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Synthesis of β-Diketonate Chelates of the Bis(cyclopentadienyl)titanium(IV) Moiety: Infrared and Proton Magnetic Resonance Spectra[1]

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Received December 2, 1966

A series of compounds of the type $[(\pi\text{-}C_5H_5)_2TiL^+]X^-$ has been synthesized where L is the conjugate base of acetylacetone, benzoylacetone, dibenzoylmethane, dipivaloylmethane, and tropolone and where X^- may be ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, or $F_3CSO_3^-$. The infrared spectra have been obtained, and assignments are made for the acetylacetonate by examination of the spectra of $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$, $[(\pi\text{-}C_5D_5)_2Ti(acac)]ClO_4$, and $[(\pi\text{-}C_5H_5)_2Ti(acac)]F_3CSO_3$. In all cases the ligand L appears to be chelating, and the titanium atom is essentially four-coordinate. The pmr spectra were also obtained, and the =C—H resonance of the acetylacetonate appears to be the lowest field value observed for any acetylacetone complex. The bonding in these compounds is discussed, and they are compared with the organometallic chelates of the group IVb metals.

Introduction

Studies with the group IVb elements have shown that six-coordinate chelates of the type ML_2X_2, where L is a β-diketonate and X is a σ-bonded carbanion, can be synthesized readily. Among the complexes prepared are those with L = acetylacetonate, M = Sn, and X = CH_3[3-5] or C_6H_5[3-6] as well as M = Pb, X = CH_3[5] or C_6H_5.[7] In general, the *trans* configuration seems to be the thermodynamically favored one.[3,5,6] With X ligands other than the carbanions, the *cis* configuration is energetically more favorable as, for example, with $Sn(acac)_2Cl_2$.[8,9]

In contrast to the spate of work recently on chelates containing organotin(IV) moieties,[10] there have been very few studies of analogous organotitanium chelates. Compounds of the type $Ti(acac)_2Cl_2$ have been reported to have the same *cis* structures as the analogous tin compounds,[11] but no organotitanium compounds containing a chelate group with nitrogen or oxygen donor atoms seem to have been prepared. Recently, dithiolate compounds such as $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$ have been synthesized.[12,13] In these compounds, the titanium(IV) is still four-coordinate. Jensen originally suggested that $(\pi\text{-}C_5H_5)_2TiX_2$ (X = Br or NCS) compounds were dimeric in acetone, presumably with six-coordination for the titanium,[14] but this appears to have been erroneous in the light of the work of Langford and Aplington.[15]

In order to determine if the bis(cyclopentadienyl)titanium(IV) moiety could be forced into a sandwich structure with parallel rings and six-coordinate titanium, it was decided to study the reactions of $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$ with ligands having small, highly electronegative donor atoms.

Experimental Section

Reagents.—Bis(cyclopentadienyl)titanium dichloride was obtained from Alfa Inorganics, Inc., and recrystallized from toluene. Acetylacetone was Fisher reagent, and benzoylacetone and dibenzoylmethane were Eastman White Label. Dipivaloylmethane was obtained from K and K Laboratories and tropolone from Aldrich Chemical. Barium trifluoromethylsulfonate was generously provided by the 3M Company.

Preparation of Complexes.—Most of the compounds were synthesized several times. Microanalyses were carried out by the Clark Microanalytical Laboratory, Urbana, Ill.

2,4-Pentanedionatobis(cyclopentadienyl)titanium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$.—A solution containing 0.01 mole of bis(cyclopentadienyl)titanium perchlorate was prepared by adding a slight excess of silver perchlorate to a suspension of 2.49 g (0.01 mole) of bis(cyclopentadienyl)titanium dichloride in 75 ml of water and filtering off the precipitated silver chloride. The filtrate was cooled to 0° and 10 g (0.10 mole) of acetylacetone was added. The gray-violet precipitate which formed immediately was collected on a glass frit and washed several times with water, ethanol, and diethyl ether. Recrystallization from methanol gave a 70% yield of violet crystals. *Anal.* Calcd for $C_{15}H_{17}ClO_6Ti$: C, 47.83; H, 4.55; Cl, 9.41. Found: C, 48.25; H, 5.10; Cl, 8.86.

Bis(cyclopentadienyl)titanium Dichloride-d_{10}.—To a 5% solution of NaOD in D_2O was added 66 g (1.0 mole) of cyclopentadiene. The mixture was kept at 0° for 5 days with constant stirring. After this time, the organic layer was separated from the aqueous layer and dried over anhydrous $MgSO_4$. The cyclopentadiene dimer was cracked after drying[16] and the monomer was allowed to react with a fresh NaOD–D_2O solution. This process was repeated a total of seven times yielding 5.0 g of cyclopentadiene-d_6. This (5.0 g, 0.07 mole), dissolved in 50 ml of tetrahydrofuran, was slowly added to a stirred supension of 1.6 g (0.07 g-atom) of sodium metal in 100 ml of THF. The mixture was stirred for 3 hr until D_2 was no longer evolved. The solution of NaC_5D_5 was then added over a period of 1 hr to a stirred solu-

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[1] Supported, in part, by the National Science Foundation, Grant GP-5022.

[2] NASA Predoctoral Fellow.

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[9] W. H. Nelson, Abstracts of Papers Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 12–16, 1966, Paper O-061.

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[14] A. Jensen, "Proceedings of the Seventh International Conference on Coordination Chemistry," Stockholm-Uppsala, June 1962, p 254.

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tion of 6.5 g (0.034 mole) of titanium tetrachloride in 100 ml of THF. The mixture was stirred an additional 2 hr and then filtered through a large sintered glass funnel to remove the NaCl which was formed. The filtrate was evaporated to dryness on a steam bath and the residue extracted with several portions of boiling toluene until the extracts were no longer colored red. The toluene solution was cooled to −80°, and the red crystals of $(\pi\text{-}C_5D_5)_2TiCl_2$ which formed were filtered off. The product was recrystallized once from acetone and twice from toluene; yield 4.2 g (48%). Comparison of the mass spectrum of the deuterated compound with that of the nondeuterated product indicated an enrichment of 97 ± 2%.

2,4-Pentanedionatobis(cyclopentadienyl-d_5)titanium(IV) Perchlorate, $[(\pi\text{-}C_5D_5)_2Ti(acac)]ClO_4$.—The deuterio bis(cyclopentadienyl)titanium dichloride was used to prepare this compound according to the procedure used for $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$.

2,4-Pentanedionatobis(cyclopentadienyl)titanium(IV) Trifluoromethanesulfonate, $[(\pi\text{-}C_5H_5)_2Ti(acac)]F_3CSO_3$.—This compound was prepared in the same manner as the perchlorate. *Anal.* Calcd for $C_{16}H_{17}F_3O_5STi$: C, 45.08; H, 4.02. Found: C, 45.13; H, 4.22.

2,4-Pentanedionatobis(cyclopentadienyl)titanium(IV) Tetrafluoroborate, $[(\pi\text{-}C_5H_5)_2Ti(acac)]BF_4$.—Synthesis was by the same procedure as was used for the perchlorate. *Anal.* Calcd for $C_{15}H_{17}BF_4O_2Ti$: C, 49.49; H, 4.71. Found: C, 49.39; H, 4.97.

The above three compounds as well as a variety of other salts of the type $[(\pi\text{-}C_5H_5)_2Ti(acac)]^+X^-$ such as the hexafluorophosphate, hexafluoroarsenate, hexafluoroantimonate, and tetraphenylborate could be prepared in lower yields by the addition of the sodium or potassium salt of the desired anion to a solution of bis(cyclopentadienyl)titanium dichloride in water containing an excess of acetylacetone.

1-Phenyl-1,3-butanedionatobis(cyclopentadienyl)titanium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2Ti(bzac)]ClO_4$.—A solution of 1.62 g (0.010 mole) of benzoylacetone dissolved in 20 ml of tetrahydrofuran was added to 50 ml of an aqueous solution containing 0.005 mole of bis(cyclopentadienyl)titanium perchlorate. The uncovered solution was allowed to stand for 2 days at room temperature, during which time deep purple crystals formed in the bottom of the flask. These were collected on a frit and washed with large portions of water and diethyl ether; yield 51%. *Anal.* Calcd for $C_{20}H_{19}ClO_6Ti$: C, 54.75; H, 4.36; Cl, 8.08. Found: C, 54.77; H, 4.29; Cl, 8.40.

1,3-Diphenyl-1,3-propanedionatobis(cyclopentadienyl)titanium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2Ti(dbzm)]ClO_4$.—Dibenzoylmethane (0.90 g, 0.004 mole) dissolved in 10 ml of THF was added to an aqueous solution of 0.002 mole of bis(cyclopentadienyl)titanium perchlorate. After standing for 24 hr, violet crystals and some yellow-orange powder formed at the bottom of the flask. Infrared examination of the orange product showed it to contain no cyclopentadienyl groups. The solid was collected on a frit and washed with water, ethanol, and ether which left only the violet crystals. Recrystallization from acetone gave 0.21 g of product; yield 21%. *Anal.* Calcd for $C_{25}H_{21}ClO_6Ti$: C, 59.96; H, 4.23; Cl, 7.08. Found: C, 60.34; H, 4.68; Cl, 6.65.

2,2,6,6-Tetramethyl-3,5-heptanedionatobis(cyclopentadienyl)titanium Perchlorate, $[(\pi\text{-}C_5H_5)_2Ti(dpm)]ClO_4$.—A solution of 1 g (0.0065 mole) of dipivaloylmethane in 20 ml of THF was added to 0.004 mole of bis(cyclopentadienyl)titanium perchlorate in 50 ml of water. The solution was allowed to stand uncovered for 5 days, at the end of which time a mixture of deep purple needles and orange crystals in approximately equal amounts was deposited on the bottom of the flask. The solid was collected on a frit and recrystallized twice from a mixture of THF and diethyl ether giving only the purple needles; yield 0.51 g (27%). *Anal.* Calcd for $C_{21}H_{29}ClO_6Ti$: C, 54.73; H, 6.34. Found: C, 54.46; H, 6.47.

2-Hydroxy-2,4,6-cycloheptatriene-1-onatobis(cyclopentadienyl)titanium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2Ti(trop)]ClO_4$.—Tropolone (0.61 g, 0.005 mole) dissolved in 10 ml of THF was added to an equivalent amount of bis(cyclopentadienyl)titanium perchlorate in 50 ml of water at 0°. The deep green crystals which formed immediately were filtered off and washed with large amounts of water and ether; yield 1.1 g (55%). *Anal.* Calcd for $C_{17}H_{15}ClO_6Ti$: C, 51.22; H, 3.79; Cl, 8.89. Found: C, 51.17; H, 4.24; Cl, 9.04.

Bis(cyclopentadienyl)titanium(IV) Perchlorate, $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$.—To a solution of 1.25 g (0.005 mole) of bis(cyclopentadienyl)titanium dichloride dissolved in 100 ml of anhydrous THF was added a slight excess of anhydrous silver perchlorate. The precipitated silver chloride was filtered off, and the filtrate was cooled to −80°. Orange crystals of bis(cyclopentadienyl)titanium perchlorate formed and were collected on a glass frit under a dry nitrogen atmosphere. Because of the explosive nature of the compound, it was not analyzed. The infrared spectrum showed that no solvent was contained in the product.

All of the compounds containing the perchlorate ion were very shock sensitive and detonated frequently during the preparation of mulls for the determination of the infrared spectra. Only very small quantities were handled.

Infrared and Pmr Spectra.—The infrared spectra were obtained with a Perkin-Elmer Model 521 grating spectrometer using split halocarbon–Nujol mulls and NaCl or CsI windows. Calibration of the instrument was effected with polystyrene film. The pmr spectra were obtained with a Varian A-60 spectrometer at 40°, and the chemical shifts are believed to be accurate to ±0.01 ppm.

Conductivity Data.—Conductance measurements were made on nitrobenzene solutions with a Leeds and Northrup AC Jones bridge. The cell constant was obtained by measuring the resistance of a 0.0200 *M* KCl solution.

Results

Infrared Spectra.—The infrared spectra of $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ and of $[(\pi\text{-}C_5D_5)_2Ti(acac)]ClO_4$ are illustrated in Figure 1, and the frequencies together with the assignments are listed in Table I. The spectra are consistent only with a chelated acetylacetonate ligand. The identification of vibrations arising from the chelate ligand and those from internal vibrations of the cyclopentadienyl groups was made by comparison of the chelate as the perchlorate and trifluoromethylsulfonate salts and the d_{10} perchlorate with $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5D_5)_2TiCl_2$. The assignments for the acetylacetonate are based on the normal coordinate analysis of metal acetylacetonates carried out by Nakamoto,[17] modified slightly as a result of more recent studies of the deuterated ligand.[18] The internal vibrations of the cyclopentadienyl groups were assigned on the basis of the compilations by Huggins and Kaesz[19] and Fritz[20] and the normal coordinate calculations of Majanc, Loksin, and Saltuper.[21]

Table II lists characteristic vibrational frequencies for several of the bis(cyclopentadienyl)titanium(IV) compounds together with the conductivity data.

Proton Magnetic Resonance Spectra.—Since the chelate complexes were salts, a solvent of relatively high dielectric constant was required in order to obtain adequate concentrations for the measurements of the spectra. Dimethylformamide was found to be suit-

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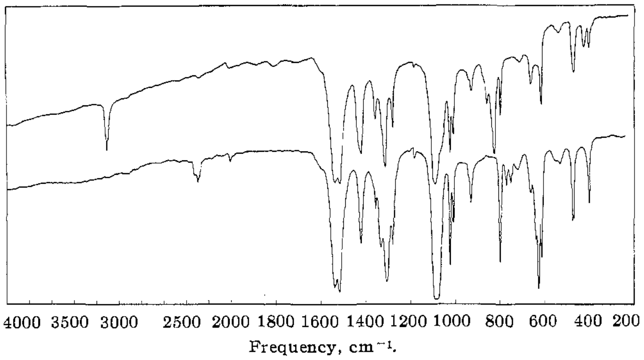

Figure 1.—Infrared spectrum of acetylacetonatobis(cyclopentadienyl)titanium(IV) perchlorate; the lower spectrum is that of the d_{10} compound.

TABLE I
INFRARED SPECTRA OF $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ AND $[(\pi\text{-}C_5D_5)_2Ti(acac)]ClO_4$[a]

ν, cm^{-1}		
$[(\pi\text{-}C_5H_5)_2Ti\text{-}(acac)]ClO_4$	$[(\pi\text{-}C_5D_5)_2Ti\text{-}(acac)]ClO_4$	Assignment
3114 m	2308 m	(π-Cp) C—H str
1543 vs	1544 vs	(acac) $C\overset{\cdots}{-}O$ str
1522 vs	1523 vs	(acac) $C\overset{\cdots}{-}C$ str
1437 sh	1340	(π-Cp) ring str
1427 s	1426 s	(acac) CH_3 deg def
1363 m	1363 m	(acac) $C\overset{\cdots}{-}O$ str
1321 s	1312 s	(π-Cp) ring str
1284 m	1289 m	(acac) $C\overset{\cdots}{-}C$ str + C—CH_3
1182 vw	1185 vw	(acac) in-plane bend
1096 vs, br	1090 vvs, br	(ClO_4^-) ν_3
1033 m	1032 s	(acac) CH_3
1017 m	1017 m	(acac) CH_3 rock
1017 m	776 m	(π-Cp) def
934 m	931 m	(acac) C—CH_3 str + $C\overset{\cdots}{-}O$ str
865 m	647 m	(π-Cp) C—H out-of-plane bend
834 s	635 s	(π-Cp) C—H out-of-plane bend
805 m	806 w	(acac) out-of-plane bend
670 m	671 m	(acac) ring def + Ti—O str
622 m	622 m	(ClO_4^-) ν_4
542	536	(acac) C—H out-of-plane bend
480 s	482 s	TiO_2 str
433 m	. . .	Ti–Cp_2 str
412 m	413 m	(acac) out-of-plane bend

[a] Cp = (C_5H_5); v, very; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

able, and a solution of $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ gave three sharp resonances at −2.27, −6.33, and −6.90 ppm relative to an internal TMS standard. The integrals of these three signals were in the approximate ratio 6:1:10, and they are assigned to the methyl protons of the acetylacetonate ligand, the γ proton on the acetylacetonate, and the cyclopentadienyl protons, respectively. Table III lists data for several of the perchlorate salts.

Discussion

Bis(cyclopentadienyl)titanium dichloride dissolves in water with aquation to give cationic species. It has been suggested that $(\pi\text{-}C_5H_5)_2TiOH^+$ predominates, since the hydroxo compound $(\pi\text{-}C_5H_5)_2Ti(OH)Br\cdot H_2O$ and the picrate $(\pi\text{-}C_5H_5)_2Ti(OH)C_6H_2N_3O_7$ can be precipitated from aqueous solutions.[22] It seems likely that polynuclear complexes also exist, at least in the solutions. Recent solution pH measurements indicate essentially complete hydrolysis in dilute aqueous solutions to $(\pi\text{-}C_5H_5)_2TiOH^+$ or some polymer thereof.[23] Several nonhydroxy salts such as the chromate also have been precipitated from aqueous solutions.[24]

All of the perchlorate chelates reported in this work were prepared easily by reaction 1. Even with very

$$(\pi\text{-}C_5H_5)_2TiOH^+(aq) + ClO_4^-(aq) + HL(aq) = [(\pi\text{-}C_5H_5)_2TiL]^+ClO_4^-(s) + H_2O(l) \quad (1)$$

high concentrations of the chelating ligand conjugate acid it was impossible to produce the bis chelate. The actual free ligand concentrations in these solutions were very low, since above about pH 2.8 the $(\pi\text{-}C_5H_5)_2Ti^{IV}$ group is decomposed with the breaking of the titanium–ring bonds. The mono chelates are only slightly soluble in water and virtually insoluble in most organic solvents. The dipivaloylmethane complex was synthesized in an effort to obtain a chelate which would be more soluble in organic solvents; however, its solubility was not significantly greater. With SO_4^{2-}, NO_3^-, or I^-, no precipitation occurred, but other large uninegative ions besides ClO_4^- such as BF_4^-, AsF_6^-, SbF_6^-, $F_3CSO_3^-$, and $B(C_6H_5)_4^-$ also gave insoluble compounds.

Both the infrared and pmr spectra indicate that the ligands are chelating, and the bis(cyclopentadienyl)-titanium(IV) moiety undoubtedly possesses a wedge-like sandwich structure with essentially tetrahedral coordination about the titanium atom similar to that found for the dichloride.[25] The vibrational frequencies assigned to the perchlorate ion in the various chelate salts are typical of the "free" anion, and no appreciable splitting of degenerate vibrations was observed. The spectra of $[(\pi\text{-}C_5H_5)_2Ti(acac)][F_3CSO_3^-]$ also showed the spectrum of the free trifluoromethylsulfonate anion.[26]

If a ligand like the acetylacetonate ion were bound by simple hard sphere coulombic interactions to a $(\pi\text{-}C_5H_5)_2Ti^{2+}$ ion, it seems likely that a bis complex with four oxygen atoms in the xy plane and parallel cyclopentadienyl rings (ω = 180°) could be synthesized. This structure would maximize the coordination number for the metal atom in an electrostatically favorable configuration and simultaneously maximize the total metal–cyclopentadienyl ring overlap.

There is a question of whether repulsions of the ligands by the cyclopentadienyl π electron clouds would lead to unfavorably long Ti–O bonds, *i.e.*, whether this structure is reasonable on steric grounds. For example, water molecules do not appear to interact strongly with ions like $(\pi\text{-}C_5H_5)_2Co^+$ in aqueous solution. Figure 2 illustrates a titanium atom buried in the π electrons of two parallel cyclopentadienyl rings. The distance between rings is calculated using the Ti–C and C–C distances reported for $(\pi\text{-}C_5H_5)_2TiCl_2$.[25] If

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Table II

Infrared and Conductance Data for Several Bis(cyclopentadienyl)titanium(IV) Compounds

	ν, cm^{-1}					
	Cyclopentadienyl ring		Perchlorate			
Compound	$\bar{\nu}$ C–H str	$\bar{\nu}$ C–H out-of-plane bend	$\bar{\nu}_3$	$\bar{\nu}_4$	Molar conductivity, cm^2 ohm^{-1} [a]	Concn, M
$[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$	3114 m	834 s	1096 vs	622 m	31.6 35.2	0.00130 0.00043
$[(\pi\text{-}C_5H_5)_2Ti(bzac)]ClO_4$	3111 w	840 s	1105 vs	628 s	30.0	0.00108
$[(\pi\text{-}C_5H_5)_2Ti(dbzm)]ClO_4$	3114 m	830 s	1098 vs	626 s	30.4	0.00133
$[(\pi\text{-}C_5H_5)_2Ti(dpm)]ClO_4$	3114 m	835 s	1095 vs	622 s	36.2	0.00024
$[(\pi\text{-}C_5H_5)_2Ti(trop)]ClO_4$	3101 m	835 s	1096 vs	623 s	32.6	0.00064
$[(\pi\text{-}C_5H_5)_2TiCl_2$	3114 m	819 s	...	...	...	
$(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$	3114 m	852 s	1130 vs, 1072 vs, 1009 vs, 920 w, 624 s, 460 w		...	

[a] Nitrobenzene solution at 25°; the values are typical of a 1:1 electrolyte.

Table III

Proton Chemical Shifts for Several Bis(cyclopentadienyl)titanium(IV) Compounds Dissolved in N,N-Dimethylformamide[a]

Compound	τ ring protons, ppm	τ other protons, ppm
$(\pi\text{-}C_5H_5)_2TiCl_2$	3.28	
$(\pi\text{-}C_5H_5)_2Ti(trop)ClO_4$	3.17	
$(\pi\text{-}C_5H_5)_2Ti(dpm)ClO_4$	3.11	—C(CH$_3$)$_3$, 8.70
$(\pi\text{-}C_5H_5)_2Ti(acac)ClO_4$	3.10	—CH=, 3.67; —CH$_3$, 7.73
$(\pi\text{-}C_5H_5)_2Ti(bzac)ClO_4$	3.03	—CH$_3$, 7.53
$(\pi\text{-}C_5H_5)_2Ti(dbzm)ClO_4$	2.95	

[a] Sample temperature *ca.* 40°; the solutions were saturated, *ca.* 0.1 M; τ_{TMS} = 10 ppm.

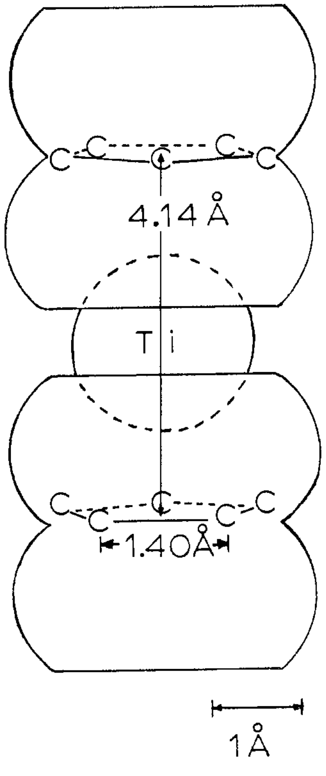

Figure 2.—Model of the bis(cyclopentadienyl)titanium(IV) moiety in a parallel ring configuration.

the ring–Ti–ring angle is decreased to 121.5°, this gives the bond distances for the bis(cyclopentadienyl)-titanium(IV) moiety in the dichloride. A value of 3.4 A, the usual value for aromatic systems, is taken for the π cloud thickness.[27] The univalent radius (0.96 A)[28] is used for the titanium atom, and this is somewhat smaller than the covalent radius of 1.24 A estimated from the 2.24 A[25] Ti–Cl distance reported for $(\pi\text{-}C_5H_5)_2TiCl_2$. Since the π clouds are used in the ring–metal bonds and would exert less of a steric effect on the equatorial ligands, there seems to be no reason *a priori* why this configuration should be unstable.

If, on the other hand, the titanium–oxygen bonds have appreciable covalent character, interaction with only one acetylacetonate ligand would be expected. Ballhausen and Dahl have discussed the bonding in wedge-like sandwich complexes in terms of molecular orbitals.[29] The titanium 3d, 4s, and 4p orbitals can be mixed to produce nine hybrid orbitals. Six of these are strongly directed toward the two cyclopentadienyl rings, and two are employed in σ bonding while four more are π bonding. The molecular orbitals which result from the interaction of these metal hybrids with the ring molecular orbitals contain the 12 bonding electrons characteristic of all covalent bis(cyclopentadienyl) complexes. Although the total ring orbital–metal orbital overlap is a maximum in the configuration with parallel rings, the total integral does not decrease rapidly as the angle ω decreases from 180°; see Figure 3.

In a covalent model, the one acetylacetonate ligand would be bound using the two strongly directed metal hybrids ψ_y and ψ_{-y} which are presumed to be used in $(\pi\text{-}C_5H_5)_2TiCl_2$. Coordination of four oxygen atoms in the xy plane by strong covalent bonds would lead to weakening of the metal–ring bonds and would be expected to be energetically unfavorable.

Efforts to produce "octahedral" coordination by reaction of a solution of $(\pi\text{-}C_5H_5)_2Ti^{2+}(aq)$ with high concentrations of fluoride ion produced only $(\pi\text{-}C_5H_5)_2TiF_2$ rather than salts containing $[(\pi\text{-}C_5H_5)_2TiF_4]^{2-}$. The same difluoride was the only product obtained when solutions of $(\pi\text{-}C_5H_5)_2TiCl_2$ in THF and other nonaqueous solvents were allowed to react with $AgBF_4$ or $NaBF_4$. Similar results were obtained with ions such as PF_6^-, SbF_6^-, and AsF_6^-. The anhydrous perchlorate was prepared, but its structure is not known. The

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(27) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 262.

(28) Reference 27, p 514.

(29) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

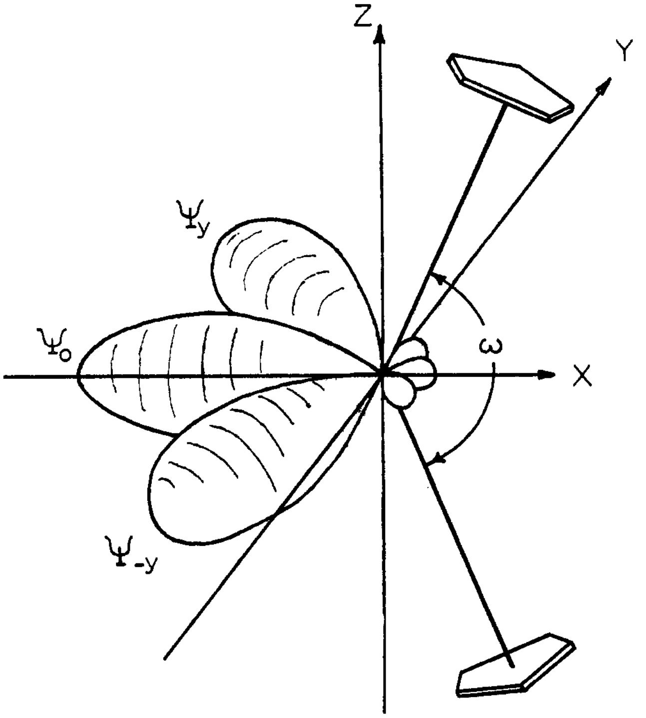

Figure 3.—Orbitals for bonding of ligands in wedge-like sandwich complexes.

degenerate perchlorate vibrations are split by the strong interaction with the bis(cyclopentadienyl)titanium(IV) moiety.

The pmr spectra of DMF solutions of $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ and $[(\pi\text{-}C_5H_5)_2Ti(dpm)]ClO_4$ are simple and easily interpreted. They showed no traces of free ligand indicating that the chelates do not dissociate upon dissolution in DMF. The γ proton resonance of the acetylacetonate complex occurs at a lower field than that reported for any other acetylacetonate. This value, $\tau = 3.67$ ppm, can be compared to the average value of several acetylacetonate complexes found by Smith and Thwaites of 4.66 ppm.[30] The most similar value is that of the tris(acetylacetonate)silicon(IV) ion, $\tau = 3.74$ ppm, found for a $CHCl_3$ solution of $[Si(acac)_3]Cl\cdot HCl$. Hester has suggested that this very low-field resonance results from a ring current effect arising from extensive π donation of the oxygen lone pairs into the vacant silicon 3d orbitals.[31] Since the two resonances observed at very low field occur with cationic acetylacetonates, it is probably true as suggested by Fackler[32] that this results, at least in part, from the net positive charge on the complex. The corresponding γ proton resonances of the dialkoxobis(acetylacetonato)titanium(IV) complexes $Ti(acac)_2X_2$ occur in the range $\tau = 4.417$ ($X = CF_3CH_2O\text{-}$) to 4.628 ($X = t\text{-}C_4H_9O\text{-}$).[33] When X is a halide, the resonance occurs at a considerably lower field; *e.g.*, in the sequence of compounds $Ti(acac)_2F_2$, $Ti(acac)_2Cl_2$, and $Ti(acac)_2Br_2$, the τ values are 4.11, 3.99, and 3.96 ppm, respectively.[34] The vibrational frequencies reported by Bradley and Holloway[33] for the coordinated acetylacetonate in $Ti(acac)_2Cl_2$, ν C$\overset{...}{—}$O, 1550; ν C$\overset{...}{—}$C, 1520; and ν Ti—O, 472 cm^{-1}, also are quite similar to the corresponding values assigned here for $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$, 1544, 1523, and 480 cm^{-1}.

The τ value of the methyl protons of the acetylacetonate group was 7.73 ppm, the same value reported for chloroform solutions of $[Si(acac)_3]Cl\cdot HCl$.[31] This is also lower than the values reported for any other acetylacetonate (Co(III) 7.87 to Th(IV) 8.10) and also can probably be attributed to the cationic charge on the complexes.

The ring proton resonances for the $(\pi\text{-}C_5H_5)_2Ti^{IV}$ chelates also occur at slightly lower field than reported for other bis(cyclopentadienyl)titanium(IV) compounds.[35] This resonance shifts downfield in the sequence acac, bzac, dbzm $\tau = 3.10$, 3.03, 2.95, respectively, and this is generally the order of increasing donor strength and thermodynamic stability with these ligands as indicated by stability constants determined for aqueous solutions. The same trend in the resonances of the methyl groups bound to tin in the compounds $(CH_3)_2SnL_2$ was observed where the resonances occur at τ values of 9.51, 9.25, and 9.07 ppm[36] with L = acac, bzac, and dbzm, respectively.

As shown by the data in Table II, the C–H stretching and out-of-plane bending vibrations are not at all sensitive to the other ligands coordinated to the titanium atom. These vibrations occur with the highest infrared intensities and give rise to the only bands which are easily assigned in the spectra of the coordination compounds.

All of the mono chelates were easily synthesized and, with the exception of the perchlorates which detonated easily, they were very stable. Giddings has suggested on the basis of the ease of preparation and stability of the bis(cyclopentadienyl)titanium(IV) mercaptides that the $(\pi\text{-}C_5H_5)_2Ti^{IV}$ moiety is a "soft" rather than a "hard" acid.[37] The results of this investigation do not support this, and apparently the $(\pi\text{-}C_5H_5)_2Ti^{IV}$ moiety forms a wide range of stable compounds with a variety of donor atoms.

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(30) J. A. S. Smith and J. D. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962).

(31) R. E. Hester, *Chem. Ind.* (London), 1397 (1963).

(32) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

(33) D. C. Bradley and C. E. Holloway, ref 7, p 483.

(34) R. C. Fay, personal communication; the values were recorded at 37° with TMS as an internal standard in CH_2Cl_2 solution.

(35) H. C. Beachell and S. A. Butter, *Inorg. Chem.*, **4**, 1133 (1965).

(36) These values are for *ca.* 0.2 *M* solutions in $CHCl_3$: Ph.D. thesis, Mary Mercy McGrady, University of Minnesota, 1965.

(37) S. A. Giddings, Abstracts of the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965, p 121.