TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1973

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Crystal Structures

Crystal and molecular structures of $CpTi(\pi\text{-}C_7H_7)$* (1), Cp_2TiBH_4 (2), $(Cp_2TiSiH_2)_2$ (3), $Cp_2TiCl_2ZnCl_2TiCp_2$ (4), $Cp[\pi\text{-}(CH_3)_5C_5]TiCl_2$ (5), $Cp_2TiS_2(CH)_2$ (6), $Cp_2Ti(O_2CC_6H_4NO_2\text{-}p)_2$ (7), $Cp_2Ti(h^2\text{-}C_5H_5)$ (8), $[\pi\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]_2TiCl_2$ (9), $[Cp(C_5H_4)TiHAl(C_2H_5)_2]_2$ (10) and $[(C_5H_4)_2TiHAl(C_2H_5)_2]_2$ (11) have been determined by X-ray diffraction, and that of $[(\pi\text{-}C_5H_4)_2(CH_2)_3]TiCl_2$ (12) by neutron diffraction. Details of these determinations will be found in the review "Organometallic Structures - Transition Metals" elsewhere in Annual Surveys. Three features of these structures are worthy of note; the distorted tetrahedral arrangement around the metal in the bis(cyclopentadienyl) derivatives, the novel dihapto cyclopentadienyl ligand of $Cp_2Ti(h^2\text{-}C_5H_5)$, and the participation of the cyclopentadienyl rings in bridging in the titanium-aluminium complexes (see later).

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* Cp = π-cyclopentadienyl

Alkyl-and arylmetal compounds

Enhanced stability of alkylmetal compounds has been achieved by complex formation or by use of elimination - stabilized ligands. Tetramethyltitanium forms coloured (yellow to red) complexes with LiR, where R=CH_3, $CH_2C_6H_5$ or Cl, which have been isolated as solvates of type $Li[Ti(CH_3)_4R]\cdot 4L$ with pyridine, THF or dioxane (13). Phenyltitanium derivatives are formed similarly. These ionic complexes decompose in the temperature range -20^o to $+10^o$.

Full details of the preparation and characterization of the tetraneopentyls, $[(CH_3)_3CCH_2]_4M$, of titanium, zirconium (14, 15) and hafnium (15) have been published. The order of thermal stabilities is Hf>Zr>Ti, neopentane being the sole detectable thermolysis product. Infrared and Raman bands have been assigned (15); the MC_4 stretching vibrations fall in the range 540 - 485 cm^{-1}, while bending modes occur at 240-283 cm^{-1} PMR and mass spectra are also discussed. In benzene solution tetraneopentyltitanium is oxidized by air to the alkoxide in good yield.

$$[(CH_3)_3CCH_2]_4Ti + 2O_2 \longrightarrow [(CH_3)_3CCH_2O]_4Ti$$

The preparation of the tetrasilylmethyl derivatives, $[(CH_3)_3SiCH_2]_4M$, of titanium, zirconium and hafnium has been described by Lappert et. al. (16). The metal tetrahalides were alkylated with the Grignard reagent, lithium alkyl or the dialkylmagnesium, the last being preferable since it minimizes reduction of the titanium in particular. The pale yellow liquid compounds are soluble in hydrocarbon solvents. The titanium derivative distils at 25-30°/10^{-3}mm and its higher stability in air has been attributed to steric effects. The PMR chemical shifts for the methyl groups are around δ0.3 while the MCH_2Si protons are found at δ0.57 (Hf), 1.18 (Zr) and 2.37 (Ti). The Ti-C stretching vibrations are at 470-500cm^{-1}.

Of greater stabilities are the cyclopentadienyl compounds, $Cp_2M[CH_2Si(CH_3)_3]_2$, which are described in the same paper (16). Although stable only briefly on exposure to air, these compounds were found to be indefinitely stable at 20° and to decompose to black solids above 100°. The thermal stabilities lie in the order Hf~Zr>Ti and parallel those of the aryls and benzyls. Also described are some analogous alkyls, $Ti[CH_2Si(CH_3)_2CH_2C_6H_5]_4$, $Ti[CH_2Si(CH_3)(C_6H_5)_2]_4$, $Zr[CH_2Si(CH_3)_2C_6H_5]_4$, $Ti[CH_2Si(CH_3)_2C_6H_5]_4$, $Cp_2Zr(Cl)CH_2Si(CH_3)_3$ and $Cp_2Ti[CH_2Ge(CH_3)_3]_2$. Stability trends in neopentyl, trimethyl silyl, benzyl and other derivatives have been discussed by Lappert et. al. (15).

Vinyltitanium trichloride, $CH_2{=}CHTiCl_3$, has been obtained as a purple solid from $TiCl_4$ and tetravinyllead at -78° (17). Although β-elimination of hydrogen was expected to be less facile in vinylmetal compounds than in simple alkyl derivatives, it was found that vinyltitanium trichloride decomposed above -30° to $TiCl_3$, ethylene, butadiene and some acetylene.

It is therefore less thermally stable than methyltitanium trichlori but like the latter compound its stability increases on adduct formation.

Several papers describe miscellaneous studies on known compounds. Thermal decomposition (and other reactions) of tetrabenzylzirconium gave evidence for the formation of dibenzylzirconium (18). By reaction of $(C_6H_5CH_2)_4Zr$ with stoichiometric amounts of iodine, benzylzirconium iodides were obtained as slightly soluble solids whose low thermal stability could be improved by complexation with bipyridyl,

$$(C_6H_5CH_2)_4Zr + (4-n)I_2 \longrightarrow (C_6H_5CH_2)_nZrI_{4-n} + (4-n)C_6H_5CH_2I.$$

The nature of the active site in the polymerization of butadiene by tribenzyltitanium iodide has been studied by Guzman *et. al.* (19) The iodide was shown to be a more efficient catalyst than tetrabenzyltitanium. The results indicated that there were two benzyl groups and one growing polymer chain at the titanium atom of the active center.

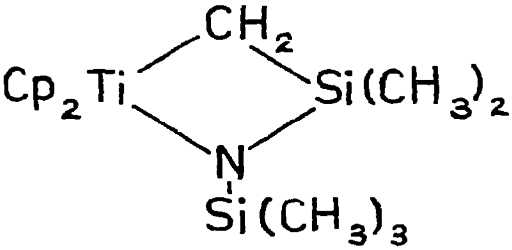
PMR exchange studies of 3,5-lutidine adducts of tetrabenzylhafnium and tetrabenzylzirconium have shown that dissociation of the mono-adduct, $(C_6H_5CH_2)_4Hf.Lut$, is the rate controlling step in the exchange. The similar activation energies in both systems (15.3 kcal mole^{-1} for Hf and 17.1 kcal mole^{-1} for Zr) suggest that the exchange mechanism is the same in both cases (20).

Thermal decomposition of methyltitanium trichloride in various solvents has been investigated (21). The mechanism is probably similar to that in other alkyltransition metal derivatives The fluxional behaviour of tetra(trihapto-allyl)zirconium has been reinvestigated (22). It was concluded that the interchange of syn and anti terminal hydrogens occurs at one end of the allyl group at a time rather than a simultaneous interchange at both ends.

Cyclopentadienylmetal(IV) derivatives

Several types of compounds have been made by simple ligand exchange of the halides of Cp_2MCl_2. Issleib and coworkers have prepared the crystalline derivatives, $Cp_2M[N(CN)_2]_2$, $Cp_2M[C(CN)_3]_2$ and $Cp_2M[ONC(CN)_2]_2$, where M=Ti or Zr, from the silver salt of the "pseudohalide" anion (23). The infrared spectra are discussed.

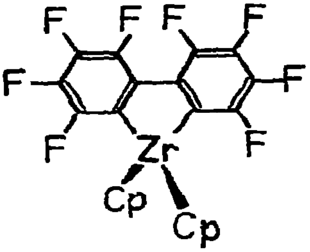
With lithium bis(trimethylsilyl)amide and Cp_2TiCl_2, Bennett and Bradley observed the formation of the four-membered heterocycle $\boxed{1}$, disilazane being a by-product (24).



$\boxed{1}$

Full details of the preparation of 1,1'-methylenebis(cyclopentadienyl)titanium dichloride from $TiCl_4$ and bis(cyclopentadienyl)methane have now been published (25) together with its use with lithium/naphthalene in fixing nitrogen and with $(C_2H_5)_2AlCl$ in ethylene polymerization.

In addition to the Ti-Si-N heterocycle described above, two other metallocyclic compounds have been made. Cp_2ZrCl_2 and 1,1'-dilithiooctafluorobiphenyl gave the zirconafluorene [2] in 4% yield (26), while dilithiobiphenyl and bis(indenyl)titanium dichloride afforded the titanafluorene [3] (27)



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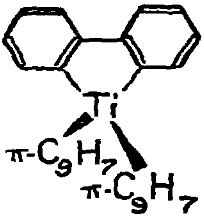


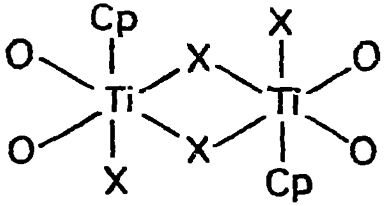
[3]

These compounds are hydrolytically more stable than the corresponding bis(σ-phenyl) derivatives.

Cyclopentadienyl derivatives of lower valent metals.

The synthesis and characterization of bis(cyclopentadienyl)titanium(III) fluoride completes the halide series, $(Cp_2TiX)_2$, where X=F, Cl, Br or I. (28). In this paper the methods of preparation of these compounds are reviewed and new methods are introduced. These are; reduction of the titanium(IV) dihalides with aluminium, and (for bromide and iodide) treatment of Cp_2TiCl with boron tribromide or triiodide. The infrared and visible spectra of this series are reported and assignments made. The metal-metal interaction in these dimers has been studied by measurement of the temperature dependence of the magnetic susceptibility (29). Characteristic singlet-triplet behaviour was observed with the strength of the Ti-Ti interaction increasing in the order $F < Cl \approx I < Br$.

Monocyclopentadienyltitanium(III) halides, $CpTiX_2$, where X=Cl or Br, form complexes with oxygen-containing ligands, $CpTiX_2 \cdot nL$. When L is dimethoxyethane, n=1, and when L is methanol or ethanol, n=2 (30). Magnetic and electronic spectral data were reported and interpreted on the basis of six-coordinate titanium atoms in a structure such as $\boxed{4}$



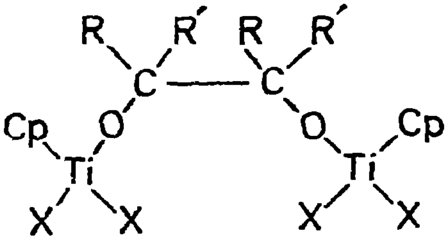
O = oxygen atom of chelating ligand

$\boxed{4}$

The green alcohol complexes were not stable and when left for one week at room temperature in the alcohol, or refluxed for one hour, alcoholysis of the Cp groups occurred giving polymeric titanium(III) alkoxides (31); e.g.

$$nCpTiCl_2 + 3nCH_3OH \longrightarrow [(CH_3O)TiCl_2 \cdot 2CH_3OH]_n + nC_5H_6$$

With ketones or aldehydes in THF/diethyl ether mixtures, $CpTiCl_2$ (or bromide) gave yellow crystalline compounds showing strong alkoxide bands in the infrared around 1000-1150 cm^{-1} and no C=O bands around 1700 cm^{-1}. The dimeric compounds were formulated as $\boxed{5}$



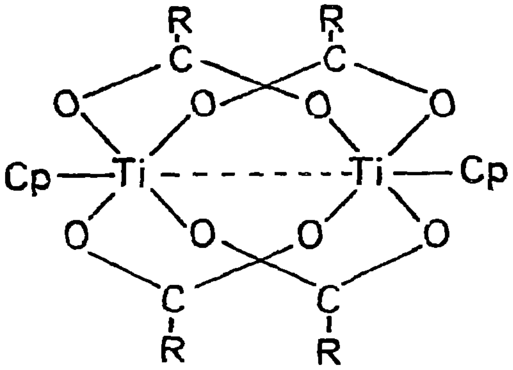
$\boxed{5}$

When R=R'=CH_3, pinacol was obtained on hydrolysis. The benzopheno complex, R=C_6H_5, R'=C_6H_5,reverted to free benzophenone and $CpTiX_2$ when dissolved in tetrahydrofuran, so in this case the coupling is reversible (32). In pure dry acetone, the halides $CpTiX_2$, where X=Cl, Br or I, dissolved to give brown solutions from which yellow crystalline polytitanoxanes, $(CpTiXO)_4$, precipitated over several days (33). Only the chloride has been reported previously.

Carboxylates of monocyclopentadienyltitanium(III) have been prepared from $CpTiCl_2$ and the sodium salt of the acid, or from the acid in the presence of an amine (34)

$$CpTiCl_2 + 2RCO_2H + 2\ amine \longrightarrow CpTi(O_2CR)_2 + 2\ amine{\cdot}HCl$$

The derivatives, R=CH_3, CF_3, C_2H_5, C_3H_7 and C_6H_5 were found to be green to brown dimers which in some case are volatile. They are virtually diamagnetic over the temperature range 100-300 K. The presence of pronounced magnetic exchange between pairs of titanium atoms was indicated by X-band ESR spectra in which $\Delta m=1$ and $\Delta m=2$ were clearly visible. The structure $\boxed{6}$ containing bridging carboxylate groups is analogous to that of the corresponding vanadium compound.



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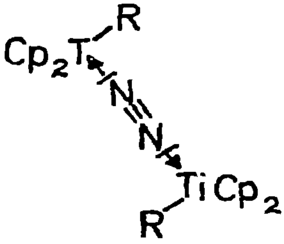
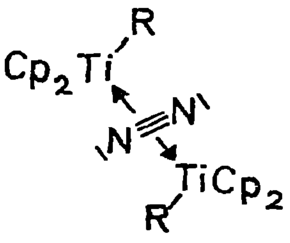
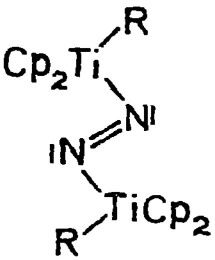
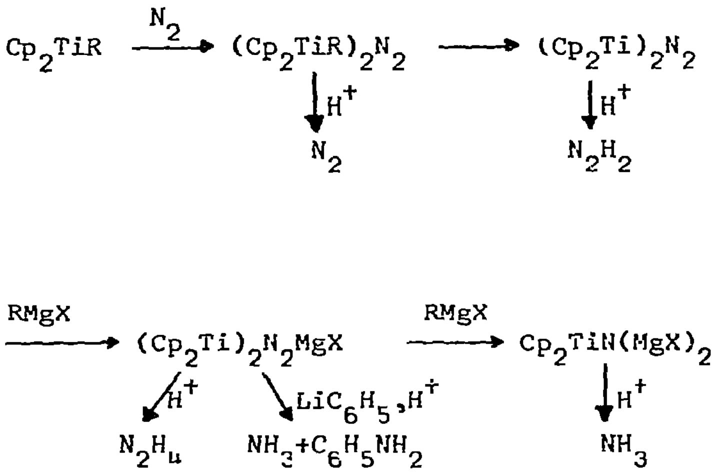
A series of bis(cyclopentadienyl)titanium(III) aryl and benzyl derivatives, Cp_2TiR, where $R=C_6H_5$, 2-, 3-, and 4-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, C_6F_5 and $CH_2C_6H_5$, was described by Teuben and de Liefde Meijer in 1972 (35). It has now been shown that all but the 2,6-$(CH_3)_2C_6H_3$ and 2,4,6-$(CH_3)_3C_6H_2$ derivatives absorb nitrogen at low temperatures (-80° to -100°) giving the binuclear complexes, $(Cp_2TiR)_2N_2$, which are deep blue in colour and absorb in the visible around 17 kK (36). The heats of formation of these complexes lie in the range -9 to -20 kcal mole^{-1}. The complexed nitrogen could be reduced by a strong reducing agent and recovered as hydrazine or ammonia after hydrolysis. Several centrosymmetric arrangements were suggested for the complexes





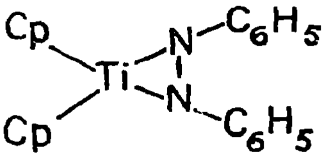


In connection with nitrogen fixation, the complexes $(Cp_2TiR)_2N_2$ and $(Cp_2Ti)_2N_2$ are now regarded by Shilov and co-workers as successive intermediates in the reduction of dinitrogen to nitride in the system, Cp_2TiCl_2+*iso*-$C_3H_7MgCl+N_2$. The paramagnetic complex $(Cp_2Ti)_2N_2MgCl$ has been isolated (37).



Chivers and Ibrahim have prepared the derivatives Cp_2TiR, where R=C_6F_5, $CH_2C(CH_3)_3$ and $CH_2Si(CH_3)_3$, and have observed the formation of a nitrogen complex of the pentafluorophenyl compound (38) (but not of the alkyls). All of the derivatives slowly formed blue colours in ethereal solvents, even in vacuo, an effect which was attributed to interaction with solvent or to isomerization (39).

Equilibration of the carbonyl, $Cp_2Ti(CO)_2$, with either Cp_2TiCl_2 or $TiCl_4$ has given the halides Cp_2TiCl or $CpTiCl_2$, carbon monoxide being evolved (40). In the presence of cyclohexylisocyanide the halides formed the monomeric complexes, $Cp_2TiCl \cdot C_6H_{11}NC$ and $CpTiCl_2 \cdot (C_6H_{11}NC)_2$. The titanium carbonyl also underwent an oxidative-addition reaction with azobenzene giving $\boxed{7}$ as maroon-black crystals (41).

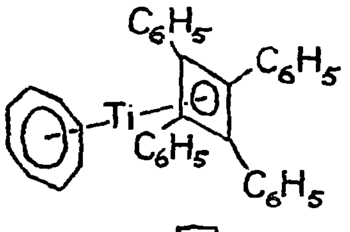


$\boxed{7}$

A series of methyl-substituted cyclopentadienylcycloheptatrienyltitanium compounds, $(\pi\text{-}C_5H_4R)Ti(\pi\text{-}C_7H_6R)$, has been prepared (42) following the procedure used for the parent compound (43); namely, by reaction of $(\pi\text{-}C_5H_4R)TiCl_3$ with *iso*-C_3H_7-MgBr in the presence of excess C_7H_7R. The compounds are thermally stable to over 300° and can be sublimed. The mass spectra indicate that the parent ions undergo an initial rearrangement to a bis(arene) species before degrading by loss of benzene or toluene; e.g.

$$\begin{array}{ccc} (\pi\text{-}CH_3C_5H_4)Ti(\pi\text{-}C_7H_7) & & (CH_3C_6H_5)Ti^+ \\ \text{or} & \longrightarrow (CH_3C_6H_5)Ti^+(C_6H_6) \longrightarrow & \text{and} \\ CpTi(\pi\text{-}CH_3C_7H_6) & & (C_6H_6)Ti^+ \end{array}$$

A similar procedure ($TiCl_3$+*iso*-$C_3H_7MgBr+C_8H_8+C_6H_5C\equiv CC_6H_5$) gave the green, thermally stable cyclooctatetraenetetraphenylcyclobutadiene complex 8 . From PMR, infrared and mass spectral evid it was deduced that both ligands are π-bonded (44).



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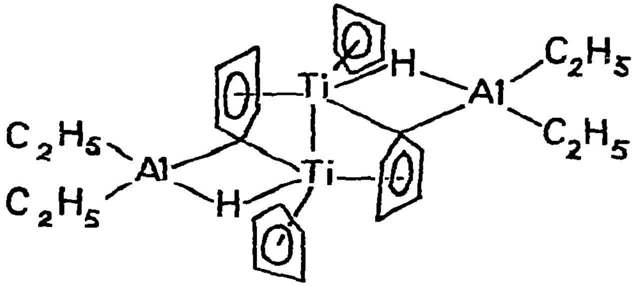
The complexities of the reactions between triethylalumini and cyclopentadienyltitanium compounds have been investigated furt by Tebbe and Guggenberger. From Cp_2TiCl_2, Cp_2TiCl or $Cp_2Ti(C_6H_5)$ and $(C_2H_5)_3Al$ at 70° for 12h, a red-purple complex was obtained (1 which is probably the same as that isolated by Natta and co-workers in 1959 (45). PMR, molecular weight and analytical data defined t composition as $Cp(C_5H_4)TiHAl(C_2H_5)_2$, the hydrido and C_5H_4 ligands bridging between titanium and aluminium atoms. The structure 9 was confirmed by an X-ray crystal study (10).



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A second complex, obtained originally by Wailes and Weigold (46) from "titanocene", $[Cp(C_5H_4)TiH]_2$, and $(C_2H_5)_3Al$, has now been shown by Guggenberger and Tebbe (11) to contain a fulvalenide ligand, $(C_5H_4-C_5H_4)^{2-}$, formed by loss of a proton from each Cp of the first complex followed by joining of the rings giving $[(C_5H_4)_2TiHAl(C_2H_5)_2]_2$ (see Crystal structures). An intermediate in this reaction is the complex, $(CpTi)_2H[H_2Al(C_2H_5)_2](C_5H_4{\cdot}C_5H_4)$.

An authentic sample of bis(benzene)titanium has now been isolated (47) by electron beam evaporation of titanium metal followed by co-condensation with benzene at 77K. The volatile, orange-red compound was extremely air-sensitive, moderately soluble in light petroleum and acetone but more soluble in benzene. The PMR spectrum showed a single band [+2.29 relative to $(CH_3)_2CO$ in $(CD_3)_2CO$, and -2.23 relative to C_6H_6 in C_6D_6]. Prominent bands were found in the infrared spectrum at 411, 452, 946 and 979 cm^{-1}.

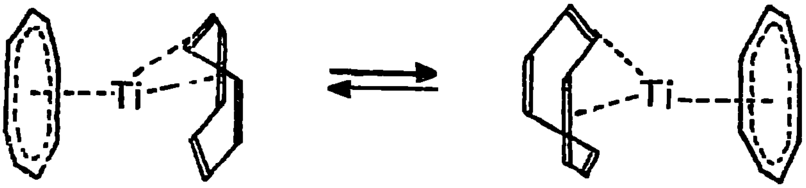
Cyclooctatetraene compounds.

Bis(cyclooctatetraene)zirconium has been prepared by reaction of the metal alkoxide with triethylaluminium in the presence of cyclooctatetraene (COT), and also from tetra-allylzirconium + COT (98% yield) (48). Although nearly insoluble, $(COT)_2Zr$ dissolved in toluene containing $HAl(C_2H_5)_2$ giving the mono- or bis-adduct. Other mono-adducts of hexamethylphosphoramide and tetrahydrofuran were isolated.

With gaseous HCl, $(COT)_2Zr$ formed $(COT)ZrCl_2$ which reacted with organomagnesium halides to give $(COT)ZrR_2$, where $R=CH_3$, C_2H_5, allyl and crotyl, while sodium cyclopentadienide gave (COT)CpZrCl. Since the alkyl derivatives have moderate thermal stability it was suggested that the β-elimination decomposition route may be impeded in the case of the ethyl compound by lack of a suitable coordinatio site on the metal. The allyl groups all exhibited dynamic behaviou in their PMR spectra. The stereospecific dimerization of butadiene at 65° by (COT)$Zr(C_3H_5)_2$ was also studied (48).

A dark green hydride, (COT)ZrH_2, was obtained by reaction of $Zr(OC_4H_9)_4$ with cyclooctatetraene and $HAl(C_2H_5)_2$ at 60°. The Zr vibrations were found at 1537 and 1310 cm^{-1} in the infrared (48), values very similar to those found for Cp_2ZrH_2 (49).

Schwartz and Sadler have shown by variable temperature PMR studies that the two (COT) rings of $(COT)_2Ti$ are fluxional, bending and flattening in turn, and have suggested (50) that this process involves an intramolecular redox reaction with an activatio energy of 16.7 ± 0.2 kcal $mole^{-1}$ at 63°.

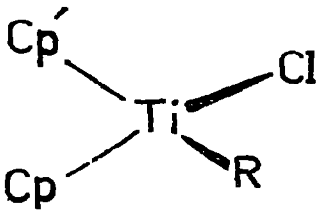


Miscellaneous Studies

By reaction of mono- and bis-lithioferrocene with dialkylamidotitanium bromide, ferrocene derivatives substituted in one or both rings with tris(dialkylamido)titano groups have been isolated (51). PMR, ^{13}C NMR and infrared spectra established that the C_5H_4 groups are π-bonded to iron and σ-bonded to titanium.

The full paper on PMR trends in the compounds Cp_2MR_2, where M=Ti, Zr or Hf and R=CH_3, C_6H_5 or C_6F_5, has now been published (27). Some bis(indenyl)metal(IV) methyl and phenyl derivatives were included.

Two research groups have been investigating diastereoisomerism in cyclopentadienyltitanium compounds. Brunner and Schindler (63) have prepared chiral molecules of type $\boxed{10}$ and $\boxed{11}$, while Le Moigne *et. al.* (64) have made similar compounds and have extended the range to include disubstituted derivatives of type $\boxed{12}$.



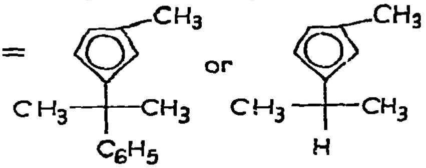
$\boxed{10}$ Cp'= π-indenyl, R=$SCH(CH_3)_2$

$\boxed{11}$ Cp'= π-$C_5H_4CH_3$, R=mentholato

Cp'= π-$C_5H_4CH(CH_3)C_6H_5$, R=$OC_6H_4CH_3$-*p*

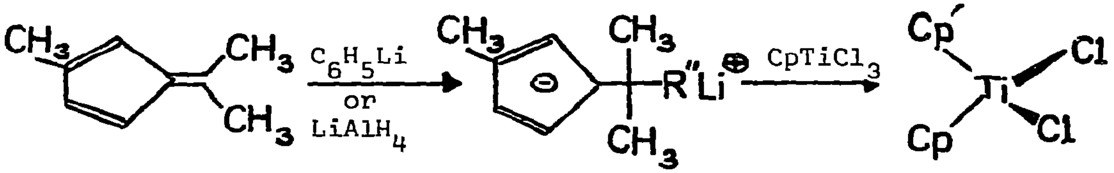
Cp'= π-$C_5H_4CH(CH_3)_2$, R=Cl

$\boxed{12}$ Cp'=



R = $OC_6H_3(CH_3)_2$-2,6

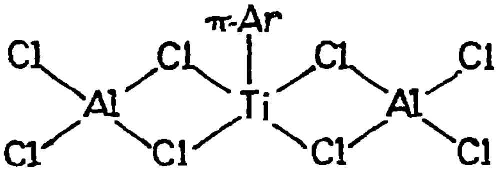
The disubstituted cyclopentadienyl derivatives were prepared from fulvenes



R'' = H or C_6H_5

The isomerism in these compounds has been studied by PMR spectroscopy and assignments made (64).

The methyl-substituted benzene complexes of titanium(II)-aluminium compounds $\boxed{13}$, analogues to the unsubstituted derivative obtained earlier by Natta et. al. (65) and by Vohwinkel (66,67), have been obtained by reduction of $TiCl_4$ with aluminium in the presence of $AlCl_3$ and the arene (68)



13

Ar = tetra, penta- or hexamethylbenzene

All are purple solids, highly sensitive to air and to moisture.

Several papers describe physical measurements carried out on known cyclopentadienyl compounds. The mass spectra of Cp_2TiX_2, where X=F, Cl, Br or I, and of $CpTiX_3$, $(\pi\text{-}CH_3C_5H_4)TiX_3$ and $[\pi\text{-}(CH_3)_5C_5]TiX_3$, where X=Cl, Br or OC_2H_5, show that the molecular ions decompose by two routes leading to elimination of X and of the cyclopentadienyl ligand (52). Elimination of X from $CpTiX_3$ is facile, but loss of the two remaining X's and of the Cp is difficult. The spectra of $[\pi\text{-}(CH_3)_5C_5]TiX_3$ showed an intense peak, $(M\text{-}HX)^+$, due to loss of a proton from one CH_3 group leading to a fulvene-type structure.

PMR spectra of a number of compounds of type Cp_2TiRCl and Cp_2TiR_2, where $R=C_6H_5$ or $CH_2C_6H_5$, and also of $CpTi(CH_2C_6H_5)_3$, have been measured in different solvents (53). The results of Beachell and Butter are critically discussed.

Low frequency infrared and Raman spectra of Cp_2MX_2, where M=Ti, Zr or Hf and X=F, Cl, Br, I or CH_3, and of $CpTiX_3$, have been measured and assignments made for metal-ring and metal-ligand stretching modes (54).

^{13}C NMR spectra of $CpZr(acac)_2Cl$, $CpTi(OC_2H_5)_3$, $CpTiCl_3$, Cp_2ZrCl_2 and Cp_2HfCl_2 have been recorded and the factors influencing the shielding of the ligand nuclei discussed (55).

The transmission of electronic effects through the ligands of certain bis(cyclopentadienyl) and bis(substituted-cyclopentadienyl)titanium difluorides as well as mono(cyclopentadienyl)titanium alkoxide chlorides has been studied by means of ^{1}H, ^{13}C and (where appropriate) ^{19}F NMR spectroscopy (56).

An authoritative article by Ballard describes the use in the polymerization of vinyl monomers and olefins of π- and σ-bonded compounds of titanium and zirconium (57). Emphasis is placed on allyl and benzyl derivatives of these metals and the active catalysts obtained by treatment of the benzyl derivatives with silanols.

To investigate the role of aluminium compounds in Ziegler-type catalysis, the activation (and cleavage) of the carbon-titanium bond in CH_3TiCl_3 on interaction with organoaluminium compounds has been studied by Yamamoto by volumetric and spectroscopic methods (58). The reaction was first order with respect to the concentration of CH_3TiCl_3.

A combination of tetrabenzylzirconium or tetraallylzirconium with alkylchloroaluminium forms an active catalyst which has been shown to produce linear α-olefins in the C_4 - C_{20} range (59) (see also 4th page of this survey).

In the formation of active homogeneous hydrogenation catalysts from Cp_2TiCl_2 and a reducing agent, dimerization and consequent loss of vacant coordination sites can be avoided by attaching the Cp_2TiCl_2 to a cross-linked polymer before reduction with butyllithium or sodium/naphthalene (60). Titanium alkoxide and thioalkoxide polymers have been made from Cp_2TiCl_2 and diols (61) or dithiols (62).

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