co(CO)_4]$ and $Na[Co(CO)_3L]$, $L = P(C_6H_5)_3$ or $P(OC_6H_5)_3$ with $(C_5H_5)_2MCl_2$, M = Ti or V, are more akin to those of Cenini and coworkers.$^{(74)}$ These workers used these types of cobalt derivatives in an attempt to synthesize M-M bonded compounds of cobalt and the members of the nickel triad. Whereas these authors$^{(74)}$ report relatively stable isolable products, although none contain M-M bonds, the compounds isolated in this study were extremely unstable. While drying <u>in vacuo</u>, all of the reaction products liberated a yellow compound which turned into a red liquid after a few minutes at room temperature. Also this same yellow compound was observed as a "sublimate" whenever melting points were taken. In an attempt to characterize this compound, it was collected from the reaction between $Tl[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$ (see experimental). The carbonyl region of the infrared spectrum of this yellow compound was shown to contain four bands at 2062, 2052, 1992 and 1987 cm^{-1} in the vapour phase. Only two carbonyl bands$^{(67)}$ (2028 and 1967 cm^{-1}) were reported for the solution spectra of $C_5H_5Co(CO)_2$ by Cotton and his coworkers.$^{(67)}$ Thus, the reaction product does not appear to be $C_5H_5Co(CO)_2$ on the basis of infrared data. However, mass spectra seemed to indicate $C_5H_5Co(CO)_2$.

The mass spectra of $C_5H_5Co(CO)_2$$^{(75,76)}$ are characterized by the successive removal of carbon monoxide (28 amu) fragments more readily than the removal of the cyclopentadienyl ring system. The mass spectrum of this yellow compound has been reproduced in Figure III. Table II lists the relative intensities of various ions at their respective m/e values. From this table, m/e values at 180, 152, 124, 98, 59, and 39 tend to support the identification of one product in the sample as $C_5H_5Co(CO)_2$.$^{(75,76)}$ High relative intensities of ions occurring at other m/e values (e.g. 40, 41, 42, 43, 71, or 72) suggest the presence of other species. These species are not readily indetifiable but they are hydrocarbons to a large extent. Two distinct possibilities can be thought of with respect to their nature. First, the sample introduced into the mass spectrometer was not completely dry and these m/e values (i.e. 40, 41, 42, and 43) represent the fragmentation pattern of tetrahydrofuran used as solvent. Second, the sample was

Figure III - Line Graph for the Volatile Product(s) from the Reaction Between Tl[Co(CO)$_4$] and $(C_5H_5)_2TiCl_2$.

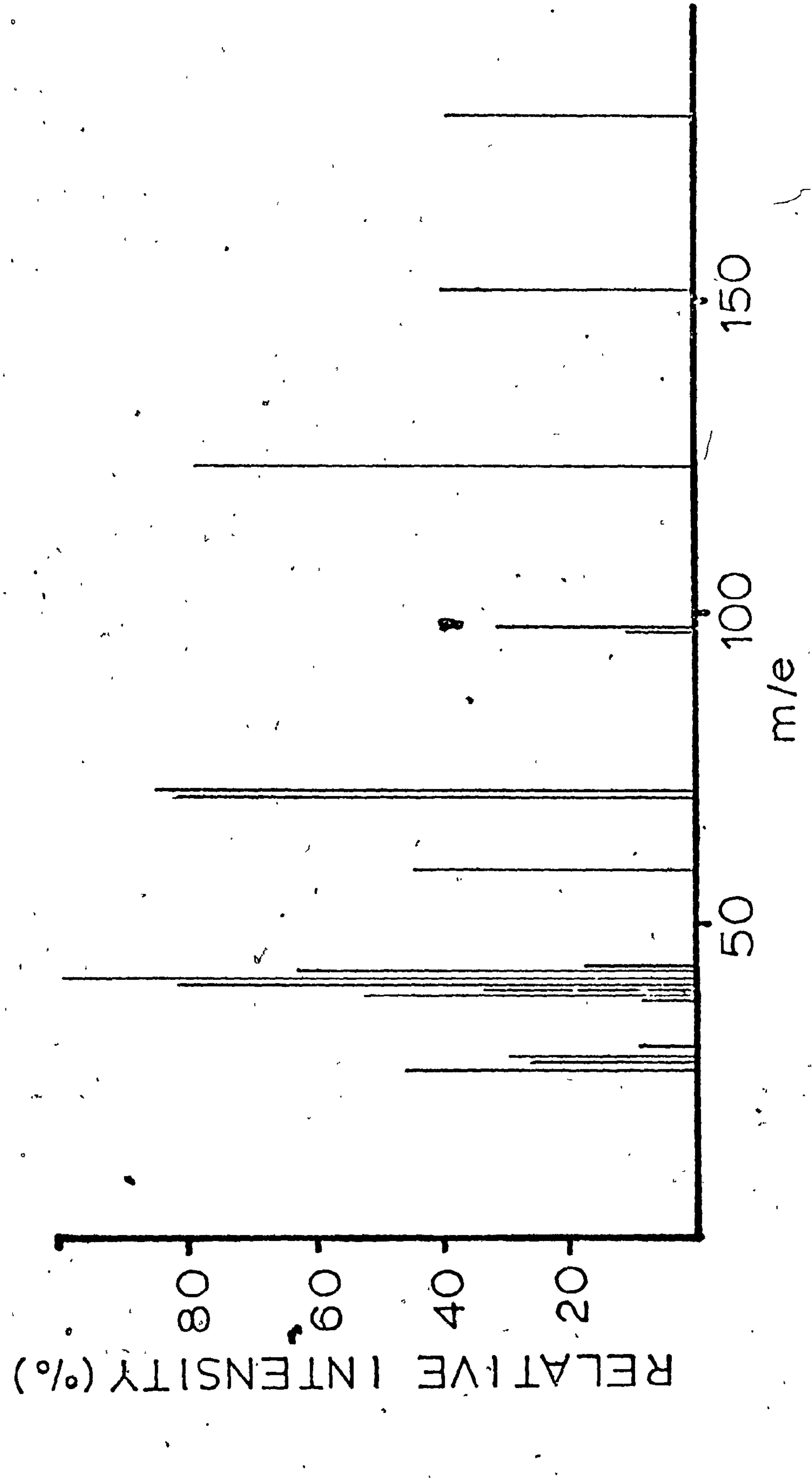

RELATIVE INTENSITY (%)
80
60
40
20
m/e
50
100
150

Table II - Mass Spectral Data[a] for the Volatile Product(s) from the Reaction Between $Tl[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$

m/e	Relative Intensity (%)	Possible Ion(s)
180	38.73	$C_5H_5Co(CO)_2^+$
152	39.79	$C_5H_5Co(CO)^+$
124	88.73	$C_5H_5Co^+$
105	5.84	
98	31.97	$C_3H_3Co^+$
97	11.27	$C_3H_2Co^+$
91	9.85	
87	8.10	$CoCO^+$
84	5.35	
72	85.21	$HCCo^+$, $C_4H_8O^+$
71	83.30	CCo^+, $C_4H_2O^+$
59	45.07	Co^+
44	18.31	$C_3H_8^+$, $C_2H_4O^+$, CO_2^+
43	63.38	$C_3H_7^+$, $C_2H_3O^+$
42	100.00	$C_3H_6^+$, $C_2H_2O^+$
41	80.99	$C_3H_5^+$
40	34.86	$C_3H_4^+$
39	54.22	$C_3H_3^+$
38	10.20	$C_3H_2^+$
31	10.49	CH_3O^+
29	29.58	$C_2H_5^+$, HCO^+

Table II - cont'd

m/e	Relative Intensity (%)	Possible Ion(s)
28	27.32	CO^+, $C_2H_4^+$
27	46.48	$C_2H_3^+$
18	5.49	H_2O^+

[a] Because it is not always possible to distinguish between even and odd electron ions, the notation adopted here is to write all ions as Y^+. This notation will be used throughout the text.

obtained by sublimation of the product(s) of the reaction between Tl[Co(CO)$_4$] and $(C_5H_5)_2TiCl_2$. If during sublimation, decomposition had occurred, then these hydrocarbon moieties could be the decomposition product(s) of an unstable compound formed on reaction of $Co(CO)_4^-$ with $(C_5H_5)_2TiCl_2$.

These hydrocarbon species do not seem to arise from the tetrahydrofuran used as solvent nor does it represent the fragmentation pattern of C_5H_6 (Table III). Further credence is given to the latter possibility if it is noted that a yellow ring was observed near the top of the capillary, whenever melting points were recorded, even after the volatile materials had been removed <u>in vacuo</u>. Since these hydrocarbon moieties, as well $C_5H_5Co(CO)_2$ result from the "sublimation" of the products of the reaction between Tl[Co(CO)$_4$] or Na[Co(CO)$_4$] and $(C_5H_5)_2TiCl_2$, it is not unreasonable to suggest that $C_5H_5Co(CO)_2$ is a "decomposition" product of the reaction.

The product of the reaction between Na[Co(CO)$_4$] and $(C_5H_5)_2TiCl_2$, after the removal of volatile materials was a pyrophoric black solid. A sample sent out for elemental analysis proved too unstable to give reliable results. However, the analysis did show that the compound was of high molecular weight and contained both titanium and cobalt. At first the inconsistent analysis

Table III - Relative Intensities of the Ten Most Intense Peaks of Tetrahydrofuran and Cyclopentadiene[a]

Tetrahydrofuran, C_4H_4O		Cyclopentadiene, C_5H_6	
m/e	Relative Intensity	m/e	Relative Intensity
39	100.0	66	100.0
68	62.1	65	64.7
38	16.5	39	49.9
29	15.8	40	41.3
40	11.5	38	15.3
37	10.5	63	9.9
42	7.0	31	9.2
14	4.0	37	8.8
26	3.7	62	7.8
31	6.9	67	5.7

[a] Taken from reference (76).

was believed to arise from impurities in the sample. Thin layer chromatography (tlc) was attempted to verify the presence of these impurities, however, the samples decomposed quickly and visibly once applied to the tic plate. This was probably due to the presence of oxygen trapped in the silica gel on the plate. Analysis performed on another sample, more carefully purified by washing, again gave results not conforming to any reasonable molecular formula (Table IV).

Table IV - Analysis for the Product(s) of the Reactions Between Na$[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$[a]

Sample	% C	% H	% Co	% Ti	MW	Solvent
1	38.69	3.49	15.58	15.39	740	Benzene
2	32.85	3.16	19.60	14.72	-	-

[a] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

The mass spectra of this compound have been recorded (Figure IV) and the relative intensities of ions occuring at different m/e values has been tabulated (Table V). Again a familiar pattern (m/e 180, 152, 124, 98) emerges, and it is tempting to postulate the loss of $C_5H_5Co(CO)_2$ from a higher molecular weight species. Decomposition of the sample, either thermally or because of

Figure IV - Line Graph for the Product(s) from the Reaction Between Na$[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$.

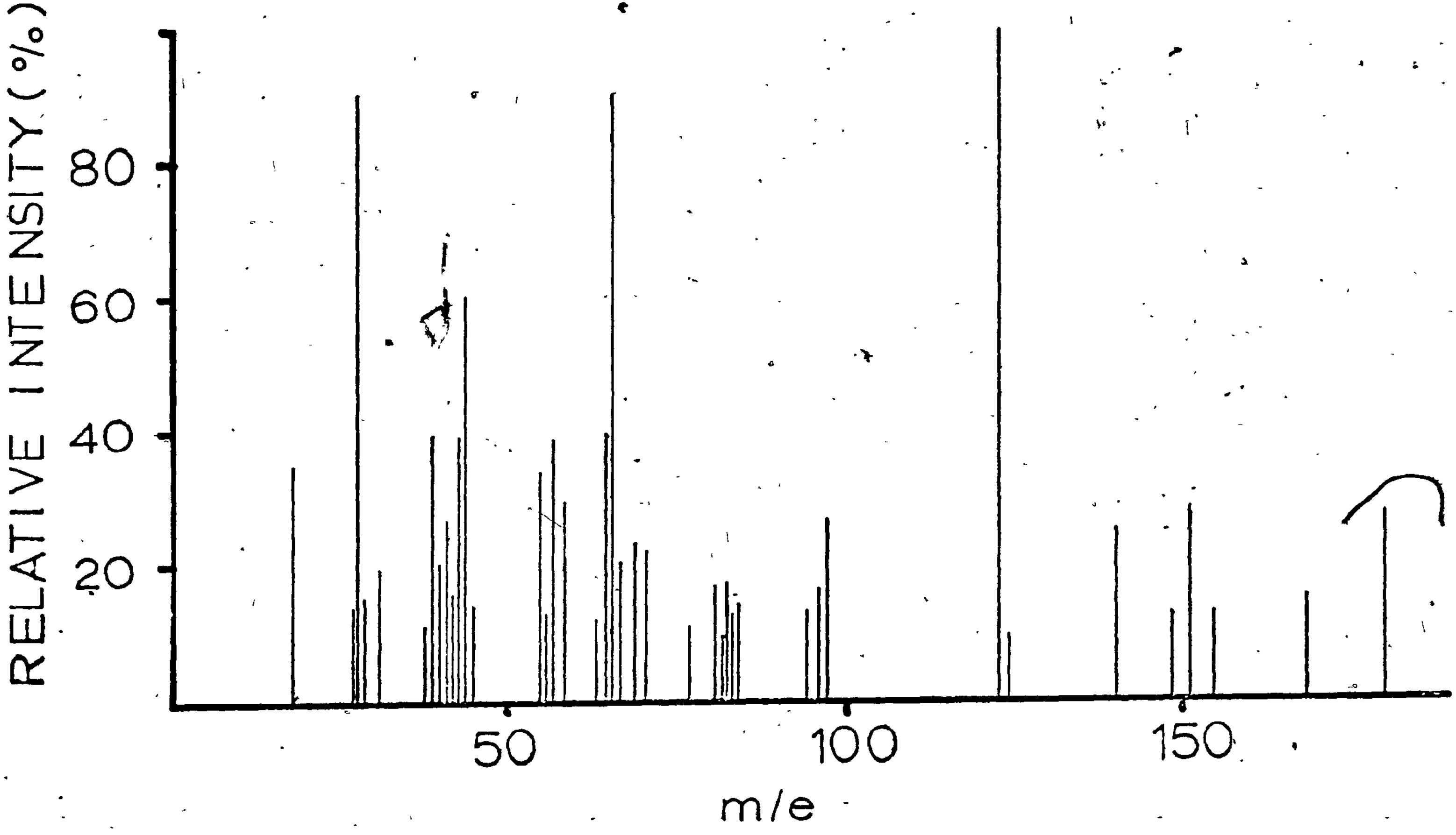

RELATIVE INTENSITY (%)
80
60
40
20
50
100
150
m/e

Table V - Mass Spectral Data for the Products of the Reaction Between Na$[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$

m/e	Relative Intensity (%)	Possible Ion(s)
191	5.02	
180	28.39	$C_5H_5Co(CO)_2^+$
169	14.82	$C_5H_5Ti(CO)_2^+$
155	13.06	$C_4H_3Ti(CO)_2^+$, $C_3H_4Co(CO)_2^+$
153	5.02	
152	29.40	$C_5H_5CoCO^+$
149	13.06	
142	5.68	
141	25.98	$C_5H_5TiCO^+$
125	10.05	
124	100.00	$C_5H_5Co^+$
123	6.83	
115	5.78	$C_3H_3TiCO^+$
112	5.93	
111	8.64	
109	9.04	
105	5.53	
103	5.83	$C_2H_3TiCo^+$
98	27.04	$C_3H_3Co^+$
97	17.94	$C_3H_2Co^+$
96	8.04	

Table V - cont'd.

m/e	Relative Intensity (%)	Possible Ion(s)
95	13.06	
94	7.18	
93	8.99	
91	5.68	
87	6.03	$C_3H_3Ti^+$, $CoCO^+$, $C_2H_4Co^+$
85	14.07	
84	11.96	
83	17.59	
82	10.05	
81	17.08	
79	6.93	
78	6.93	
77	10.80	$HTiCo^+$
76	5.63	$TiCO^+$
71	22.91	
70	10.90	
69	24.12	$C_4H_5O^+$, $HC_3O_2^+$
68	8.04	
67	21.10	$C_5H_7^+$, $C_4H_3O^+$
66	89.95	$C_5H_6^+$
65	39.70	$C_5H_5^+$

Table V - cont'd

m/e	Relative Intensity (%)	Possible Ion(s)
64	5.73	
63	11.66	
62	8.44	
61	5.02	
59	29.90	Co^+
58	8.04	
57	38.99	$C_4H_9^+$
56	13.22	
55	33.52	$C_4H_7^+$, $C_3H_3O^+$
54	5.93	
53	6.63	
51	9.55	
50	6.03	
46	9.80	
45	13.62	
44	60.80	$C_2H_4O^+$, $C_3H_8^+$, CO_2^+
43	40.20	$C_2H_3O^+$, $C_3H_7^+$
42	15.58	
41	26.88	$C_2H_2O^+$, $C_3H_5^+$
40	21.10	
39	39.70	$C_3H_3^+$
38	10.80	

Table V - cont'd

m/e	Relative Intensity (%)	Possible Ion(s)
37	5.83	
32	9.25	
31	20.10	H_3CO^+
29	15.48	
28	90.45	CO^+, $C_2H_4^+$
27	14.02	
18	34.17	H_2O^+

electron impact, is suspected because of the relatively high intensity of CO^+ (90%, m/e = 28), $C_5H_6^+$ (90%, m/e = 66), and $C_5H_5^+$ (40%, m/e = 65).(77)

Table IV above shows that besides cobalt, the sample contains titanium. However, only a few ions in the mass spectrum (Figure IV) that may possibly contain titanium (m/e = 169, 141, and 115) may be indentified. Being unable to perform a chromatographic seperation, it was impossible to determine whether the titanium containing moieties were authentic species or just part of the fragmentation pattern of a higher molecular weight product. In either case, it seems that the fragmentation pattern observed in the mass spectra (Table V) is of the type expected for $(C_5H_5)_2Ti(CO)_2$.

The infrared spectrum of $(C_5H_5)_2Ti(CO)_2$ contains two solvent dependent carbonyl stretching bands at 1975 and 1897 cm^{-1}.(78,79) These bands were not observed in either the infrared spectrum of the volatile materials, which were shown by mass spectroscopy to be mainly $C_5H_5Co(CO)_2$, or the infrared spectrum of the remaining sample. Again it appears that decomposition of a high molecular weight product is responsible for moieties indentified as $C_5H_5Ti(CO)_2^+$ (m/e = 169), $C_5H_5TiCO^+$ (m/e = 141), and $C_3H_3TiCO^+$ (m/e = 115).

Decomposition is again observed (at least in the mass spectrometer) for the product(s) formed by the reaction between $Na[Co(CO)_4]$ and $(C_5H_5)_2VCl_2$. However, in this case, the instability is reflected mainly in the loss of carbon monoxide. (Table VI, Figure V) The products of the reaction seem to be quite stable to the loss of cyclopentadiene. In fact this "extra stability" of the cyclopentadiene in this sample, as compared to that of the product(s) of the reaction between $Na[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$, is only apparent and is due to the excessively large relative intensity of the CO^+ ion. If the relative intensity of CO^+ is minimized (Table VII), then it is seen that cyclopentadiene is appreciably lost (Table VII). This is represented graphically in Figure VI.

Since product stability was rather poor in the reactions with carbonyl compounds, it was reasoned that a substituted carbonyl, $Na[Co(CO)_3L]$ ($L = P(C_6H_5)_3$ or $P(OC_6H_5)_3$) might give better stability. The replacement of a carbonyl ligand with a poorer π-acceptor such as triphenylphosphine or triphenylphosphite has the effect of increasing the negative charge on the cobalt. This results in the $[Co(CO)_3L]^-$ anion being a better nucleophile than the $[Co(CO)_4]^-$ anion.(80) It was hoped that this increase in nucleophilicity would be sufficient to isolate a pure compound and not just a decomposition product.

It was shown(81,82) that the most acidic hydrides

Table VI - Mass Spectral Data for the Product(s) from the Reaction Between Na[Co(CO)$_4$] and $(C_5H_5)_2VCl_2$

m/e	Relative Intensity (%)	Possible Ion(s)
180	8.72	$C_5H_5Co(CO)_2^+$
152	8.43	$C_5H_5Co(CO)^+$
124	28.52	$C_5H_5Co^+$
98	6.45	$C_3H_3Co^+$
84	5.00	
82	6.95	
66	22.61	$C_5H_6^+$
65	10.34	$C_5H_5^+$
59	7.70	Co^+
49	5.17	
44	18.30	$C_3H_8^+$, CO_2^+
40	5.20	
39	11.22	$C_3H_3^+$
28	100.00	CO^+

Figure V - Line Graph of the Product(s) from the Reaction Between Na$[Co(CO)_4]$ and $(C_5H_5)_2VCl_2$.

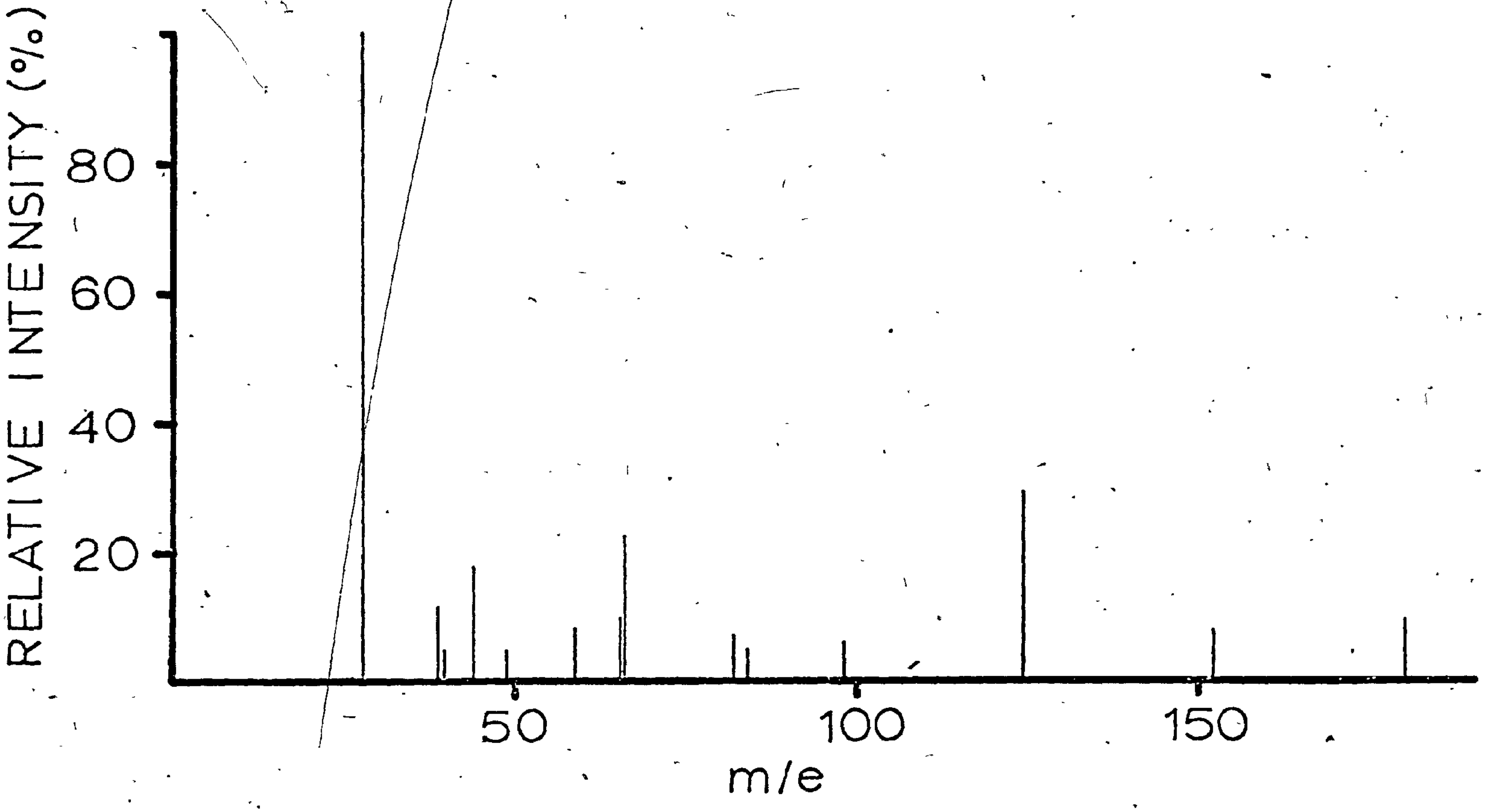

RELATIVE INTENSITY (%)
20
40
60
80
50
100
150
m/e

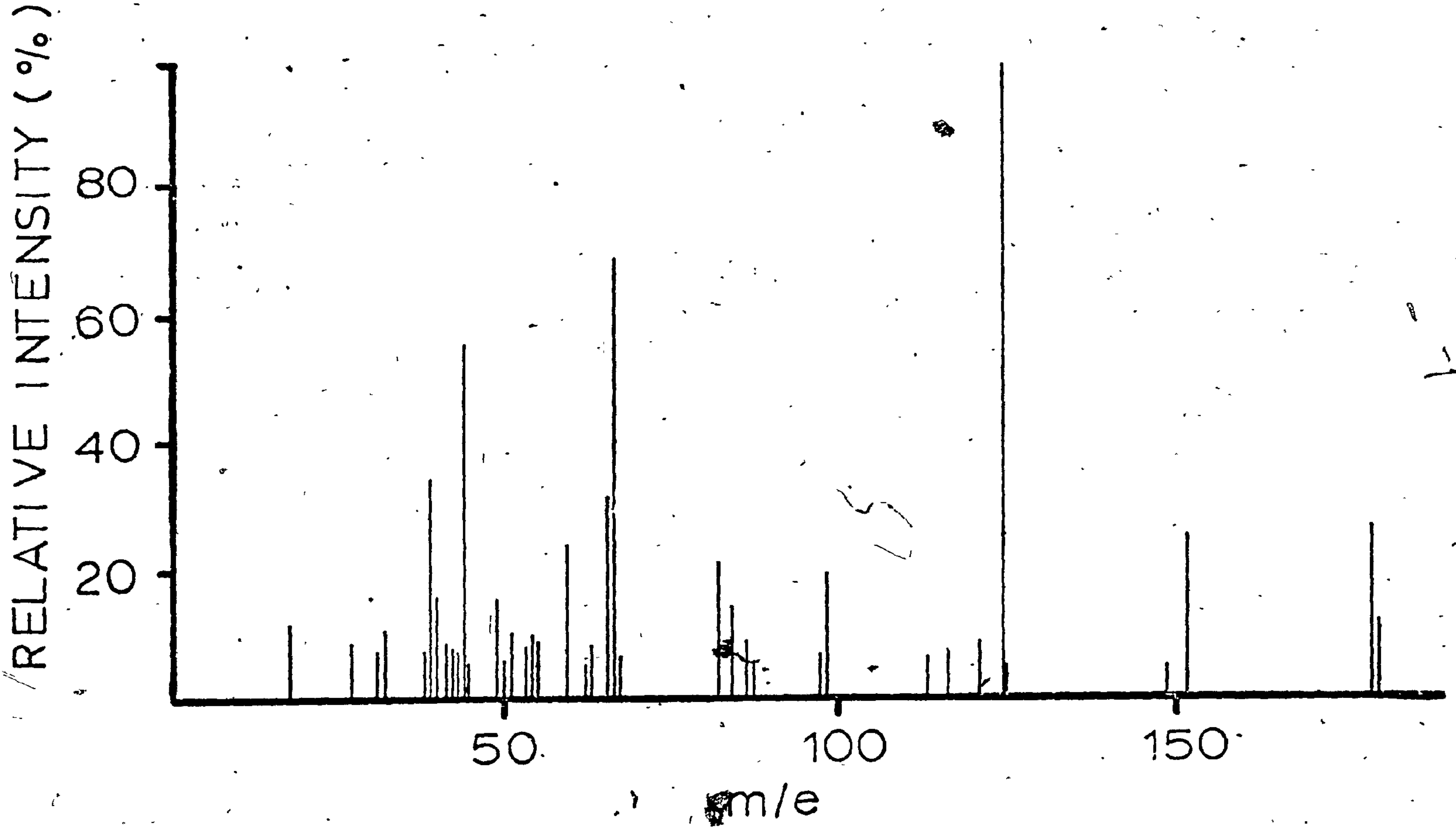
Table VII - Mass Spectral Data for the Product(s) from the Reaction Between Na[Co(CO)$_4$] and $(C_5H_5)_2VCl_2$ Assuming Excess CO in the Sample

m/e	Relative Intensity (%)	Possible Ion(s)
181	12.62	$(C_5H_5)_2V^+$
180	26.89	$C_5H_5Co(CO)_2^+$
152	26.02	$C_5H_5CoCO^+$
149	6.28	
125	5.61	
124	100.00	$C_5H_5Co^+$
121	9.01	
106	7.40	
103	6.91	$C_4H_4V^+$
98	19.92	$C_3H_3Co^+$
97	6.94	
87	5.96	$COCo^+$
86	9.08	
84	15.43	
82	21.46	
67	7.01	
66	69.78	$C_5H_6^+$
65	31.91	$C_5H_5^+$
63	8.76	
62	6.31	
59	23.77	Co^+

Table VII - cont'd

m/e	Relative Intensity (%)	Possible Ion(s)
55	9,75	
54	11,15	
53	9,12	
51	11.22	V^+
50	6.24	
49	15,95	
45	5.33	
44	56,45	CO_2^+, $C_3H_8^+$, $C_2H_4O^+$
43	7.78	
42	7,71	
41	9,12	
40	16,06	$C_3H_4^+$
39	34,61	$C_3H_3^+$
38	7,85	
32	10,52	
31	7.01	
29	9,89	
28	-	
27	8,42	
18	11,92	H_2O^+

Figure VI - Line Graph for the Product(s) from the Reaction Between Na$[Co(CO)_4]$ and $(C_5H_5)_2VCl_2$ Assuming Excess CO in the Sample.


RELATIVE INTENSITY (%)
20
40
60
80
50
100
150
m/e

are the least stable to thermal decomposition. Those ligands which are particularly efficient in removing electron density from the metal (i.e. cobalt) by back-bonding increase the acidity of the hydride and decrease its thermal stability.(81,82) Conversely, the substitution of a ligand which is less efficient in removing electron density from cobalt should increase the thermal stability of the cobalt derivative. By such a substitution, both the thermal stability of the resulting product and the nucleophilicity of the $[Co(CO)_3L]^-$ anion should have been increased. This was observed for the reaction between $Tl[Co(CO)_3P(OC_6H_5)_3]$ and $(C_5H_5)_2TiCl_2$. The reaction time was much less, and although some volatile materials were removed, decomposition was not as extensive as with $Tl[Co(CO)_4]$. It is doubtful that an M-M bonded species was isolated. Had this occurred, a charge transfer from the cobalt to the titanium would have resulted in a shift to higher ν(CO) frequencies in the product than in $Tl[Co(CO)_3P(OC_6H_5)_3]$. The carbonyl frequencies for the product, (ν(CO) = 1995, 1900 cm^{-1}) are in the same frequency range as those in the starting material (ν(CO) = 2012, 1907, and 1895 cm^{-1}). This limits the possibilities of the product to either an ionic compound containing titanium or a cluster compound of cobalt.

No apparent reaction occurred after two hours if the sodium salt, $Na[Co(CO)_3P(OC_6H_5)_3]$, was used. However, a reaction seemed to proceed between $Na[Co(CO)_3-P(C_6H_5)_3]$ and $(C_5H_5)_2TiCl_2$. Again from the infrared spectrum ($\nu(CO) = 2000, 1940\ cm^{-1}$) no M-M bonding may be inferred. The nmr spectrum showed two peaks ($\delta = 6.60, 6.35$ ppm); one ($\delta = 6.60$ ppm) may be assigned $(C_5H_5)_2TiCl_2$, while the other ($\delta = 6.35$ ppm) occurs very close to the chemical shift for the product in the reaction between $Na[Co(CO)_4]$ and $(C_5H_5)_2TiCl_2$ (i.e. $\delta = 6.33$ ppm). The products are probably very similar in both cases.

In a recent article(69) R. M. G. Roberts claimed the synthesis of $Cl_3Ti-Fe(C_5H_5)(CO)_2$ by the reaction of $TiCl_4$ with $(CH_3)_3Sn-Fe(C_5H_5)(CO)_2$. Ths displacement of $(CH_3)_3SnCl$ was followed by nmr. He inferred that because he observed the chemical shift of $(CH_3)_3SnCl$ in the reaction products between $(CH_3)_3Sn-Fe(C_5H_5)(CO)_2$ and $TiCl_4$, the above M-M bonded derivative must have been obtained. In hopes of applying this reaction scheme to the cobalt system, the reactions were successfully reproduced. (Table VIII) Furthermore, infrared spectra were determined at each stage of the process. Thus the two bands observed in the carbonyl region of the infrared spectrum of $(CH_3)_3Sn-Fe(C_5H_5)(CO)_2$ ($\nu(CO) = 1963, 1910\ cm^{-1}$) were shifted to higher frequencies ($\nu(CO) = 2044, 1981\ cm^{-1}$) in the reaction product. Such a shift was

Table VIII.- Evidence for the Synthesis of $Cl_3Ti-Fe(C_5H_5)(CO)_2$[a]

Sample	C_5H_5 (ppm)	CH_3 (ppm)	CO cm^{-1}
$(CH_3)_3SnCl$	–	0.55, 0.55 (69)	–
$(CH_3)_3SnFe(C_5H_5)(CO)_2$	4.67, 4.68 (69)	0.33, 0.32 (69)	1963 vs, 1910 vs
$TiCl_4$ + $(CH_3)_3SnFe(C_5H_5)(CO)_2$	5.26, 5.31 (69)	0.58, 0.55 (69)	2044 s, 1981 s

[a] The solvent was DMSO-d_6.

expected upon M-M bond formation with titanium because of the greater effective nuclear charge on the titanium atom than on the tin. Note that these products were observed only in solution and no attempts were made at isolating them.

When these reactions were applied to cobalt (i.e. $(CH_3)_3SnCo(CO)_4$ + $TiCl_4$), decomposition was observed within a few minutes. The colorless $(CH_3)_3SnCo(CO)_4$/DMSO-d_6 solution turned blue with the evolution of a gas upon addition of $TiCl_4$. The nmr spectrum of this blue solution was not appreciably different from that of $(CH_3)_3SnCo(CO)_4$.(83) In the blue solution, methyl group chemical shifts occurred at δ = 0.57 ppm while in the reactant, $(CH_3)_3SnCo(CO)_4$, the chemical shifts were observed at δ = 0.54 ppm. Had a reaction similar to that of $(CH_3)_3SnFe(C_5H_5)(CO)_2$ occurred, the chemical shift of the $(CH_3)_3SnCl$ formed would have been at δ = 0.55 ppm. Clearly, the expected and the observed chemical shifts are in too close proximity to be able to draw significant conclusions. Perhaps, a change of solvent would have provided larger chemical shift differences and thus more conclusive results.

To summarise, then, it appears that the direct reaction between the sodium or thallium salt of $[Co(CO)_4]^-$ and a titanium halide may not be a good method for the synthesis of metal-metal bonded compounds between cobalt and titanium. Although this method is applicable for a large variety of metal carbonyls and substituted metal carbonyls, only decomposition products of high molecular weight derivatives were obtained in this work. Substitution of metal centers (i.e Ti for Sn) bonded to cobalt also gave intractable products.

A method that has been successfully used in the synthesis of M-M bonded derivatives and could possibly give the desired products is photolysis. Simultaneous photolysis of Mn_2CO_{10} and $[C_5H_5Mo(CO)_3]_2$ gave $(CO)_5Mn$-$Mo(CO)_3(C_5H_5)$ as a final product.(84) On the surface, the method seems simple. However, a large variety of compounds in the product soup could also prove difficult to separate and product isolation would still remain a problem.

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