

TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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Work published in this area has followed the same pattern as in previous years, the main emphasis being on π -cyclopentadienyl (Cp) derivatives, with some attention being paid to cycloarene compounds and dinitrogen complexes of lower valent metal derivatives. Two texts have been published; the book "Organometallic Chemistry of Titanium, Zirconium and Hafnium" (1) and "Organozirconium Compounds" and "Organohafnium Compounds" in Gmelin's Handbook (2).

CRYSTAL STRUCTURES

Crystal and molecular structures of $[(\text{PhCH}_2)_3\text{Ti}]_2\text{O}$ (3), (fluorenyl) $_2\text{ZrCl}_2$ (4), $[(\pi\text{-C}_5\text{H}_4)_2(\text{CH}_2)_3]\text{ZrCl}_2$ (5) [also Hf (76)], $\text{Cp}_2\text{Zr}(\text{Cl})(\text{CH}_2\text{CH}(\text{AlEt}_2))_2$ (6) and the racemic form of $\text{Cp}[\pi\text{-3-Me C}_5\text{H}_3\text{C}(\text{Me})\text{Ph}]\text{Ti}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})\text{Cl}$ (7) have been determined by X-ray diffraction. All show distorted tetrahedral stereochemistry around the metal. The fluorenylzirconium compound is unique in that one of the fluorenyl ligands is bonded to the metal through only three carbon atoms of the five-membered ring in a π -allylic fashion. The Zr-Al complex contains Zr-Cl-Al, Zr-C-C-Al and Al-C-Al bridge structures.

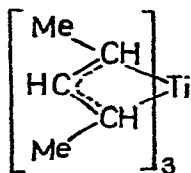
ALKYL- AND ARYLMETAL COMPOUNDS (see also Cyclopentadienyl)

Several simple alkyl derivatives of these metals have been prepared and isolated including methyltriisopropoxo-

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titanium, $\text{MeTi}(\text{OPr}^i)_3$. The increased molecular weight shown in benzene indicates some association. On exposure to nitrogen for some hours the colour changed to blue (8). Some corresponding aryl derivatives are described below.

The tris(π -allyl)titanium(III) derivative was



obtained (9) by the action of $\text{C}_5\text{H}_9\text{MgCl}$ on either TiCl_3 or TiCl_4 . Other alkyls isolated include the bis(trimethylsilyl)methyltitanium(III) derivative, $\text{Ti}[\text{CH}(\text{SiMe}_3)_2]_3$, and the zirconium and hafnium compounds, $\text{ClM}[\text{CH}(\text{SiMe}_3)_2]_3$, where $\text{M}=\text{Zr}$ or Hf (10). Tetrabenzylzirconium forms complexes with oxygen- and nitrogen-containing ligands of type $(\text{PhCH}_2)_4\text{Zr} \cdot 2\text{L}$, where $\text{L}=\text{3- or 4-cyanopyridine, pyrazidine or quinoline; } (\text{PhCH}_2)_4\text{Zr} \cdot \text{L}$, where $\text{L}=\text{2-cyanopyridine, 2,2'- or 4,4'-bipyridyl, 2-methylpyridine, pyrazine, p-phenylene diamine, THF; } 2(\text{PhCH}_2)_4\text{Zr} \cdot \text{L}$, where $\text{L}=\text{thioxan}$. The complexes showed enhanced thermal stabilities over $(\text{PhCH}_2)_4\text{Zr}$. In all of the $^1\text{H-NMR}$ spectra of the soluble complexes the resonance of the methylene protons of the benzyl ligands was shifted downfield (11).

In liquid SO_2 , tetrabenzylzirconium formed the tris(O-sulphinate), $\text{PhCH}_2\text{Zr}(\text{SO}_2\text{CH}_2\text{Ph})_3$. Insertion of phenylisocyanate, PhNCO , and methylisothiocyanate occurred also giving $\text{Zr}[\text{N}(\text{Ph})\text{C}(=\text{O})\text{CH}_2\text{Ph}]_4$ and $\text{Zr}[\text{N}(\text{Me})\text{C}(=\text{S})\text{CH}_2\text{Ph}]_4$ respectively. With nitric oxide a mixture resulted containing compounds substituted with two or three N-benzyl-N-nitrosohydroxylamino ligands, *ie.* $-\text{ON}(\text{CH}_2\text{Ph})\text{NO}$ (11).

Prolonged heating (24 h) of tetrabenzyltitanium in ether was found to give the oxygen-bridged species,

$[(\text{PhCH}_2)_3\text{Ti}]_2\text{O}$, by oxygen-abstraction from ether (12). The X-ray crystal structure determination of this orange moisture-sensitive compound was reported above (3).

Autoxidation of tetrabenzylzirconium as well as $(\text{Me}_3\text{SiCH}_2)_4\text{Ti}$ and $(\text{Me}_3\text{SiCH}_2)_4\text{Zr}$ appears to involve formation of peroxyalkyl derivatives, ROOM-, which then decompose to alkoxides (13). At 20° the half-life of peroxybenzylzirconium, the most stable of the species, was found to be 50 minutes.

The He(I) photoelectron spectra of the tetra-nor-pentyl and tetra(trimethylsilylmethyl) derivatives of titanium, zirconium and hafnium have been assigned in terms of a localized bond model assuming a tetrahedral MC_4 framework. The highest occupied molecular orbital, assigned to $\sigma\text{-M-C}$, was found to be in the range 8-9 eV (14).

Titanium hydrides and alkyls are undoubtedly present in certain reaction systems but have never been isolated. For example the system, $\text{TiCl}_4 + \text{Mg} + \text{THF}$ fixes H_2 and CO giving magnesium formate and the probable intermediate is a mixed metal hydride (15).

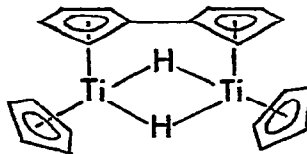
Methylene- and dimethylene-bridged titanium species have been predicted by Russian workers in the reaction between titanium tetrabutoxide and trimethylaluminium (16). Alkylation of but-3-en-1-ol to C_6 alcohols occurred in the presence of $\text{Et}_2\text{AlCl} + (\text{acac})_2\text{TiCl}_2$. The intermediate is believed to be an ethyltitanium species (17). In the formation of the efficient olefin polymerization catalyst from bis(π -allyl)nickel and TiCl_4 , the production of $(\pi\text{-C}_3\text{H}_5)\text{NiCl}\cdot\text{C}_3\text{H}_5\text{TiCl}_3$ was supported by infrared data (18). Tetramethyltitanium has been shown to remove the sulphur from phosphole sulphides giving the parent phospholes (19).

The pentafluorophenyl derivative, $\text{C}_6\text{F}_5\text{Ti}(\text{OPr}^i)_3$,

was obtained from C_8F_5Li and $ClTi(OPr^t)_3$ in the same paper reporting the corresponding methyl derivative above (8), and phenylzirconium trichloride has been isolated in complexed form. The tetrahydrofuran complex, $PhZrCl_3 \cdot 3THF$, reacted with a range of nitrogen-, phosphorus- and sulphur-containing ligands giving complexes of stoichiometry, $PhZrCl_3 \cdot THF \cdot L$, where $L = 2,2'$ -bipyridyl, $4,4'$ -bipyridyl, 2-methylpyridine or triphenylphosphine; and $PhZrCl_3 \cdot 2L'$, where $L' =$ pyridine, benzonitrile or 1,4-thioxan. Methyl cyanide formed $PhZrCl_3 \cdot 2CH_3CN$ which was converted by the appropriate ligand to $PhZrCl_3 \cdot L$, where $L = 2,2'$ -bipyridyl, $4,4'$ -bipyridyl or $Ph_2PCH_2CH_2PPh_2$ (20).

CYCLOPENTADIENYL DERIVATIVES

The ^{13}C -NMR spectrum of titanocene showed the pattern characteristic of a $\mu-(\eta^5:\eta^5\text{-fulvalene})$ ligand (21) in agreement with the structure



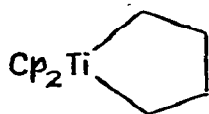
Alkylzirconium compounds formed by addition of $Cp_2Zr(H)Cl$ to 1- or 4-octene underwent rearrangement to the 1-octyl derivative, and that from isoprene rearranged to the 1-(3-methylbutyl) analogue. Acylation or halogenation of the alkyl ligand occurred on treatment with CH_3COCl or halogen respectively (22).

Insertion of carbon monoxide into these alkylzirconium compounds occurred readily; for example the hexyl

derivative formed $\text{Cp}_2\text{Zr}(\text{Cl})\text{CO}(\text{CH}_2)_5\text{CH}_3$, which gave n-heptaldehyde on hydrolysis. Oxidation gave heptanoic acid, while treatment with Br_2 or N-bromosuccinimide in methanol gave methyl heptanoate (23).

Carbon monoxide insertion occurred also with $\text{Cp}_2\text{Ti}(\text{X})\text{R}$, where $\text{R} = \text{Me}$ or CH_2Ph , $\text{X} = \text{Cl}$; $\text{R} = \text{Et}$, $\text{X} = \text{Cl}$ or I . The low CO stretching frequency in the infrared of the acyl derivatives may indicate metal-CO interaction (24).

From the reaction between Cp_2TiCl_2 and 1,4-dithiobutane the unstable metallocycle below was isolated by extraction and chromatography at -30° .

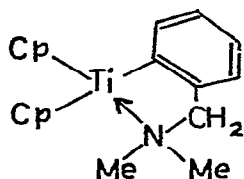


The bright orange solid was unstable above -30° , decomposing to but-1-ene. At -78° in pentane CO was absorbed giving an acyl derivative which gave cyclopentanone on warming. The properties of the metallocycle were contrasted with those of the bis(butyl) derivative and with those of the product of the reaction between ethylene and $\text{Cp}_2\text{TiN}_2\text{TiCp}_2$, which also gave cyclopentanone on carbonylation (25).

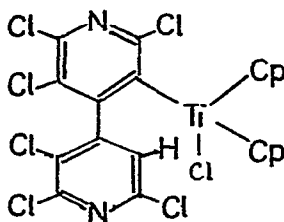
Disproportionation occurred when $(\text{Cp}_2\text{TiCl})_2$ was treated with $\text{Me}_3\text{SiCH}_2\text{Li}$ (or $-\text{MgCl}$) leading to $\text{Cp}_2\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$. Similarly $(\text{CpTiCl}_2)_n$ gave CpTiR_3 , when $\text{R} = \text{Me}$ or CH_2SiMe_3 . Unidentified divalent titanium species were formed in both cases (26). $(\text{CpTiCl}_2)_n$ formed phosphine complexes of type $\text{CpTiCl}_2 \cdot \text{L}_2$, where $\text{L} = \text{Me}_2\text{PPh}$, MePPh_2 ; $\text{L}_2 = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (26).

A series of thioanisoyl derivatives of various metals has been prepared including orange-yellow $\text{Cp}_2\text{Ti}(\text{CH}_2$

$\text{SPh})_2$, which was prepared from Cp_2TiCl_2 and LiCH_2SPh (27). The dimethylaminomethylphenyltitanium(III) derivative, $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)$ is distinguished from the corresponding vanadium compound by being internally co-ordinated and hence of greater thermal stability (28).



In an attempt to prepare a metallocyclic derivative, Cp_2TiCl_2 was treated with hexachloro-5,5'-dilithio-4,4'-bipyridine (29). Cyclization did not occur, probably for steric reasons, the product being the yellow compound,



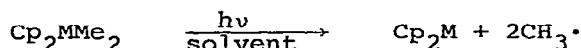
Full details of the preparation of $\text{Cp}_2\text{TiC}_6\text{F}_5$ and $\text{Cp}_2\text{TiCH}_2\text{SiMe}_3$ have been published (30), as well as that of $\text{CpTi}(\text{CH}_2\text{SiMe}_3)_3$.

Several papers describe reactions of titanium(IV) alkyls and aryls. Thermal decomposition at 120° - 136° of $\text{Cp}_2\text{-TiR}_2$, where $\text{R} = \text{CH}_2\text{Ph}$, Ph , 3- or 4- MeC_6H_4 or 3,4- $\text{Me}_2\text{C}_6\text{H}_3$, gave R-H quantitatively, the H originating from a Cp or R group, indicating more than one reaction pathway. The black solid residue did not retain the Cp_2Ti structure (31). Heating the bis(tolyl) derivative under 80-100 atm. of N_2 gave ammonia

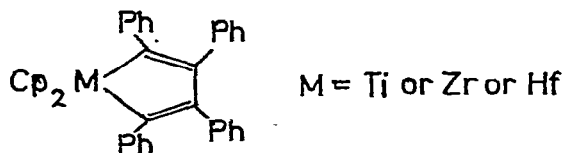
and toluidine isomers after hydrolysis. The mechanism of their formation via an intermediate benzyne complex was discussed (32).

A study of a range of titanium(III) aryls, Cp_2TiR , where $\text{R} = \text{Ph}$, C_6F_5 , 2- or 3- or 4- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ and also CH_2Ph , by differential thermal analysis showed that decomposition proceeded similarly to the bisaryltitanium(IV) compounds, R-H being formed as well as a diamagnetic residue containing Cp and C_5H_4 groups. The dinitrogen complexes of these aryls liberated N_2 before undergoing the same type of decomposition (33). An exception was the C_6F_5 derivative which gave $\text{Cp}_2\text{Ti}(\text{F})\text{C}_6\text{F}_5$ on heating to $130^\circ\text{-}160^\circ$.

The dimethyl derivatives, Cp_2MMe_2 , where $\text{M} = \text{Ti}$, Zr or Hf , decomposed readily on photolysis,



In pentane the methyl radicals appeared as CH_4 . All spectroscopic evidence indicated the presence of only π -bonded Cp rings in the diamagnetic pyrophoric residues. In the presence of diphenylacetylene, the metallocycles shown below were produced, while CO formed $\text{Cp}_2\text{Ti}(\text{CO})_2$ with the titanium residue (34).



Olefin polymerization catalyst systems have received some attention. By quenching with DCl , and the use of NMR and kinetic measurements, the presence of a range of Zr-Al complexes in the system, $\text{Cp}_2\text{ZrCl}_2 + \text{Et}_3\text{Al}$ has been demonstrated. The complexes are cyclic or linear with bridging alkyl groups

of various types formed by β -hydrogen transfer and cleavage of alkanes (35). The crystal structure of one of these products was mentioned above (6).



In connection with catalyst systems, decomposition of $\text{Cp}_2\text{Ti}(\text{Cl})\text{Et}$ was studied. In the presence of amines, the amine complex of Cp_2TiCl was formed together with ethyl radicals. The activation energy of the Ti-C bond breaking was 30.3 kcal/mole (36).

In an attempt to obtain model compounds for Ziegler-Natta catalysts, titanium-olefin interaction has been studied in the compounds, $\text{MeTiCl}_3(\text{OR})$, $\text{Cp}_2\text{Ti}(\text{Cl})\text{OR}$ and $\text{Cp}_2\text{Ti}(\text{Me})\text{OR}$, where $\text{OR} = \text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, but the olefin appeared to remain uncoordinated (37). The olefin polymerizing system, $\text{Cp}_2\text{Ti}(\text{R})\text{Cl} + \text{R}'\text{AlCl}_2$, where $\text{R}, \text{R}' = \text{Me}$ or Et , was studied spectroscopically and chromatographically in some detail with regard to rate of reduction of $\text{Ti}^{\text{IV}} \longrightarrow \text{Ti}^{\text{III}}$. The intermediate was postulated to be a titanium(IV) transient hydride (38).

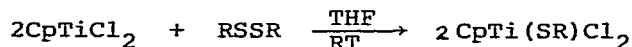
Oligomerization of butadiene occurred when atoms of titanium (produced by electrical discharge) were condensed in toluene (or benzene) in the presence of Et_2AlCl giving cyclo-dodecatriene isomers (39). The effect of phosphines on the catalyst system, $\text{Cp}_2\text{TiCl}_2 + \text{Et}_3\text{Al}$, was also studied. ESR indicated that the rate of conversion of the initially-formed complex, $\text{Cp}_2\text{TiCl}_2\text{AlEt}_2$, to a ternary complex containing titanium, aluminium and phosphine, and then into $\text{Cp}_2\text{TiCl}\cdot\text{PR}_3$, depended on the nature and amount of the added phosphine (40).

Full details of the preparation and properties of $(\text{C}_5\text{Me}_5)_2\text{TiH}_2$, $(\text{C}_5\text{Me}_5)_2\text{Ti}$ and $(\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{CH}_2)\text{TiH}$ have been published. Possible equilibria in the dinitrogen complexes, $[(\text{C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2$, $(\text{C}_5\text{Me}_5)_2\text{TiN}_2$ and $(\text{C}_5\text{Me}_5)_2\text{Ti}(\text{N}_2)_2$ were considered. At low temperature, ^1H , ^{13}C and ^{15}N -NMR spectra of $(\text{C}_5\text{Me}_5)_2\text{TiN}_2$ showed the presence of

was much slower producing a small yield of CpTiCl_2 after three weeks (46). Others have observed an increase in the lability of Cp groups on irradiation; in particular, exchange of Cp between Cp_2TiCl_2 and $(\pi\text{-C}_5\text{D}_5)_2\text{TiCl}_2$ in benzene and accelerated alcoholysis of Cp_2TiCl_2 to $\text{Cp}(\text{OR})\text{TiCl}_2$ (47).

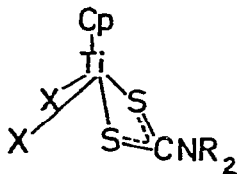
The ESR spectra of a series of binuclear titanium(III) carboxylates, $\text{CpTi}(\text{O}_2\text{CR})_2$, where R = Me, Et, Pr, Ph or CF_3 (48), and CF_3 , Ph, CCl_3 , 3- FC_6H_4 ,  or  have been measured (49). In toluene or in the solid state the spectra are characteristic of a triplet state ($S = 1$) with $g(\perp)$ close to 1.94 and $g(\parallel)$ around 2.00. The forbidden $\Delta M = 2$ resonance was observed at $g_{\text{av}} = 3.96$. The two titanium atoms in the dimeric molecule appear to be strongly coupled antiferromagnetically through a superexchange pathway.

The titanium(III) halide, CpTiCl_2 , splits the S-S bond of disulphides in an oxidative-addition reaction,



R = Me, Et or Ph

Similarly thiuram disulphides, $\text{R}_2\text{NC}(\text{S})\text{SSC}(\text{S})\text{NR}_2$, gave orange-red monomeric dithiocarbamates which are five-coordinate (50).

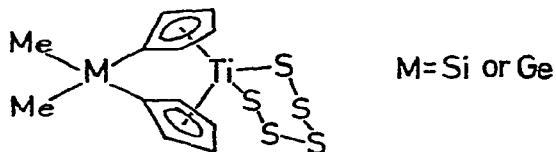


Oxidative-addition of disulphides occurred also with $\text{Cp}_2\text{Ti}(\text{CO})_2$ leading to the titanium(IV) bithiolates, $\text{Cp}_2\text{Ti}(\text{SR})_2$, with one mole of RSSR, where R = Me, Ph, 4- MeC_6H_4

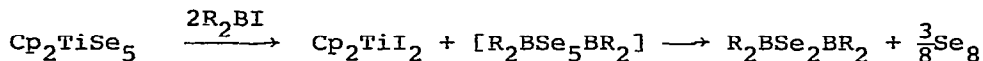
or CH_2Ph , or giving $(\text{Cp}_2\text{TiSR})_2$ with 0.5 mole of RSSR , where $\text{R} = \text{Et}$ or Ph . The latter compounds ($\text{R} = \text{Ph}$ or $4\text{-MeC}_6\text{H}_4$) were prepared also by equilibration of $\text{Cp}_2\text{Ti}(\text{SR})_2$ and $\text{Cp}_2\text{Ti}(\text{CO})_2$ in boiling toluene (51).

Treatment of Cp_2TiCl_2 with RSeMgBr in THF gave the green seleno derivatives, $\text{Cp}_2\text{Ti}(\text{SeR})_2$, where $\text{R} = \text{Me}$, CH_2Ph , Ph or $4\text{-CH}_3\text{C}_6\text{H}_4$ in good yield. Similarly the red-brown tellurium derivatives, $\text{Cp}_2\text{Ti}(\text{TeR})_2$, where $\text{R} = \text{Ph}$ or $4\text{-CH}_3\text{C}_6\text{H}_4$, were obtained. The analogous zirconium compounds with SePh , $\text{SeC}_6\text{H}_4\text{Me}$ or TePh were formed using RSeLi and RTeLi but not Grignard reagents. Infrared and NMR spectra were discussed (52).

Unusual polychalcogenides of titanium have been prepared from $(\text{C}_5\text{H}_5)_2\text{MMe}_2$, where $\text{M} = \text{Si}$ or Ge , in which the cyclopentadienyl rings are σ -bonded. Treatment with LiBu followed by TiCl_4 gave the intermediate titanium dichloride with π -bonded Cp ligands. Ammonium pentasulphide converted this into the cyclic pentasulphide,



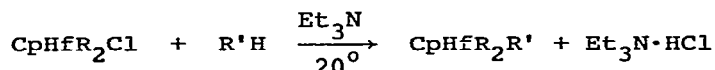
The conformation of the TiS_5 ring produced non-equivalence of the Cp rings which showed up in the $^1\text{H-NMR}$ spectra (53). Among the unusual reactions undergone by this type of polychalcogenide is the conversion of the pentaselenide to diboryldiselenanes (54)



Considerable effort continues to be applied by French workers to the preparation and study of optically active $\text{Cp}_2\text{Ti}^{\text{IV}}$ compounds. Those of type, $(\pi\text{-MeC}_5\text{H}_3\text{CHMe}_2)_2\text{TiCl}_2$, which

was prepared from 2,6,6-trimethylfulvene, showed two planes of chirality. Replacement of one of the chlorides by OR produced one derivative from one isomer and two stereoisomers from the other (55). Dynamic stereochemistry in the preparation of the similar complexes, $\text{Cp}(\text{Cp}')\text{Ti}(\text{OMe})\text{C}_5\text{F}_5$, where $\text{Cp}' = \pi\text{-C}_5\text{H}_4\text{CH}(\text{Me})\text{-Ph}$, has also been studied (56). Asymmetric decomposition in optically active mandelic acid produced complexes of type $\text{Cp}(\text{Cp}')\text{Ti}(\text{Cl})\text{OR}$, where $\text{Cp}' = \pi\text{-C}_5\text{H}_4\text{CHMe}_2$, $\pi\text{-C}_5\text{H}_4\text{CHPh}_2$, $\pi\text{-MeC}_5\text{H}_3\text{CHMe}_2$; $\text{R} = \text{aryl}$, which were chiral around the titanium atom (57,58).

β -Diketonates of hafnium, $\text{CpHfR}_2\text{R}'$, where $\text{R}, \text{R}' = \text{acetylacetonone, benzoylacetonone or dibenzoylmethane}$, were made by the reaction,



The complexes proved to be less stable than the corresponding zirconium compounds and the infrared spectra indicated that the ligands are bidentate (59). An NMR study of rearrangements in some cyclopentadienylzirconium β -diketonates, CpZrR_2Cl and CpZrR_3 , and in a new cationic species, $(\text{CpZrR}_2)^+$, has been reported. Several relationships between structure and lability are described which provide a basis for favouring twisting over bond rupture processes (60).

OTHER π -BONDED COMPOUNDS

Cycloheptatrienylcyclopentadienylzirconium has been prepared by treatment of CpZrCl_3 (or Cp_2ZrCl_2) with iso- $\text{C}_3\text{H}_7\text{-MgBr}$ and C_7H_8 in ether. Sublimation at $120^\circ/0.1 \text{ mm}$ gave violet crystals of $\text{CpZr}(\text{C}_7\text{H}_7)$ which was diamagnetic and whose $^1\text{H-NMR}$ spectrum showed two singlets in the ratio 7:5. Although thermally very stable the compound was more sensitive to air

and water than the corresponding titanium and vanadium compounds. The mass spectrum was discussed (61).

Metallation of $\text{CpTi}(\text{C}_7\text{H}_7)$ with butyllithium occurred more readily than with the corresponding vanadium compound and took place preferentially in the seven-membered ring. Qualitative molecular orbital considerations of the charge distribution in these compounds led to the conclusion that this was due to an enhanced negative charge on the C_7H_7 ring (62,63) which was estimated by X-ray photoelectron spectroscopy at 0.7-0.8 electron, whereas the Cp ring carries 0.3-0.4 electron. The two rings of $\text{CpV}(\text{C}_7\text{H}_7)$ carry about equal charge of 0.3-0.4 electron per ring (64).

The higher field resonance of the C_7 ring relative to that of the C_5 ring in the ^{13}C -NMR spectra of $\text{CpTi}(\text{C}_7\text{H}_7)$ and $\text{CpZr}(\text{C}_7\text{H}_7)$ was also taken as evidence for the greater negative charge on the larger ring (65). In the same paper the ^1H -NMR spectra indicated free rotation of both rings in these compounds but hindered rotation in the chromium and molybdenum derivatives.

He(I) photoelectron spectra of $\text{CpTi}(\text{C}_7\text{H}_7)$ and $\text{CpTi}(\text{COT})$ have been assigned using a simple molecular orbital model and the electronic structure discussed (66). The cyclo-octatetraene-titanium compounds, $(\text{h}^8\text{-C}_8\text{H}_8)(\text{h}^5\text{-R})\text{Ti}$, where $\text{R} = \text{C}_5\text{H}_4\text{Me}$, $\text{C}_5\text{H}_4\text{CMe}_3$, $\text{C}_5\text{H}_4\text{SiMe}$, indenyl or fluorenyl, have been synthesized by substitution of the chloride of $(\text{h}^8\text{-C}_8\text{H}_8)\text{TiCl}$. THF using the appropriate sodium or lithium derivative. Magnetic susceptibility measurements showed that all have one unpaired electron per titanium atom. They are sensitive to air and to moisture but thermally stable to 350° . Mass spectral evidence indicated that the strength of the $\text{Ti-h}^5\text{-R}$ bond decreased in the order $\text{C}_5\text{H}_5 > \text{indenyl} > \text{fluorenyl}$ (67).

The fundamental bands in the infrared spectrum of bis(cyclooctatetraene)titanium have been assigned using group theory. The structure of the molecule as well as the ionicity of the ring-metal bonds was considered (68).

In an NMR study of alkoxotitanium compounds the shifts in the resonances of the α - and β - protons of $\text{CpTi}(\text{OR})_3$, where $\text{R} = \text{CHMe}_2$, CMe_3 or CH_2CMe_3 , have been compared with those of $\text{XTi}(\text{OR})_3$, where $\text{X} = \text{Cl}$, OR or NET_2 . Overlap of ligand p orbital with titanium d orbital ($p_\pi-d_\pi$) was found to increase in the order $\text{Cl} < \text{OR} < \text{NR}_2 < \text{Cp}$ (69).

The ^{35}Cl , ^{81}Br and ^{127}I -NQR spectra of $\text{Cp}_n\text{TiX}_{4-n}$, where X is halogen, have been measured. The increase in the quadrupole coupling constant with increasing number of Cp rings in the molecule was related to the decreasing multiplicity of the titanium-halogen bond (70). The nature of the bonding of the carboxyl groups in acylates of type, $\text{Cp}_n\text{Ti}(\text{O}_2\text{CR})_{4-n}$, where $n = 1$ or 2 , has also been studied. The infrared spectra of a number of these compounds, together with some methyl and pentamethylcyclopentadienyl derivatives, were measured. The large separation of the symmetric and asymmetric COO frequencies ($200\text{-}390\text{ cm}^{-1}$) established the presence of monodentate carboxyl (71).

Oxidation of Cp_2TiBH_4 with oxygen and polarographic reduction of the titanium(IV) product have been investigated. It was suggested that both of these processes are reversible. Polarography of Cp_2TiCl_2 was also reported (72). A number of organometallic polymers containing cyclopentadienyltitanium, -zirconium or -hafnium alternating with nitrogen- or oxygen-bonded organic ligands have been prepared (73, 74 and refs. therein)

Activation of alkylmagnesium halides by Cp_2TiCl_2 produced useful stereospecific reducing agents similar in activity

to LiAlH_4 and which were useful for the reduction of alkoxy-chloro- and fluorosilanes (75).

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