

TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1972

F. CALDERAZZO

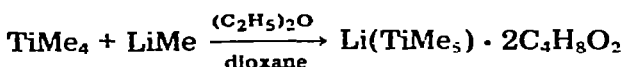
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Two articles dealing with alkyl and aryl derivatives of titanium, zirconium and hafnium, taken from main lectures by Thiele [1] and Rausch [2] have appeared.

I. Titanium(IV) derivatives containing four one-electron donors*

Elimination-stabilised alkyls of titanium(IV) and zirconium(IV) have been reported by Mowat and Wilkinson [3]. The organic radical is neo-pentyl and the compounds were $(\text{Me}_3\text{CCH}_2)_4\text{M}$ ($\text{M} = \text{Ti}$ and Zr) obtained by treatment of the corresponding tetrahalides with the lithium or Grignard reagents obtained from $\text{Me}_3\text{CCH}_2\text{Cl}$. The titanium and zirconium compounds, $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$ and $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$, were reported to be yellow and off-white, melting at 99 and 103°C, respectively.

Treatment of an ethereal solution of TiMe_4 with LiMe results in the formation [4] of an adduct, which upon addition of dioxane, precipitates out as a yellow solid:



The product behaves as a 1/1 electrolyte in tetrahydrofuran and is thermally unstable (dec. about 0°C). Similar compounds were obtained with phenyllithium and with benzyllithium and also by treating TiPh_2Me_2 with phenyllithium.

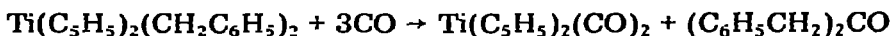
Alkyl group exchange was observed [5] between $\text{Al}_2(\text{CH}_3)_6$ and $\text{Ti}(\text{CD}_3)_4$ as evidenced by ^2H NMR spectra at variable temperatures from -75°C to room temperature. The appearance of the Al-CD_3 signal at 10.8 ppm from internal C_6D_6 was followed. Additional evidence of methyl group exchange was gathered by the observation of CD_4 , CD_3H and CDH_3 formed by thermal decomposition of the titanium complex resulting from the exchange.

It has been pointed out [5a] that the compound previously reported [5b] as $\text{Ti}(\text{SiPh}_3)_4$ might in fact be $\text{Ti}(\text{OSiPh}_3)_4$.

* A one-electron donor is a σ -bonded alkyl, aryl or cyclopentadienyl group. Hydrido species and compounds containing metal-silicon bonds are included.

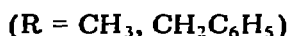
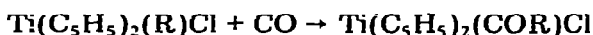
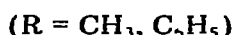
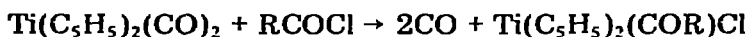
II. Titanium(IV) derivatives containing two one-electron donors

Carbonylation of dicyclopentadienyldibenzyltitanium(IV), $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)_2$, results in reductive elimination of the benzyl radicals and formation of the ketone [6]:



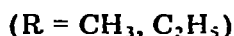
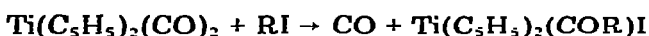
The reaction was suggested to take place via pre-coordination of CO to $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)_2$, followed by formation of an intermediate acyl derivative, unstable under the reaction conditions. The acyl intermediate would then undergo ketone elimination and addition of CO to give the final dicyclopentadienyldicarbonyltitanium(II).

The postulated formation of the acyl intermediate in the reaction of CO with $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)_2$ has obtained support from the isolation of some acyl derivatives of dicyclopentadienyltitanium(IV) [7, 8]. These compounds were isolated by one of the following methods:



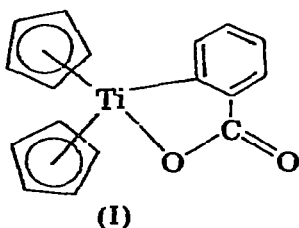
In the case of the methyl derivative, the latter reaction is completely shifted to the right hand side [8], thus showing that the acyl is more stable relative to the alkyl. In the case of the benzyl derivative an equilibrium situation is set up at room temperature.

A further possibility [7] of obtaining the acyl compounds is the reaction of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ with alkyl iodides:

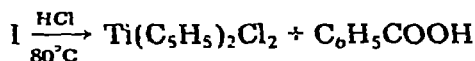


These compounds are characterized by low values of the acyl stretching vibration in the $1600\text{-}1620\text{ cm}^{-1}$ range. This is rather surprising in view of the high oxidation state of the central metal atom. An interaction between lone pairs of the acyl oxygen and empty *d* orbitals of titanium may be suggested.

The insertion reactions of CO_2 into Ti—C bonds of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Me}_2$ and $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Ph}_2$ have been reported [9]. The dimethyl derivative reacts with CO_2 in toluene at 80°C giving the bis-acetato complex $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{OOCCH}_3)_2$. As it had



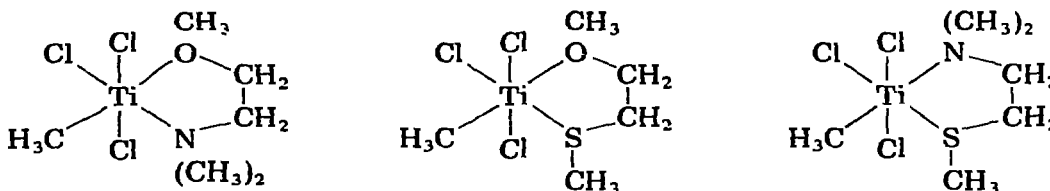
been reported already earlier [10], the diphenyl compound reacts with CO_2 giving the carboxylato complex (I). This is a rather stable compound, either toward air oxidation or chemically. The reactions with HCl and CH_3I take place only under rather drastic conditions:



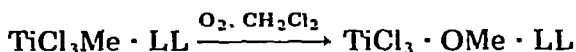
It is interesting to note that $\text{Ti}(\text{C}_6\text{H}_5)_2\text{Ph}_2$ can react with a second molecule of CO_2 giving a phthalato complex in small yields.

III. Titanium(IV) derivatives containing one one-electron donor

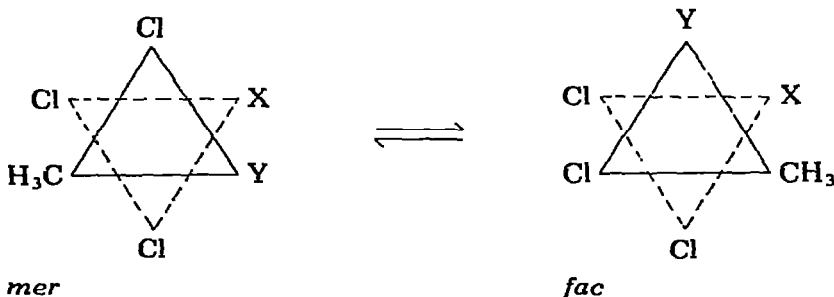
Methyltrichlorotitanium(IV) reacts with some asymmetrical bidentate ligands to give hexacoordinate complexes [11]. The following complexes were isolated: $\text{TiCl}_3\text{Me} \cdot \text{MeO}(\text{CH}_2)_2\text{NMe}_2$, $\text{TiCl}_3\text{Me} \cdot \text{MeO}(\text{CH}_2)_2\text{SMe}$ and $\text{TiCl}_3\text{Me} \cdot \text{Me}_2\text{N}(\text{CH}_2)_2\text{SMe}$. ^1H NMR spectra suggest that the complexes, which are thermally unstable and decompose slowly, at low temperature have the *mer* configurations:



The methyltrichloro complexes of titanium(IV) are oxidised [12] by oxygen in methylene chloride to give the corresponding methoxy derivatives:

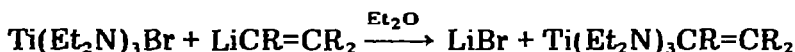


where LL is an asymmetrical bidentate ligand with nitrogen, sulphur and oxygen donor atoms. ^1H NMR spectra at variable temperatures suggest that the complexes undergo *mer* \rightleftharpoons *fac* rearrangement. It has been suggested that the *fac* isomer is obtained from the *mer* isomer by turning one of the trigonal faces of the



pseudo-octahedron by an angle of 120° with respect to the opposite face (twisting mechanism). This mechanism, of course, does not require bond breaking.

Vinyldialkylamide derivatives of titanium(IV) were obtained by the following reactions [13]:

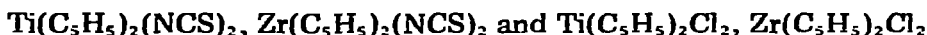


The compounds are liquids at room temperature, and can be purified by distillation under reduced pressure.

IV. Titanium(IV) derivatives containing cyclopentadienyl groups and nitrogen, oxygen, sulfur and halogen donors

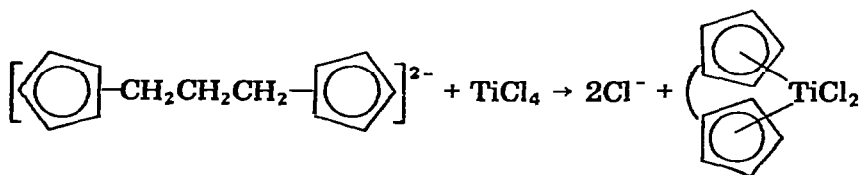
A theoretical approach to the interpretation of electronic spectra of dicyclopentadienyltitanium(IV) derivatives has been presented [13a].

Dipole moments measurements have been carried out [14] on NCS, NCO, and halogeno complexes of dicyclopentadienyltitanium(IV). The results obtained for the following two titanium—zirconium couples:



suggests a similar type of bonding for the NCS complexes of titanium and zirconium. The infrared spectra suggest that the complexes are nitrogen-bonded in both cases. On the other hand, in the case of the NCO ligand, it appears that the titanium complex is nitrogen-bonded, $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{NCO})_2$, whereas the zirconium derivative is oxygen-bonded, i.e. $\text{Zr}(\text{C}_5\text{H}_5)_2(\text{OCN})_2$. The latter result applies also to the corresponding hafnium compound.

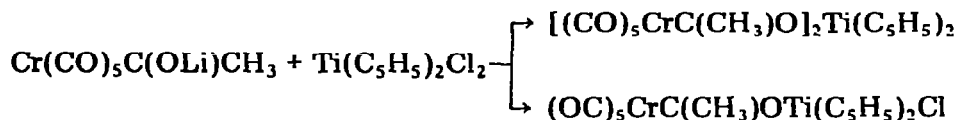
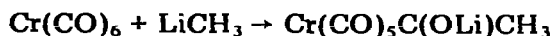
The preparation and properties of a dicyclopentadienyldichloro derivative of titanium(IV) in which two C_5H_4 rings are joined together by a $(\text{CH}_2)_3$ bridge have been reported [15]. The X-ray structure [16] had shown that the ring—ring angle of the bent dicyclopentadienyl system is 47.4° . The preparation consists of treating the trimethylene-bridged dianion with TiCl_4 :



The ^1H NMR spectrum shows two resonances for the ring protons. This has been explained in terms of non-equivalence due to tilting of the rings, the spinning of which is hindered by the trimethylene bridge.

Equimolar quantities of (acetylithium)pentacarbonylchromium(0) and

$\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ react [17] giving two products:



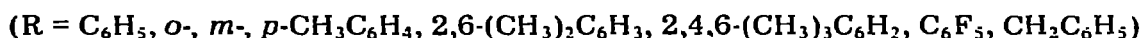
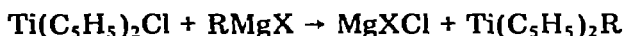
The complexes are better described as carbene complexes of chromium(0) oxygen bonded to titanium(IV), in agreement with the observed diamagnetism. On the basis of the measured chemical shifts for the ring protons, it was concluded that the chromium-containing substituents have an electronegativity similar to chlorine.

The proton resonance spectra of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ and $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{N}_3)_2$ in the presence of a β -diketonato complex of europium(III) have been reported [18]. Downfield shifts of 0.10 and 0.47 ppm, respectively, were observed in the presence of the paramagnetic lanthanide complex at given concentrations.

Chemical ionization mass spectrometric data were reported [19] for $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ and the corresponding zirconium and hafnium complexes. The measurements were carried out with methane as reagent gas affording CH_5^+ and C_2H_5^+ . These ions do not act as proton donors for the cyclopentadienyl complexes since no $M + 1^+$ peaks (M is the parent molecule) were observed in the mass spectrum. On the contrary the most abundant fragment is $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}^+$ arising from protonation at the titanium-chlorine bond and elimination of HCl.

V. Titanium(III) derivatives containing one-electron donors

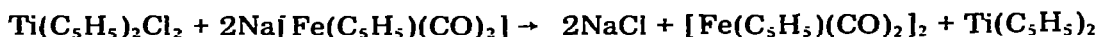
The synthesis of dicyclopentadienyl derivatives of titanium(III) of formula $\text{Ti}(\text{C}_5\text{H}_5)_2\text{R}$ has been reported [20]. The compounds were obtained by treating dicyclopentadienylchlorotitanium(III) with the proper Grignard reagent:



The solvent used was diethyl ether containing dioxane in equimolar quantities with respect to the starting titanium complex. The aryl derivatives obtained by the above reaction were isolated and most of them analysed correctly. They are very sensitive to air, monomeric in benzene and have magnetic moments close to the spin-only value for one unpaired electron. These data suggest that the complexes are monomeric both in the solid state and in solution. The existence of a dimeric phenyl derivative mentioned [21] earlier could not be confirmed. By application of this reaction to alkyl-Grignard reagents intractable reaction mixtures and no pure product could be obtained. Nitrogen reacts with some of the aryl derivatives giving dimeric thermally unstable complexes of formula $\text{R}(\text{C}_5\text{H}_5)_2\text{-TiN}_2\text{Ti}(\text{C}_5\text{H}_5)_2\text{R}$.

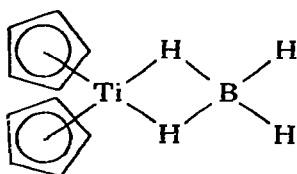
Work aimed at identifying nitrogen-fixing intermediates has been reported

[22]. The reducing agent used for $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ was $\text{Na}[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]$:



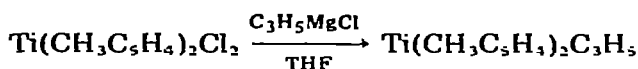
Of course, dicyclopentadienyltitanium(II) would be present in the reaction mixture only as a metastable species. It was found that when four moles of reducing agent per titanium were used, the yields of ammonia obtained under nitrogen would correspond to those obtained by carrying out the reduction of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ with sodium, under comparable conditions.

The vibrational spectra of some borohydrido complexes of Group IVB have been examined [23]. Dicyclopentadienylborohydridotitanium(III) has an infrared spectrum consistent with the double hydrogen-bridging structure shown below. A dimeric hydrogen-bridged structure is excluded by the fact that the compound is monomeric in dioxane and the solution spectra between 2600 and 1900 cm^{-1} are the same in both benzene and tetrahydrofuran.



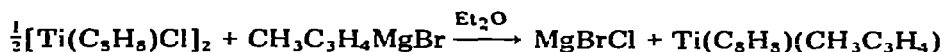
VI. Organometallic derivatives of titanium(III) with carbon, nitrogen, phosphorus, oxygen, sulphur and halogen donors

It has been shown [24] that dicyclopentadienyl(1-methylallyl)titanium(III) can be hydrogenated to give butane and a titanium complex which is a catalyst for the hydrogenation and isomerisation of olefins. The similar bis(methylcyclopentadienyl)allyltitanium(III) was prepared by the following reaction:



The product obtained, once hydrogenated, is capable of undergoing exchange with deuterium gas. Hydrogen is found in the gas phase and the soluble products show presence of deuterium. However, of the fourteen possible exchangeable hydrogens, only four undergo exchange and no exchange was observed for the methyl group. In addition it was found that exchange especially occurred at the β -position of the five-membered rings:

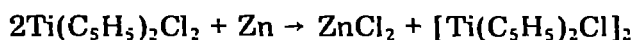
Cyclooctatetraene(1-methylallyl)titanium was prepared by the following Grignard reaction [25]:



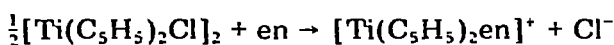
Infrared evidence suggest that the cyclooctatetraene and the allyl groups are *octahapto* and *trihapto*, respectively. The compound is sensitive to both air and moisture and starts decomposing at 110°C .

The EPR spectra of cyclooctatetraenecyclopentadienyltitanium have been measured [26]. The results suggest that the unpaired electron of this d^1 system is in an orbital which has predominant d_{z^2} character. The spectrum showed some hyperfine structure, due to coupling with the protons which was not completely resolved.

A simplified experimental procedure for the synthesis of dicyclopentadienylchlorotitanium(III) has been reported [27]. It consists of reducing $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ with zinc in tetrahydrofuran, followed by recrystallization from diethyl ether:

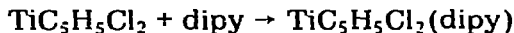
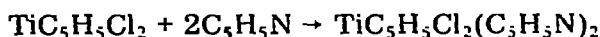


Addition of monodentate Lewis bases to the titanium(III) complex leads to the formation of products of general formula $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl} \cdot \text{L}$ ($\text{L} = \text{pyridine}, \text{NH}_2\text{R}$). Interestingly enough, no addition products could be obtained with PPh_3 and $\text{P}(\text{C}_6\text{H}_{11})_3$, whereas adduct formation takes place with PPh_2Me and PPhMe_2 . With bidentate nitrogen bases, ionic products were obtained, e.g.:

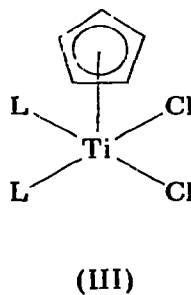
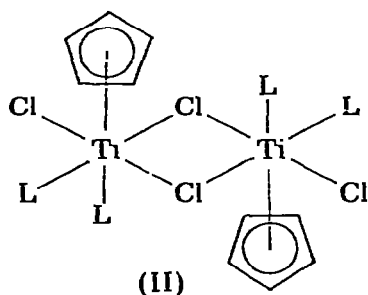


(en = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

Adducts of nitrogen bases [28] with cyclopentadienyldichlorotitanium(III) were obtained in tetrahydrofuran, e.g.:



(dipy = 2,2'-dipyridyl). The magnetic susceptibilities follow a Curie-Weiss law, with μ_{eff} in the range 1.55-1.75 BM at room temperature. This suggests a very low degree of titanium-titanium interaction. However, mainly in view of the low solubility suggesting some degree of association, the dimeric chlorine-bridged structure II was preferred to the monomeric III containing pentacoordinate titanium(III). On the other hand, structure III could not be excluded on the basis of the available data.

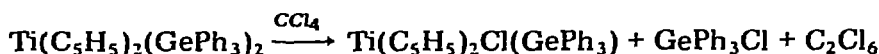
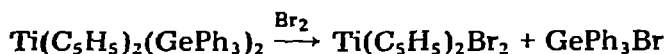


Carboxylato complexes of titanium(III) of formula $\text{TiC}_5\text{H}_5(\text{COOR})_2$ ($\text{R} = \text{CH}_3, \text{CF}_3, \text{C}_6\text{H}_5$), have been reported [29]. These compounds have rather anomalous magnetic behavior, thus suggesting considerable titanium-titanium interactions in the solid state.

VII. Intermetallic derivatives of titanium

The titanium-germanium complex $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{GePh}_3)_2$ has been obtained from the reaction [30] of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ with LiGePh_3 in tetrahydrofuran at -78°C .

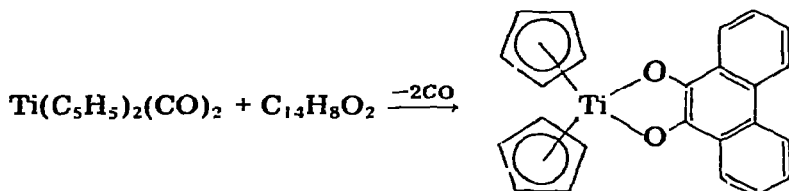
No reduction takes place during the reaction as shown by the absence of EPR signals. The titanium(IV) derivative so obtained, $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{GePh}_3)_2$, was shown to undergo reactions with bromine and carbon tetrachloride:



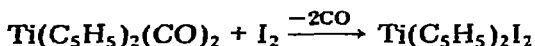
VIII. Organometallic derivatives of titanium(II)

Dicyclopentadienyldicarbonyltitanium(II) may be regarded as a source of "Ti(C₅H₅)₂" in solution. Apart from the coordinative oxidations described above (see eqns. 3 and 5 reported in ref. 7), other oxidations of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ have been described [31].

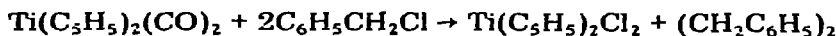
9,10-Phenanthrenequinone adds to $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ with carbon monoxide evolution:



Reaction with iodine results in the formation of the iodotitanium(IV) derivative in substantially quantitative yield:



The reaction with benzyl chloride [7] leads to $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ and bibenzyl in substantially quantitative yields:



It was suggested that the reaction may go through the intermediate formation of an unstable chlorobenzyl derivative of titanium(IV), the latter undergoing further attack by benzyl chloride to give the final products.

Also the "titanocene dimer" of formula $\text{Ti}_2\text{C}_{20}\text{H}_{20}$, as obtained from the reduction of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$, dehalogenates organic halides [32], with the exception of aromatic halides. Benzyl chloride was shown to give bibenzyl in about 19% yield. The metal-containing portion of the reaction mixture was not $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$, but rather a green colored substance analyzing for $\text{Ti}_2\text{Cl}_4\text{C}_{20}\text{H}_{19}$.

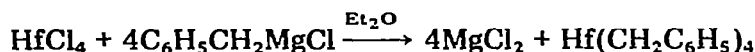
This is again consistent with the fact that the so-called "titanocene dimer" most probably does not contain symmetrically bonded cyclopentadienyl rings.

A bonding model for bent dicyclopentadienyl systems of d^0-d^2 configurations has been proposed [33]. A MO energy-level diagram has been derived from that of ferrocene by considering a deformation of the sandwich structure to C_{2v} symmetry. This model, which follows earlier bonding models [34, 35], explains some structural features of titanium, zirconium, niobium, molybdenum, vanadium and rhenium complexes.

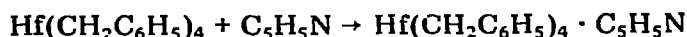
Titanocene dimer was found [35a] to be an effective catalyst for the hydrogenation of olefins. Similar properties were mentioned also for $Ti(C_5H_5)_2(CH_3)Cl$ and $Ti(C_5H_5)_2(C_6H_5)_2$.

IX. Zirconium(IV) and hafnium(IV) derivatives

Tetrabenzylhafnium was synthesized [36] by the usual Grignard reaction on the tetrachloride:



Tetrabenzylhafnium is a pale yellow solid, sensitive to air, reported to be more stable thermally than the corresponding titanium and zirconium analogs. Solutions of $Zr(CH_2C_6H_5)_4$ and $Hf(CH_2C_6H_5)_4$ in equimolar quantities did not show two distinct resonances for the methylene protons, thus suggesting that no or slow (on the NMR time scale) ligand exchange was taking place. NMR evidence of complex formation was obtained between $Hf(CH_2C_6H_5)_4$ and pyridine, quinoline, tetrahydrofuran and PMe_3 . In the case of pyridine, evidence for the formation of a 1/1 adduct was gathered with little or no 1/2 adduct being present:



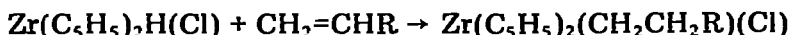
In the 1/1 adduct the hafnium atom is probably five-coordinate. On the other hand, the hafnium complex gives a 1/1 adduct also with 2,2'-dipyridyl in which the central metal atom was suggested to be six-coordinate.

The catalytic properties of tetrakis(trimethylsilylmethyl)zirconium(IV), $Zr(CH_2SiMe_3)_4$ for the polymerization of some silacyclobutanes were investigated [37]. The zirconium complex was found to have no or very low activity.

The tetrahydridoborato complexes of zirconium and hafnium have been studied [38] with special concern for their infrared, Raman and proton NMR spectra. The infrared spectra of the two compounds as Nujol solutions are very similar, thus suggesting that both compounds have the same structure, namely that with tridentate BH_4 groups as it has been determined earlier by X-ray [39] and electron diffraction [40] methods. 1H NMR spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ show very similar temperature dependence. The conclusion was reached that, even at $-80^\circ C$, rapid intramolecular interchange of bridging and terminal hydrogens takes place.

The preparation of alkyl complexes of zirconium(IV) of formula ZrX_3R and ZrX_2R_2 has been reported [1]. The compounds were isolated as diethyl ether or 2,2'-dipyridyl adducts, e.g. $ZrCl_3CH_3 \cdot 2Et_2O$ and $ZrCl_2Et_2 \cdot dipy$.

The reactions of $\text{Zr}(\text{C}_5\text{H}_5)_2\text{H}_2$ and $\text{Zr}(\text{C}_5\text{H}_5)_2\text{H}(\text{Cl})$ with olefins have been reported [35a]. From the latter, monoalkyl derivatives, resulting from the insertion of the olefin into the zirconium—hydrogen bond have been isolated:

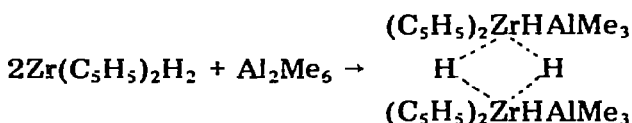


No isolable products could be obtained from the dihydrido species, however, the formation of intermediate unstable dialkyls could be evidenced chemically. In fact, from the reaction of $\text{Zr}(\text{C}_5\text{H}_5)_2\text{H}_2$ with 4-vinyldiphenyl, ethyldiphenyl, complexed vinyldiphenyl and "zirconocene" were obtained:



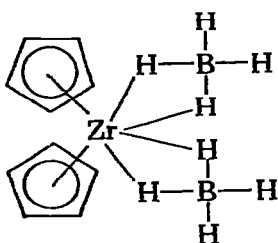
It is interesting to note that formation of the alkane (ethyldiphenyl in this case) would occur by hydrogen migration within the alkyls bonded to zirconium rather than from the cyclopentadienyl rings. In titanium chemistry hydrogen migrations from cyclopentadienyl are usually involved [6, 41, 42, 43].

Dicyclopentadienyldihydrido-zirconium(IV) reacts with trimethylaluminum [44] to give a blue adduct, unstable even at room temperature:

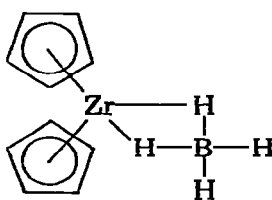


The structure shown in the above equation was suggested by the ^1H NMR results and cryoscopic molecular-weight determinations, the latter being somewhat imprecise due to partial decomposition. The infrared vibrations associated with the $\text{Zr}-\text{H}-\text{Zr}$ and $\text{Zr}-\text{H}-\text{Al}$ groups in the adduct were localized at 1350 and 1780 cm^{-1} , respectively.

Spectroscopic results [23] on $\text{Zr}(\text{C}_5\text{H}_5)_2(\text{BH}_4)_2$ suggest that the tetrahydridoborato ligand has two bridging hydrogens in this compound, as indicated in structure IV. Also the tetrahydridoboratohydrido complex $\text{Zr}(\text{C}_5\text{H}_5)_2(\text{BH}_4)\text{H}$ has been investigated [23]. Infrared spectra are again in agreement with a bidentate BH_4 and a terminal hydrido ligand. The compound is monomeric and the terminal $\text{Zr}-\text{H}$ stretching vibration was located at 1595 cm^{-1} (in benzene solution).



(IV)



(V)

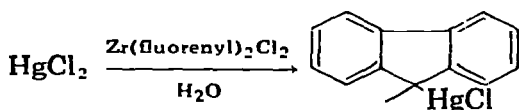
This is substantially the only well authenticated example of a tetrahydridoborato-hydrido mixed complex of a transition element. The molecular structure of this compound would then be V.

The Raman and infrared spectra of $Zr(C_5H_5)_4$, together with the elevated value of the dipole moment ($\mu = 3.56$ D) suggest [45] that the cyclopentadienyl rings are not equivalent in this compound. On the other hand, fast exchange of the proton sites must occur even at low temperature: in the lowest temperature range investigated (between -100 and -150°C) only one single cyclopentadienyl resonance could be observed. The X-ray structure of $Hf(C_5H_5)_4$ has not been carried out as yet. However, also in this case the nonequivalence of cyclopentadienyl rings is suggested by spectroscopic data and by the dipole moment value ($\mu = 3.76$ D). The ^1H NMR spectrum again shows only one cyclopentadienyl resonance.

Dicyclopentadienyldimethyl-, dicyclopentadienyldiphenyl- and dicyclopentadienylbis(pentafluorophenyl) derivatives of zirconium(IV) were announced in a plenary lecture by Rausch [2]. These compounds have been reported as having a quite high thermal stability. In this connection it is also interesting to note that dicyclopentadienyldibenzylzirconium(IV), $Zr(C_5H_5)_2(CH_2C_6H_5)_2$, was described [6] as crystallizable from boiling heptane. This behavior contrasts drastically with the high thermal lability of the corresponding titanium analog.

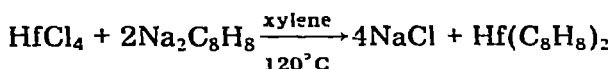
The preparation and properties of dicyclopentadienyldichloro derivatives of zirconium(IV) and hafnium(IV) in which, similar to the corresponding titanium(IV) analog, two C_5H_4 rings are joined together by a $(CH_2)_3$ chain have been reported [15].

Difluorenyldichlorozirconium has been used [46] for preparing fluorenyl-chloromercury(II):

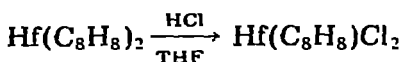


Water is necessary for obtaining the mercury derivative: this suggests that this is not a simple intermolecular exchange reaction.

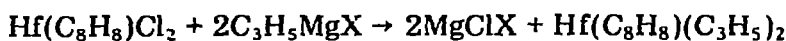
Dicyclooctatetraenehafnium(IV) has been prepared [47] by treating $HfCl_4$ with $Na_2C_8H_8$:



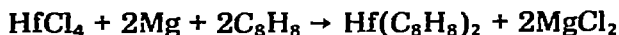
The deep red compound shows the molecular ion in its mass spectrum. With two equivalents of HCl the corresponding dichloro derivative was obtained:



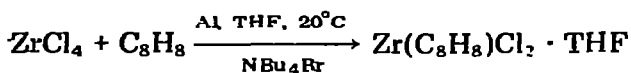
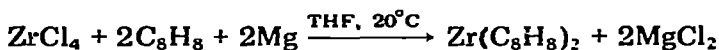
The dichloro derivative crystallizes out as the tetrahydrofuran adduct $Hf(C_8H_8)Cl_2 \cdot \text{THF}$, which then can be converted into $Hf(C_8H_8)Cl_2$ by heating in vacuo. A further reaction which was reported was the synthesis of a mixed cyclooctatetraeneallyl complex:



Dicyclooctatetraenehafnium was also synthesized [48] by a one-step reaction of hafnium tetrachloride with magnesium and cyclooctatetraene:



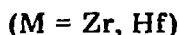
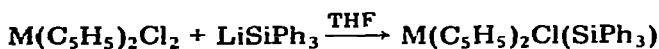
The same paper [48] reports electrochemical syntheses of $\text{Zr}(\text{C}_8\text{H}_8)_2$ and $\text{Zr}(\text{C}_8\text{H}_8)\text{Cl}_2$:



Magnesium and aluminum are the anodes in these reactions; the yields are 15 and 83%, respectively.

The molecular structure of dicyclooctatetraenezirconium as its tetrahydrofuran adduct has been solved [49]. As shown in Fig. 1, the structure consists of a planar cyclooctatetraene ring and a non-planar C_8 ring, four carbon atoms of the latter ring being at bonding distances.

Zirconium—silicon and hafnium—silicon containing compounds have been reported [5a]. The compounds were obtained by the following reaction:



The same paper reports the preparation and properties of several intermetallic derivatives of dicyclopentadienylzirconium(IV) and dicyclopentadienylhafnium(IV) derivatives with tin and germanium of general formula $\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}(\text{M}'\text{Ph}_3)$, ($\text{M} = \text{Zr, Hf}$; $\text{M}' = \text{Ge, Sn}$).

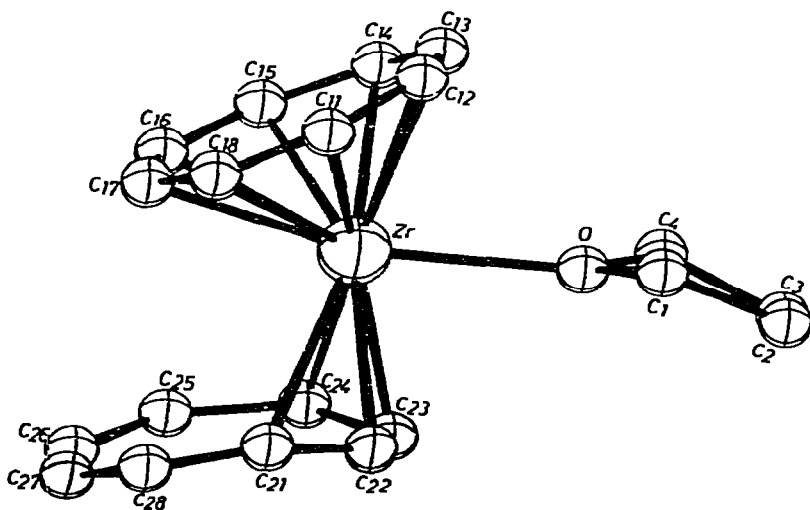


Fig. 1. Molecular structure of $\text{Zr}(\text{C}_8\text{H}_8)_2 \cdot \text{THF}$. (From D.J. Bauer and C. Krüger, *J. Organometal. Chem.*, 42 (1972) 129.)

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