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sublimes under vacuum at 100°C as the adduct $Hf(NO_3)_4.N_2O_5$.

Zirconium phosphates (α-form: $Zr(HPO_4)_2$-H_2O, β-form: $Zr(HPO_4)_2.2H_2O$) have layered structures with cation-exchange properties due to the replaceable, acidic hydrogens. Intercalation of organic molecules causes swelling of the structures and increases their versatility as ion-exchangers.

In oxidation states lower than +4, only Ti^{III} forms a sulfate and this gives rise to the alums, $MTi(SO_4)_2.12H_2O$ (M = Rb, Cs), containing the octahedral hexaaquotitanium(III) ion.

21.3.5 Complexes[4,15]

Oxidation state IV (d^0)

A very large number of these complexes, particularly of titanium, have been prepared and, as is to be expected for the d^0 configuration, they are invariably diamagnetic. Hydrolysis, resulting in polymeric species with –OH– or –O– bridges, is common especially with titanium and is still a preparative problem with zirconium and hafnium, though acidic solutions if sufficiently dilute ($<10^{-4}$ M) probably contain the Zr^{4+}(aq) ion[16]. A coordination number of 6 is the most usual for Ti^{IV} but 7- and even 8-coordination is possible. However, these high coordination numbers are much more characteristic of Zr^{IV} and Hf^{IV}, whose complexes are more labile (consistent with greater electrostatic character in the bonding). Furthermore, because changes in geometry entail smaller changes in energy for higher coordination numbers, these include a greater variety of stereochemistries.

The neutral and anionic adducts of the halides constitute a large proportion of the complexes of Ti^{IV}, and the alkoxides (also prepared from $TiCl_4$) are of commercial importance (p. 968).

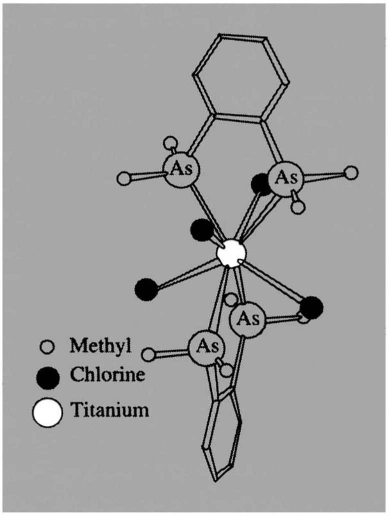

Figure 21.5 Molecular structure of $[TiCl_4(diars)_2]$. The dodecahedral coordination is produced by two interpenetrating tetrahedra (slightly distorted) of chlorine and arsenic atoms.

TiF_4 forms 6-coordinate adducts mainly with *O*- and *N*-donor ligands, and complexes of the type TiF_4L have all the appearances of fluorine-bridged polymers. $TiCl_4$ and $TiBr_4$ are especially prolific and are clearly "softer" acceptors than the fluoride. They form mainly yellow to red adducts of the types $[MX_4L_2]$ and $[MX_4(L\text{-}L)]$ with ligands such as ethers, ketones, $OPCl_3$, amines, imines, nitriles, thiols and thioethers. Zirconium and hafnium analogues occur but are often less well characterized because of insolubility and also difficulty in preparing samples suitable for X-ray analysis. Phosphorus- and *As*-donor ligands also complex readily with the chlorides of all three metals, particularly as chelates, and are of interest in that they produce coordination numbers which, for titanium, are unusually high. Thus *o*-phenylenebis(dimethyldiarsine), diars, and its phosphorus analogue form not only the 6-coordinate $[MX_4(L\text{-}L)]$ but also the 8-coordinate $[MX_4(L\text{-}L)_2]$. $[TiCl_4(diars)_2]$ (Fig. 21.5) was in fact one of the first examples of an 8-coordinate complex of a first-row transition element. The terdentate arsine, $MeC(CH_2AsMe_2)_3$, forms a 1:1

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[15] N. Serpone, M. A. Jamieson and E. Pelizzetti, *Coord. Chem. Revs.* **90**, 243–315 (1988); R. Fay *ibid.* **80**, 131–56 (1987).

[16] D. H. Devia and A. G. Sykes, *Inorg. Chem.* **20**, 910–13 (1981).

adduct with $TiCl_4$ which is monomeric and so presumably 7-coordinate. $[TiCl_4L]$ adducts are usually 6-coordinate dimers with double chloride bridges.

Octahedral, anionic complexes, $[MX_6]^{2-}$, show a marked increase in susceptibility to hydrolysis and consequent difficulty in preparation, in passing from the stable fluorides to the heavier halides, with the result that the hexaiodo complexes cannot be isolated. The fluorozirconates and fluorohafnates display considerable variety, complexes of the types $[MF_7]^{3-}$, $[M_2F_{14}]^{6-}$, and $[MF_8]^{4-}$ having been prepared, often by fusion of the appropriate fluorides. In Na_3ZrF_7 the anion has the 7-coordinate pentagonal bipyramidal structure; in $Li_6[BeF_4][ZrF_8]$ the zirconium anion is 8-coordinate, dodecahedral (distorted); in $Cu_6[ZrF_8].12H_2O$ it is 8-coordinate, square antiprismatic, and in $Cu_3[Zr_2F_{14}].18H_2O$ dimerization by the edge-sharing of two square antiprisms maintains 8-coordination. Stoichiometry does not, however, define coordination type, and this is very well illustrated by the ostensibly $[MF_6]^{2-}$ complexes which may contain 6-, 7-, or 8-coordinate Zr^{IV} or Hf^{IV} depending on the counter anion. In Rb_2MF_6, M is indeed octahedrally coordinated, but in $(NH_4)_2MF_6$ and K_2MF_6 polymerization occurs to give respectively 7- and 8-coordinate species.

Alkoxides of all 3 metals are well characterized but it is those of titanium which are of particular importance. The solvolysis of $TiCl_4$ with an alcohol yields a dialkoxide:

$$TiCl_4 + 2ROH \longrightarrow TiCl_2(OR)_2 + 2HCl$$

If dry ammonia is added to remove the HCl, then the tetraalkoxides can be produced:

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl$$

These alkoxides are liquids or sublimable solids and, unless the steric effects of the alkyl chain prevent it, apparently attain octahedral coordination of the titanium by polymerization (Fig. 21.6). The lower alkoxides are especially sensitive to moisture, hydrolysing to the dioxide. Application of these "organic titanates" (as they are frequently described) can therefore give a thin, transparent, and adherent coating of TiO_2 to a variety of materials merely by exposure to the atmosphere. In this way they are used to waterproof fabrics and also in heat-resistant paints. They are also used on glass and enamels which, after firing, retain a coating of TiO_2 which confers a resistance to scratching and often enhances the appearance. However, the most important commercial application is in the production of "thixotropic" paints which do not "drip" or "run". For this the $Ti(OR)_4$ is chelated with ligands such as β-diketonates to give products of the type $[Ti(OR)_2(L\text{-}L)_2]$ which are water soluble and more resistant to hydrolysis. In concentrations of 1% or less, they form gels with the cellulose ether colloids used to thicken latex paints and so produce the desired characteristics. Titanium tartrate complexes, probably dimeric species such as $[Ti_2(tartrate)_2(OR)_4]$, are also useful catalysts in asymmetric epoxidations of allylic alcohols.[17]

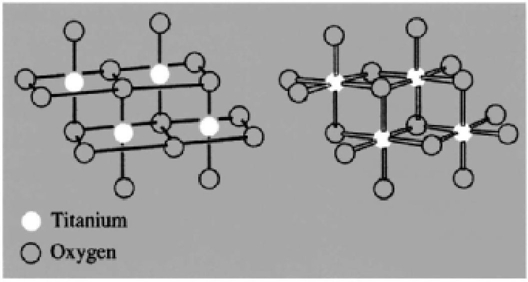

Figure 21.6 Two representations of the tetrameric structure of $[Ti(OEt)_4]_4$.

One of the most sensitive methods for estimating titanium (or, conversely, for estimating H_2O_2) is to measure the intensity of the orange colour produced when H_2O_2 is added to acidic solutions of titanium(IV). The colour is due[18] to the peroxo complex, $[Ti(O_2)(OH)(H_2O)_x]^+$, though alkaline solutions are needed before crystalline solids such as $M^I_3[Ti(O_2)F_5]$ or $M^I_2[Ti(O_2)(SO_4)_2]$

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[17] R. A. JOHNSON and K. B. SHARPLESS, Chap. 3.2, pp. 389-436 in *Comprehensive Organic Synthesis*, Vol. 7, Pergamon Press, Oxford, 1991.

[18] E. M. NOUR and S. MORSY, *Inorg. Chim. Acta* **117**, 45-8 (1986).

can be isolated. The peroxo ligand is apparently bidentate, the 2 oxygen atoms being equidistant from the metal (see also p. 615).

Not surprisingly, in view of their greater size, zirconium and hafnium show a greater preference than titanium for *O*-donor ligands as well as for high coordination numbers, and this is shown by the greater variety of β-diketonates, carboxylates and sulfato complexes which they form. Bis-β-diketonates such as $[MCl_2(acac)_2]$ of all 3 metals are made by the reaction of MCl_4 and the β-diketone in inert solvents such as benzene. They are octahedral with *cis*-chlorides. In addition, Zr and Hf form the monomeric, 7-coordinate $[MCl(acac)_3]$ complexes which have a distorted pentagonal bipyramidal stereochemistry. Also, providing alkali is present to remove the labile proton, Zr and Hf will yield the tetrakis complexes in aqueous solution:

$$MOCl_2 \xrightarrow[+Na_2CO_3]{4acacH} [M(acac)_4]$$

These too are monomeric, and the 8-coordinate structure has a square-antiprismatic arrangement of oxygen atoms around M.

Monocarboxylates of the types $[Zr(carbox)_4]$, $[ZrO(carbox)_3(H_2O)_x]$ and $[ZrO(OH)(carbox)(H_2O)_x]$ are well known, as are the corresponding dicarboxylates. It is interesting that the tetrakis(oxalates), $Na_4[M(C_2O_4)_4].3H_2O$, adopt the dodecahedral stereochemistry in contrast to the square-antiprismatic stereochemistry of $[M(acac)_4]$, possibly because the smaller "bite" of the oxalate ion compared to that of acac favours the dodecahedral form (p. 916). It may also be noted that, although optical and geometrical isomerism is conceivable for these stereochemistries, intramolecular rearrangement of the ligands is too rapid for sets of isomers of the above compounds (or, indeed, of any compound of Zr^{IV} or Hf^{IV}) to have been isolated.

Intramolecular rearrangement evidently also occurs in the borohydride, $[Zr(BH_4)_4]$ (p. 168). X-ray analysis of a single crystal at −160°C (at which temperature thermal vibrations are sufficiently reduced to allow the positions of the hydrogen atoms to be determined) showed it to have T_d symmetry (Fig. 21.7), with triple-hydrogen bridges, implying two types of hydrogen. Yet the proton nmr distinguishes only one type of proton, so that rapid intramolecular rearrangement is indicated. The structure of the hafnium compound has not been determined but its properties are so similar that its structure may be assumed to be the same. Both compounds are rather unstable, have virtually the same mp (~29°C) and are the most volatile compounds yet known for zirconium and hafnium. The type of bonding involved is a matter of some uncertainty. The volatility is indicative of covalency, but how many electrons the borohydride groups should be regarded as donating to the metal is open to doubt.

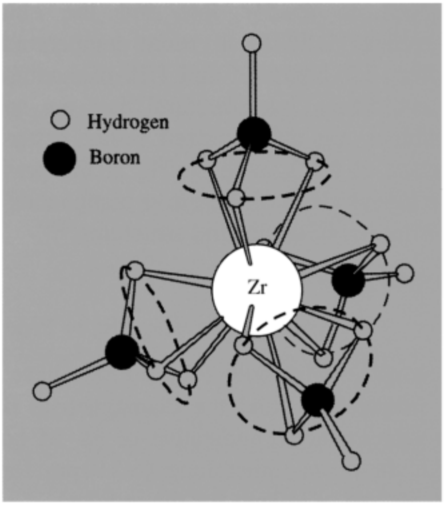

Figure 21.7 Molecular structure $[Zr(BH_4)_4]$ showing 4 trihapto BH_4 groups.

Oxidation state III (d^1)

The coordination chemistry of this oxidation state is virtually confined to that of titanium. Reduction of zirconium and hafnium from the quadrivalent to the tervalent state is not easy and cannot be attempted in water which is itself reduced by Zr^{III} and Hf^{III}. A few adducts of the trihalides of these two elements with *N*- or *P*- donor ligands have been prepared. $ZrBr_3$ treated with liquid ammonia yields a hexaammine stable to room temperature but NH_3 is readily lost and the chloride only retains $2.5NH_3$ at room temperature.^(19) Pyridine, 2,2′-bipyridyl and 1,10-phenanthroline also coordinate, but structural data are sparse. Phosphines are characterized rather better and reduction of MCl_4 with Na/Hg in the presence of the ligand yields air-sensitive compounds with edge-sharing, bi-octahedral structures:^(20)

$$[(PR_3)_2Cl_2M(\mu\text{-}Cl)_2MCl_2(PR_3)_2] \quad (M = Zr, Hf;\ PR_3 = PMe_2Ph)$$

Analogous iodides with $PR_3 = PMe_3$ have also been prepared,^(21) and the diamagnetism of all these compounds is indicative of M–M bonds, though these are rather long (~310 pm for the chlorides and ~340 pm for the iodides).

Titanium(III) is also prone to aerial oxidation. Most of the complexes of titanium(III) are octahedral and are produced by reacting $TiCl_3$ with an excess of the ligand, giving rise to stoichiometries such as $[TiL_6]X_3$, $[TiL_4X_2]X$, $[TiL_3X_3]$ and $M^I_3[TiX_6]$ (L = neutral unidentate ligand, X = singly charged anion) (Table 21.4) together with corresponding complexes involving multidentate ligands.

The first of these types is most familiarly represented by the hexaaquo ion which is present in acidic aqueous solutions and, in the solid state, in the alum $CsTi(SO_4)_2.12H_2O$. In fact few other neutral ligands besides water form a $[TiL_6]^{3+}$ complex. Urea is one of these few and $[Ti(OCN_2H_4)_6]I_3$, in which the urea ligands coordinate to the titanium via their oxygen atoms, is one of the compounds of titanium(III) most resistant to oxidation.

Hydrate isomerism of $TiCl_3.6H_2O$, yielding $[TiCl_2(H_2O)_4]^+Cl^-$ as one of the isomers, has already been referred to (p. 965) and analogous complexes are formed by a variety of alcohols. Neutral complexes, $[TiL_3X_3]$ have been characterized for a variety of ligands such as tetrahydrofuran (C_4H_8O), dioxan ($C_4H_8O_2$), acetonitrile, pyridine and picoline, while anionic complexes $[TiX_6]^{3-}$ (X = F, Cl, Br, NCS) have been prepared by electrolytic reduction of melts or by other nonaqueous methods. An interesting binuclear complex, $(NMe_4)[Ti(H_2O)_4F_2][TiF_6].H_2O$ is obtained by reacting $TiCl_3$ with NMe_4F in dimethylformamide. It contains *trans*-$[Ti^{III}(H_2O)_4F_2]^+$ cations and $[Ti^{IV}F_6]^{2-}$ anions.^(22)

Interpretation of the electronic spectrum of Ti^{III} in aqueous solution was an early landmark in the development of Crystal Field Theory, the observed broad band being assigned to the $^2E_g \leftarrow 2T_{2g}$ transition (promotion of an electron from a t_{2g} to an e_g orbital). However, the absorption band actually observed for this and for other octahedral complexes of Ti^{III} is never of the symmetrical shape expected for a single transition, but is rather an asymmetrical peak with a (usually) distinct shoulder on the low-energy side^(4). The whole absorption "envelope" is apparently made up of two superimposed bands whose positions are indicated in Table 21.4 and which are generally assumed to be a consequence of the Jahn–Teller effect (p. 1021) acting on the excited term. The value of $10Dq$ is usually identified with the energy of the stronger of the two bands rather than an average, and the results in Table 21.4 indicate that this varies with the ligand in the order:

$$Br^- < Cl^- < \text{urea} < NCS^- < F^- < H_2O$$

which agrees with the spectrochemical series established for other metals.

The t^1_{2g} ground configuration in a perfectly octahedral crystal field is expected to produce a magnetic moment of approx. 1.86 BM at room temperature, decreasing to zero at 0 K. Although observed magnetic moments of Ti^{III} compounds do indeed decrease with temperature, the effects of distortions (which split the ground $^2T_{2g}$ term) and partial covalency of the metal–ligand bond (which delocalizes the single electron from the

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[19] E. L. Boyle, E. S. Dodsworth, D. Nicholls and T. A. Ryan, *Inorg. Chim. Acta* **100**, 281–4 (1985).

[20] F. A. Cotton, P. A. Kibala and W. A. Wojtczak, *Inorg. Chim. Acta* **177**, 1–3 (1990).

[21] F. A. Cotton, M. Shang and W. A. Wojtczak, *Inorg. Chem.* **30**, 3670–5 (1991).

[22] L. Kiriazis and R. Mattes, *Z. anorg. allg. Chem.* **593**, 90–8 (1991).

Table 21.4 Spectroscopic and magnetic properties of some complexes of titanium(III)

Complex	Colour	$^2E_g \leftarrow {}^2T_{2g}/(\text{cm}^{-1})$	μ (room temperature)/BM
$[Cs(H_2O)_6][Ti(H_2O)_6][SO_4]_2$	Red-purple	19 900, 18 000	1.79
$[Ti(urea)_6]I_3$	Blue	17 550, 16 000	1.77
$[TiCl_3(NCMe)_3]$	Blue	17 100, 14 700	1.68
$[TiCl_3(NC_5H_5)_3]$	Green	16 600, Asym(a)	1.63
$[TiCl_3(thf)_3]$	Blue-green	14 700, 13 500	1.70
$[TiCl_3(dioxan)_3]$	Blue-green	15 150, 13 400	1.69
$[NH_4]_3[TiF_6]$	Purple	19 000, 15 100	1.78
$[C_5H_5NH]_3[TiCl_6]$	Orange	12 750, 10 800	1.78
$[C_5H_5NH]_3[TiBr_6]$	Orange	11 400, 9 650	1.81
$[NBu^n_4]_3[Ti(NCS)_6]$	Dark violet	18 400, Asym(a)	1.81

(a)The band "envelope" is asymmetrical with insufficient resolution to identify the position of the weaker component.

metal) lead to lower values at room temperature (see Table 21.4) and less temperature dependence than would have been expected.(23)

Amongst the few complexes of Ti^{III} which have been shown to be non-octahedral are $[TiBr_3(NMe_3)_2]$ and $[Ti\{N(SiMe_3)_2\}_3]$. The former has a 5-coordinate, trigonal bipyramidal structure while the latter is one of a series of complexes of tervalent metals which have a 3-coordinate, planar structure. It appears that the silylamide ligands are simply too bulky for the Ti^{III} ion to accommodate more than three of them, and this consideration overrides any preference which the metal might have for a higher coordination number.

Lower oxidation states

Apart from TiO and the lower halides already mentioned, the chemistry of these metals in oxidation states lower than 3 is not well established. Addition compounds of the type $[TiCl_2L_2]$ can be formed with difficulty with ligands such as dimethylformamide and acetonitrile, but their magnetic properties suggest that they also are polymeric with appreciable metal–metal bonding. However, the electronic spectra of Ti^{II} in $TiCl_2/AlCl_3$ melts and also of Ti^{II} incorporated in NaCl crystals (prepared by the reaction of $CdCl_2$ and titanium in molten NaCl and subsequent sublimation of Cd metal) have been shown to be as expected for a d^2 ion in an octahedral field.

The versatility of cyanide and bipyridyl ligands has been used to stabilize low oxidation states. By using potassium in liquid ammonia, $K_3Ti^{III}(CN)_6$ is reduced to $K_2Ti^{II}(CN)_4$ and $TiBr_3 + KCN$ to $K_4Ti^0(CN)_4$. With $ZrBr_3$ and M^ICN (M^I = K, Rb) in liquid ammonia, ammonolysis occurs and zerovalent Zr is produced:

$$4ZrBr_3 + 5M^ICN + 6NH_3 \rightarrow M^I_5Zr(CN)_5 + 3ZrBr_3(NH_2) + 3NH_4Br$$

Reduction of MCl_4 (M = Ti, Zr) in tetrahydrofuran by lithium in the presence of bipyridyl yields a series of darkly coloured, very air-sensitive compounds of the types $[M(bipy)_3]$, $Li[M(bipy)_3]$ and $Li_2[M(bipy)_3]$ with varying amounts of solvent of crystallization, implying oxidation states of 0, −1 and −2. However, delocalization of charge in the π^* orbitals of the ligands facilitates reduction of the ligands and assigning oxidation states to the metals under these circumstances is a purely formal exercise. A more "realistic" claim to zero oxidation state in Zr and Hf compounds is provided by $[M(\eta\text{-}PhMe)_2(PMe_3)]$. Metal vapour was produced from an "electron-gun furnace" and condensed with an excess of toluene and trimethylphosphine at −196°C. On warming up, a dark-green solution was produced from which the pure solids were isolated.

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[23] For a fuller account, see pp. 58–61 of R. L. Carlin, *Magnetochemistry*, Springer-Verlag, Berlin (1986).

Ziegler-Natta Catalysts(27)

The original ICI process for producing polythene involved the use of high temperatures and pressures but K. Ziegler discovered that, in the presence of a mixture of $TiCl_4$ and $AlEt_3$ in a hydrocarbon solvent, the polymerization will take place at room temperature and atomospheric pressure. G. Natta then showed that by suitable modification of the catalyst stereoregular polymers of almost any alkene (olefin), $CH_2{=}CHR$, can be produced. In general, these catalysts can be formed from an alkyl of Li, Be or Al together with a halide of one of the metals of Groups 4 to 6 in an oxidation state less than its maximum. As a result of their work, Ziegler and Natta were jointly awarded the 1963 Nobel Prize for Chemistry. Because of its commercially sensitive nature, much of the voluminous literature on this subject is in the form of patents, but a great deal of work has also been directed at ascertaining the mechanism of the catalyst. The initial reaction of $TiCl_4$ and $AlEt_3$ produces insoluble $TiCl_3$ (alternatively, preformed $TiCl_3$ can be used). The most plausible sequence of events on the surface of this catalyst is then as illustrated in Fig. A:

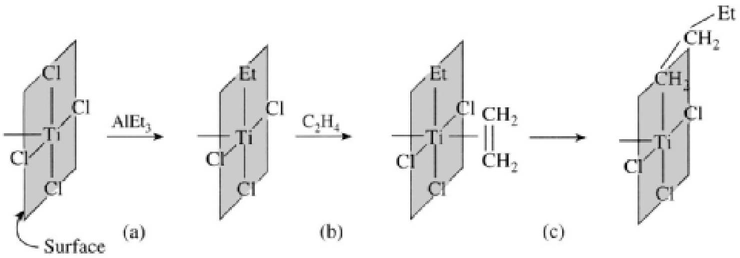

Figure A Possible mechanism of Ziegler-Natta catalyst.

(a) one of the chlorine atoms coordinated to a titanium atom is replaced by an ethyl group from $AlEt_3$,
(b) then, because the titanium atom on the surface of the solid has a vacant coordination site, a molecule of ethylene (ethene) can attach itself;
(c) migration of the ethyl group to the ethylene by a well-known process known as "*cis*-insertion" occurs.

The result of this *cis*-insertion is that a vacant site is left behind, and this can be occupied by another ethylene molecule and steps (a) and (b) repeated indefinitely.

The efficacy of the catalyst seems to lie in the fact that in the case of propylene ($CH_2{=}CH{-}CH_3$), for instance, the steric hindrance inherent in the surface coordination sites ensures that the polymer which is produced is stereoregular. Such a stereoregular polymer is stronger and has a higher mp than the non-regular (so-called "atactic") polymer. Furthermore, while the titanium provides bonds sufficiently strong to be able to hold the olefin and the alkyl in the correct orientations for reaction, they are not so strong as to prevent the migration which is essential to the reaction. For an alternative suggestion for the mechanism of catalysis, see p. 261.

21.3.6 Organometallic compounds(24,25)

Until the 1950s this was an unexplored area of chemistry, but then two events occurred: ferrocene was discovered (pp. 937, 1109) and K. Ziegler(26) catalysed the polymerization of ethylene using an organo-titanium derivative. The first event initiated a systematic study of cyclopentadienyl compounds, and so led to the preparation of the most stable of the organometallic compounds of this group, while the second event provided a strong commercial incentive for the investigation of this field (see Panel).

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[24] M. BOTTRILL, P. D. GAVENS J. W. KELLAND and J. MCMEEKING, Chap. 22, pp. 271-547, and D. J. CARDIN, M. F. LAPPERT, C. L. RASTON and P. I. RILEY, Chap. 23, pp. 549-646, in *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1982.

[25] D. J. CARDIN, M. F. LAPPERT and C. L. RASTON, *Chemistry of Organo-Zirconium and -Hafnium Compounds*, Ellis Horwood, Chichester, 1986, 451 pp. D. COZAK and M. MELNIK. *Coord. Chem. Rev.* **74**, 53-99 (1986).

[26] K. ZIEGLER, E. HOLZKAMP, H. BREILAND and H. MARTIN, *Angew. Chem.* **67**, 541-7 (1955).

[27] See pp. 475-547 of ref. 24.

In sharp contrast to the Group 14 elements Ge, Sn and Pb, Group 4 metals form relatively few alkyl and aryl compounds and those which are known are very unstable to both air and water. Thermal stabilization is provided by ligands which lack β-hydrogens (p. 926) or are bulky. Thus MEt_4 are unknown; MMe_4 can be prepared by the reactions of LiMe and MCl_4 in ether at low temperatures, but the yellow titanium and the red zirconium compounds decompose to the metals at temperatures above −20 and −15°C respectively; $M(CH_2SiMe_3)_4$ of all three metals are stable at room temperature. Another homoleptic alkyl is of interest because of its unusual structure. X-ray analysis has shown the anion of $[Li(tmed)]_2[ZrMe_6]$ to be the first ML_6 complex to have a trigonal bipyramidal structure and nmr studies indicate that this is retained in solution.(28)

Perhaps because of inadequate or non-existent back-bonding (p. 923), the only neutral, binary carbonyl so far reported is $Ti(CO)_6$ which has been produced by condensation of titanium metal vapour with CO in a matrix of inert gases at 10–15 K, and identified spectroscopically. By contrast, if MCl_4 (M = Ti, Zr) in dimethoxyethane is reduced with potassium naphthalenide in the presence of a crown ether (to complex the K^+) under an atmosphere of CO, $[M(CO)_6]^{2-}$ salts are produced.(29) These not only involve the metals in the exceptionally low formal oxidation state of −2 but are thermally stable up to 200 and 130°C respectively. However, the majority of their carbonyl compounds are stabilized by π-bonded ligands, usually cyclopentadienyl,(30) as in $[M(\eta^5\text{-}C_5H_5)_2(CO)_2]$ (Fig. 21.8).

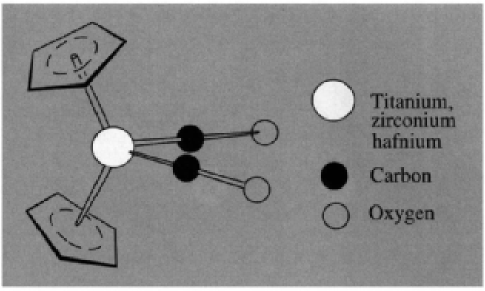

Figure 21.8 Molecular structure of $[M(\eta^5\text{-}C_5H_5)_2(CO)_2]$. For M = Ti the C_5H_5 rings are "eclipsed" as shown here, but for M = Hf they are "staggered". Essentially the same structure is found in other $[M(\eta^5\text{-}C_5H_5)_2L_2]$ molecules, but the conformation of the two C_5H_5 rings varies in an apparently unsystematic manner.

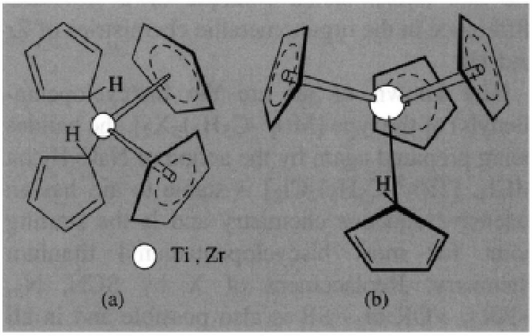

Figure 21.9 (a) Molecular structure of (a) $Ti(C_5H_5)_4$. (b) $Zr(C_5H_5)_4$.

Indeed, it is the cyclopentadienyls which provide the major part of the organometallic chemistry of this group and they are known for metal oxidation states of IV, III and II though III and II are rather sparsely represented for Zr and Hf. The compounds $M(C_5H_5)_4$ are prepared from MCl_4 and NaC_5H_5 and the structure of the green-black titanium compound is shown in Fig. 21.9a. It is therefore formulated as $[Ti(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2]$ (p. 940). Rather surprisingly, the ^1H nmr distinguishes only one type of proton at room temperature and it is evident that fluxional processes render all 20 protons indistinguishable. The yellow hafnium analogue is isostructural but the yellow-orange zirconium compound contains 1 monohapto- and 3 pentahapto-rings, $[Zr(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)_3]$ Fig. 21.9b. This formulation is unexpected since it entails a formally 20-electron

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[28] P. M. Morse and G. S. Girolami, *J. Am. Chem. Soc.* **111**, 4114–6 (1989).

[29] K. M. Chi, S. R. Frerichs, S. B. Philson and J. E. Ellis, *Angew. Chem. Int. Edn. Engl.* **26**, 1190–1 (1987) and *J. Am. Chem. Soc.* **110**, 303–4 (1988).

[30] D. J. Sikora, D. W. Macomber and M. D. Rausch, *Adv. Organometallic Chem.* **25**, 318–80 (1986).

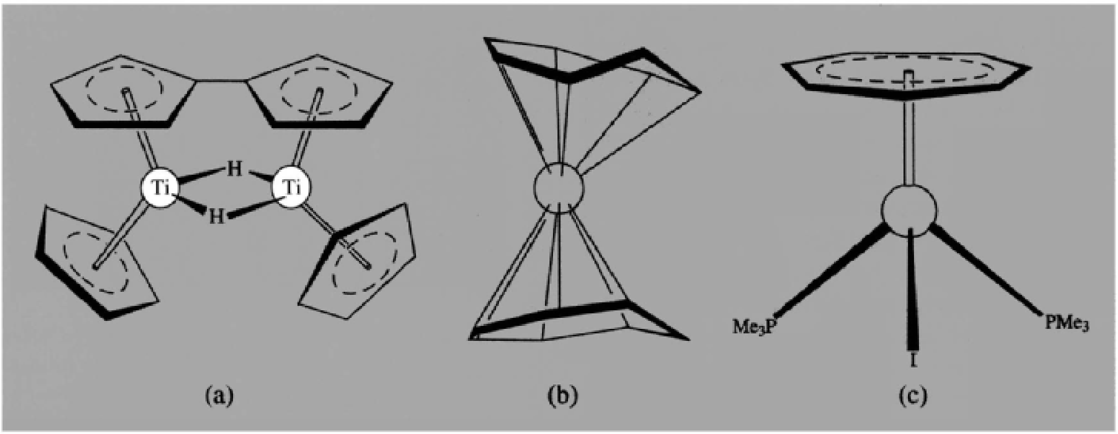

Figure 21.10 (a) "Dimeric" $Ti(C_5H_5)_2$, actually $(\mu$-$(\eta^5,\eta^5$-fulvalene(-di-(μ-hydrido)-bis(η^5-cyclopentadienyltitanium), (b) $Zr(\eta^6\text{-}C_7H_8)_2$ and (c) $Zr(\eta^7\text{-}C_7H_7)(PMe_3)_2I$.

configuration; the two compounds also provided the first authenticated example of a structural difference in the organometallic chemistries of Zr and Hf.

Best known of all are the bis(cyclopentadienyls) of the type $[M(\eta^5\text{-}C_5H_5)_2X_2]$, the halides being prepared again by the action of NaC_5H_5 on MCl_4. $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ is stable to air, has an extensive aqueous chemistry and is the starting point for most biscyclopentadienyl titanium chemistry. Replacement of X by SCN, N_3, $-NR_2$, $-OR$ or $-SR$ is also possible and in all cases the structures are distorted tetrahedral with both rings pentahapto (Fig. 21.8). Interesting derivatives of the type $[(C_5H_5)_2Ti(CH_2)_4]$ have also been produced. Amongst the many other reactions of the dihalides, ring replacement to give compounds such as $[Ti(C_5H_5)X_3]$ and reductions to $[Ti(C_5H_5)_2X]$ and $[Ti(C_5H_5)_2]$ may be noted. The last of these is of interest as a potential analogue of ferrocene. Several preparative routes have been suggested, and the usual product is a dark-green, pyrophoric, diamagnetic dimer, though a monomeric isomer may be produced in some cases as an intermediate. The structure of the dimer has been shown by X-ray crystallography(30a) to be that in Fig. 21.10a, confirming earlier results based on ^{13}C nmr. Attempts to prepare a zirconium analogue have yielded a variety of products, some dinuclear others polymeric but, as with titanium, no true mononuclear metallocene. A number of cyclopentadienyl and related compounds of titanium and zirconium have been found to absorb molecular nitrogen, which in some cases can be recovered in a reduced form (i.e. as ammonia or hydrazine) upon hydrolysis, and the first example of dinitrogen complexation by a non-cyclopentadienyl Ti system has recently been reported.(31) While this has obvious interest as a potential route to nitrogen fixation, a compound which can be regenerated and so act catalytically has so far proved elusive.

Although the chemistry of zirconium in its lower oxidation states is still relatively unexplored, it is developing. Examples which offer the possibility of further exploitation include the blue, paramagnetic zirconium(III) compound(32) $[L_2Zr(\mu\text{-}Cl)_2ZrL_2]$ $\{L = C_5H_3(SiMe_3)_2\text{-}1,3\}$, and the "sandwich" and "half-sandwich" compounds derived from cycloheptatriene: red

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$[Zr^0(\eta^6\text{-}C_7H_8)_2]$(33) and blue, $[Zr^{II}(\eta^7\text{-}C_7H_7)(PMe_3)_2I]$(34) (Fig. 21.10b and c).

Considerable attention is also being given to the anti-tumor activity of titanium compounds. Amongst these are bis(cyclopentadienyl) and bis(β-diketonate) derivatives, some of which are undergoing clinical trials,(35) in the hope that they will provide more extensive application than cisplatin (pp. 1163–4).

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