TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1971

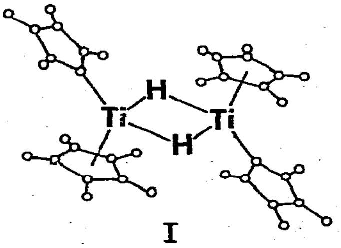
F. CALDERAZZO

Istituto di Chimica Generale ed Inorganica, University of Pisa, 56100 Pisa (Italy)

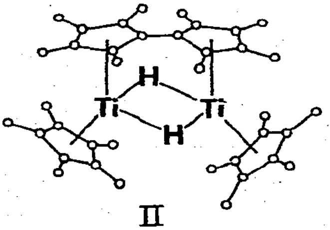
I. TITANIUM IN THE NITROGEN FIXATION PROBLEM

The nitrogen-fixing properties of organometallic derivatives of titanium and the structure of the so-called "titanocene dimer" appear to be problems so strictly related one to the other that they will be treated together under this section.

It had been suggested[1], mainly on the basis of infrared and mass spectroscopic evidence, that the "titanocene dimer" has the formula $[Ti(C_5H_5)(C_5H_4)H]_2$ and a hydrogen-bridged structure, either (I) or (II). The X-ray structure[2] of the niobium analogue, $[Nb(C_5H_5)(C_5H_4)H]_2$ has now been published. This compound has been shown to contain terminal hydrido groups rather than bridging ones and the suggestion was also made[2,3] that the "titanocene dimer" may have a similar C_5H_4-bridged structure with terminal hydrido ligands, as indicated in (III). If this suggestion is correct, the "titanocene dimer" would represent a unique example of titanium–hydrogen (to terminal hydrido ligands) bond reported in the literature. It is to be in fact recalled that the anionic titanium(III)–hydrido species[4], $[Ti(C_5H_5)H_2]^-$, which have been characterized by EPR spectra only, probably contain bridging hydrido ligands (*vide infra*).



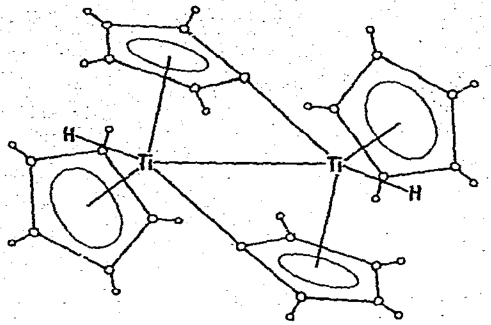
I



II

The problem concerning the structure of the "titanocene dimer" seems to be further complicated by the fact that several dimeric species approximately corresponding to the formula can be isolated depending on the reaction conditions. The situation can be summarized as follows.

(i) Reduction[5] of $Ti(C_5H_5)_2Cl_2$ with sodium in toluene at about 50° for four days



(III)

yields a green solid of formula $C_{20}H_{20}Ti_2$, whose structure may be (I) or (II), as proposed by Brintzinger and Bercaw[1] or (III).

(ii) Treatment[6] of $Ti(C_5H_5)_2(CH_3)_2$ with hydrogen at atmospheric pressure in hexane at 20° for 1 h gives a green solid of formula $C_{20}H_{20}Ti_2$, believed[7] to be identical with the product obtained according to (i).

(iii) Treatment of $Ti(C_5H_5)_2(CH_3)_2$ with hydrogen[8] at 0° without solvent yields a dimeric compound too, but this is violet rather than green and its formula was reported to be $C_{20}H_{22}Ti_2$. Its structure is that of a dimeric hydrido-bridged dicyclopentadienyl derivative of titanium(III).

(iv) Treatment[7] of a saturated hexane solution of $Ti(C_5H_5)_2(CH_3)_2$ with hydrogen at 0° and removing continuously methane formed in the reaction in order to keep the partial pressure of hydrogen as high as possible does not lead to the violet solid described at (iii), but gives a gray-green product. The latter was reported[7] to contain hydrido ligands and was suggested to be a linear polymer of composition $[-Ti(C_5H_5)_2H-]_n$.

This polymeric substance was also described[7] as a precursor of a metastable form of the titanocene dimer, of formula $[Ti(C_5H_5)_2]_2$, different from $[Ti(C_5H_5)(C_5H_4)H]_2$, especially in its reactivity towards carbon monoxide, hydrogen and nitrogen. Ether solutions of this dimer absorb 1 mole of N_2 per mole of $[Ti(C_5H_5)_2]_2$; the absorption is reversible, molecular nitrogen being released upon warming to room temperature. Since the infrared spectrum did not show any absorption due to coordinated nitrogen, the complex was suggested[7] to have the dinitrogen-bridged structure $(C_5H_5)_2Ti{-}NN{-}Ti(C_5H_5)_2$. It has to be recalled at this point that van Tamelen and coworkers had reported some time ago[9] that solutions of the green titanocene dimer would absorb approximately 1 mole of nitrogen per titanium. We have therefore to consider this additional complication, namely that two different nitrogen complexes of titanocene derivatives appear to exist.

Also Shilov and coworkers[10] have isolated a nitrogen complex obtained by treating $[Ti(C_5H_5)_2Cl]_2$ with the isopropyl Grignard reagent in the presence of N_2 at temperatures comprised between −80° and −100°. A blue precipitate was formed under these conditions. The latter was found, by its reactions, to have the formula $[Ti(C_5H_5)_2(C_3H_7)]_2N_2$.

This result is in agreement with that obtained earlier by Teuben and De Liefde Meijer[11,12]. These authors have reported the preparation of dicyclopentadienylphenyltitanium(III), obtained by the reaction of the phenyl Grignard reagent with $[Ti(C_5H_5)_2Cl]_2$:

$$\tfrac{1}{2}[Ti(C_5H_5)_2Cl]_2 + MgBrC_6H_5 \rightarrow MgClBr + Ti(C_5H_5)_2C_6H_5 \qquad (1)$$

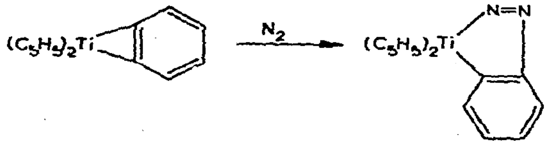
The reaction was carried out in diethyl ether at −25°. The phenyl derivative decomposes at room temperature and absorbs molecular nitrogen in toluene solution at −78°:

$$2\,Ti(C_5H_5)_2C_6H_5 + N_2 \rightarrow [Ti(C_5H_5)_2C_6H_5]_2N_2 \qquad (2)$$

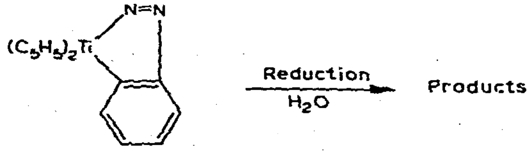
The nitrogen complex was isolated and characterized by elemental analysis, differential thermal analysis and chemical reactivity. The molecular weight of the complex could not be determined because of its thermal instability, but it is believed to be dimeric, possibly N_2-bridged.

The chemistry of cyclopentadienyl and phenyl derivatives of titanium is characterized by intramolecular hydrogen transfers. For example, whatever may be the structure of the "*titanocene dimer*", as *indicated in* (I), (II) and (III), *the hydrido ligand attached to titanium* originates from a hydrogen atom originally bonded to a cyclopentadienyl ring. Volpin and coworkers[13] have pointed out that in the course of the reduction of $Ti(C_5H_5)_2Cl_2$ with Mg and MgI_2 in the absence of nitrogen, hydrido species are formed, the source of hydrogen being the cyclopentadienyl rings, rather than the solvent.

A further application of the intramolecular hydrogen transfer has now been found[14]. When dicyclopentadienyldiphenyltitanium(IV) was thermally decomposed in the presence of nitrogen (90–100 atm), and the resulting product hydrolyzed, aniline, ammonia and phenylhydrazine were obtained. Since benzene was formed during the reaction, it has been suggested that nitrogen was inserted into an intermediate phenylene stabilized by complexation to titanium:



(3)



(4)

The thermal reaction of $Ti(C_5H_5)_2(C_6H_5)_2$ with nitrogen is paralleled by the similar result obtained with carbon dioxide[15]. Treatment of dicyclopentadienyldiphenyltitanium(IV) with CO_2 in xylene solution at 80–90° yielded a compound of formula $Ti(C_5H_5)_2(C_6H_4CO_2)$. The latter was shown by an X-ray diffraction study, to have the

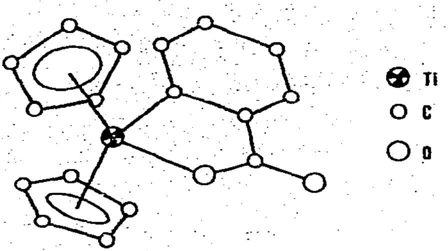


Fig. 1. Molecular structure of $Ti(C_5H_5)_2(C_6H_4CO_2)$ schematically drawn. (Adapted from I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya, G.G. Aleksandrov, Yu.T. Struchkov and M.E. Volpin, *Chem. Commun.*, (1971) 972).

structure indicated schematically in Fig. 1. Again, formation of the complex was suggested to take place via insertion of CO_2 into the titanium—carbon bond of the coordination-stabilized phenylene intermediate shown on the left-hand side of eq. (3).

It has been pointed out[16] that a group of transition metals in combination with different reducing agents will perform reductions of N_2, KCN, cyclohexylisocyanide and hexyne-1 to products in much the same way the naturally occurring nitrogenase would do. $Ti(C_5H_5)_2Cl_2$ with sodium naphthalene was one of the active combinations, according to experimental results reported in an earlier paper by the same group of research people[17].

II. SURVEY OF NEW COMPOUNDS AND REACTIONS

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

Much progress has been made in this field with the determination of the molecular structure of tetrabenzyltitanium(IV) in the solid state by X-ray diffraction methods. The results were obtained by two different research groups: the investigation[18] carried out at −40° has to be considered of better quality than that at room temperature[19] because of higher thermal motion in the latter. Despite that structural data from the two research groups are substantially in agreement. The molecular structure of tetrabenzyltitanium is schematically shown in Fig. 2. The essential features of this compound in the solid state are as follows.

(i) There is no question of the organic residue being bonded to titanium by an allylic type of arrangement involving three of the carbon atoms.

(ii) Some of the angles at the methylene carbons are much smaller than the tetrahedral value (92°, 98°, 109°, 115° according to ref. 18; 88°, 98°, 108°, 116° according to ref. 19). The corresponding distances between the central metal atom and the β-carbon atom of the organic residue are significantly small. This suggests an interaction between empty *d* orbitals of the titanium and the π-electron density at the β-carbon atom.

The interaction mentioned at point (ii) may explain most of the properties of tetra-

---

* A one-electron donor is a σ-bonded alkyl, aryl or cyclopentadienyl group. Hydrido species are also included.

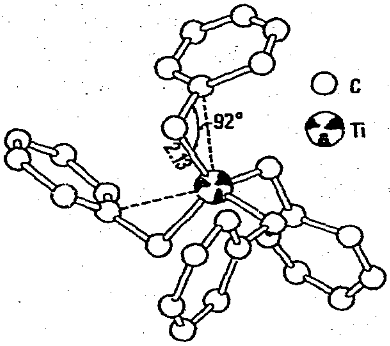


Fig. 2. Molecular structure of $Ti(CH_2C_6H_5)_4$ showing that the angle at one of the four methylene groups is 92°. (From G.R. Davies, J.A.J. Jarvis and B.T. Kilbourn, *Chem. Commun.*, (1971) 1511. See also I.W. Bassi, G. Allegra, R. Scordamaglia and G. Chioccola, *J. Amer. Chem. Soc.*, 93 (1971) 3787.)

benzyltitanium, in particular its deep-red colour and its thermal stability. The colour may be attributed to a charge-transfer type of absorption and the thermal stability assigned to a decreased tendency to the homolytic cleavage of the titanium–carbon bond as a consequence of the net increase of bond order.

It is interesting to note that in the corresponding zirconium derivative, which will be discussed in a later section, the angles at the methylene carbon atoms are even smaller[20] (85°, 90°, 92° and 101°) than in the titanium case.

Chemical and physical properties of tetrabenzyltitanium(IV) have been studied[21,22]. Giannini and coworkers[21] have reported reactions with proton-active substances, such as hydrogen halides and methanol, presumably taking place by electrophilic attack at the methylene carbon atom. With CH_3OD, $C_6H_5CH_2D$ is the product of the reaction, as expected. Tetrabenzyltitanium undergoes reactions also with carbon monoxide and isocyanides, as shown by work carried out in our laboratories at the University of Pisa. These reactions have probably to be classified as nucleophilic in character with attack at the metal. The reaction with CO was carried out with the aim at synthesizing a still unknown binary carbonyl of titanium. The reaction, which is very prompt, does not yield the desired product but rather a complicated mixture of substances which are still under investigation[23]. Giannini and coworkers have also reported[21] the thermal decomposition of $Ti(CH_2C_6H_5)_4$. Titanium(III) was obtained in solution, accompanied by the formation of toluene. The latter must arise from an intramolecular hydrogen shift, since no deuterated toluene was obtained when the decomposition was carried out in deuterated solvents. Tetrabenzyltitanium(IV) has ^1H NMR absorptions (room temperature, toluene-d_8) at $\tau 7.21$ (methylene protons), $\tau 3.39$ (*ortho* ring protons) and $\tau 2.9$ (*meta* and *para* ring protons). The absorption for the *ortho* protons is significantly shifted upfield with respect to the *meta* and *para* protons, a fact that may be now perhaps be explained on the basis of the established X-ray structure of the compound suggesting an interaction of the electron π-density of the aromatic ring with empty *d* orbitals of the metal.

Thiele and coworkers[22] have studied in detail the infrared spectrum (nujol and deuterated paraffin mulls) of tetrabenzyltitanium and found that the stretchings of the methylene group are at 2863 and 2930 cm^{-1} which would correspond to an sp^3 hydridized carbon atom. This is therefore substantially in agreement with the reported X-ray structure.

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

The full details of the X-ray work on tetracyclopentadienyltitanium(IV) have appeared[24]. The molecule contains two symmetrically bonded (*pentahapto*) cyclopentadienyl rings, the other two being σ-bonded (*monohapto*). The structure of the compound is schematically drawn in Fig. 3. The coordination around titanium is approximately tetrahedral, although substantial distortions are observed. For example, the C—Ti—C angle (at the two *monohapto* cyclopentadienyl rings) is 86.3°. The titanium—carbon distances for two of the cyclopentadienyl rings are all in the range 2.359—2.400 Å, thus showing the symmetrical arrangement. It has been pointed out[24] that this is one of the few cases in which the symmetrical arrangement of C_5H_5 rings has been demonstrated crystallographically.

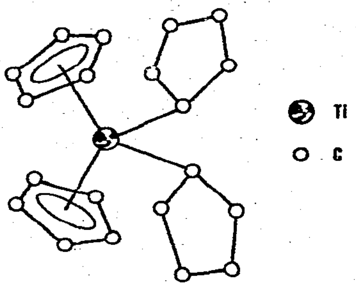


Fig. 3. Molecular structure of tetracyclopentadienyltitanium(IV). (Adapted from J.L. Calderon, F.A. Cotton, B.G. DeBoer and J. Takats, *J. Amer. Chem. Soc.*, 93 (1971) 3592.)

In solution $Ti(C_5H_5)_4$ has fluxional behaviour[25]. The ^1H NMR spectra have been studied from +80° to −140°. The temperature dependence of the spectra observed and their line shapes were interpreted as being due, *inter alia*, to interchange of the cyclopentadienyl rings. The corresponding activation energy for this process was calculated to be E_a = 16.1 ± 0.5 kcal/mole.

The structural investigation of $Ti(C_5H_5)_4$ has shown that this is a molecule belonging to the general class $Ti(C_5H_5)_2X_2$ (X = F, Cl, Br, I, alkyl and so on). In agreement with this view, the structure of $Ti(C_5H_5)_2(C_6H_5)_2$ was shown[26] to contain two symmetrically bonded cyclopentadienyl rings and two σ-bonded phenyl rings. Fig. 4 is a schematic representation of the molecular structure. Even some of the structural parameters are similar to those of $Ti(C_5H_5)_4$.

Wilkinson and coworkers have applied their concept of elimination-stabilized alkyl groups to titanium and have prepared[27] the compound $Ti(C_5H_5)_2(CH_2SiMe_3)_2$ (Me = CH_3); this was reported as a yellow crystalline substance slightly sensitive to air. The preparation involves the treatment of $Ti(C_5H_5)_2Cl_2$ with the appropriate alkyllithium:

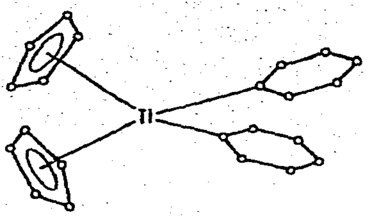
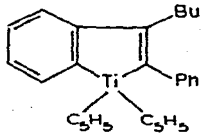


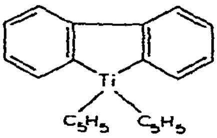
Fig. 4. Molecular structure of $Ti(C_5H_5)_2(C_6H_5)_2$ schematically drawn. (From V. Kocman, J.C. Rucklidge, R.J. O'Brien and W. Santo, *Chem. Commun.*, (1971) 1340.)

$$Ti(C_5H_5)_2Cl_2 + 2LiCH_2SiMe_3 \xrightarrow[-78^\circ\ \text{r.t.}]{(C_2H_5)_2O} 2LiCl + Ti(C_5H_5)_2(CH_2SiMe_3)_2 \quad (5)$$

Rausch and Klemann[28] have prepared two new metallocyclic compounds, namely the titanaindene(IV) and the titanafluorene(V) derivatives. The authors point out that the two compounds have a much higher thermal stability than the corresponding non-cyclic derivatives, such as, for example, $Ti(C_5H_5)_2(C_6H_5)_2$.



(IV)



(V)

Insertion of sulfur dioxide into the titanium–carbon bonds of $Ti(C_5H_5)_2(CH_3)_2$, $Ti(C_5H_5)_2(C_6H_5)_2$ and $Ti(C_5H_5)_2(CH_3)Cl$ was observed[29]. The reactions were the following:

$$Ti(C_5H_5)_2(CH_3)_2 + 2SO_2 \xrightarrow[\text{petr. ether}]{-78^\circ} Ti(C_5H_5)_2(O_2SCH_3)_2 \quad (6)$$

$$Ti(C_5H_5)_2(C_6H_5)_2 + 2SO_2 \xrightarrow[\text{room temperature}]{CH_2Cl_2} Ti(C_5H_5)_2(O_2SC_6H_5)_2 \quad (7)$$

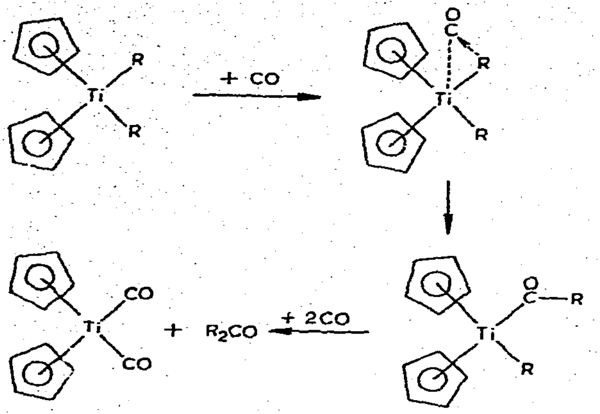
$$Ti(C_5H_5)_2(CH_3)Cl + SO_2 \xrightarrow[-78^\circ]{CH_2Cl_2} Ti(C_5H_5)_2(O_2SCH_3)Cl \quad (8)$$

The products, on the basis of their infrared spectra, were suggested to be oxygen-bonded sulphinato complexes.

It is interesting to note that also carbon monoxide insertion reactions into titanium–carbon bonds were successfully carried out. According to work by Floriani and Fachinetti in these laboratories at the University of Pisa, dicyclopentadienyldibenzyltitanium(IV) undergoes reaction with CO under mild conditions[30], similar to $Ti(CH_2C_6H_5)_4$: in this case, however, well defined products were obtained. The reaction occurs according to the following stoichiometry:

$$Ti(C_5H_5)_2(CH_2C_6H_5)_2 + 3\,CO \rightarrow Ti(C_5H_5)_2(CO)_2 + (C_6H_5CH_2)_2CO \quad (9)$$

The carbonylation to $Ti(C_5H_5)_2(CO)_2$ was suggested to occur via pre-coordination of CO to titanium, followed by alkyl migrations (Scheme 1).



Scheme 1. Proposed[30] mechanism for the carbonylation of $Ti(C_5H_5)_2(CH_2C_6H_5)_2$.

Scheme 1 postulates the intermediate formation of an acyl derivative of titanium(IV). Increased credibility for this reaction scheme was obtained by the preparation of some acyl derivatives of titanium(IV). These compounds were obtained either by the reaction of $Ti(C_5H_5)_2(CO)_2$ with acyl chloride[31]:

$$Ti(C_5H_5)_2(CO)_2 + RCOCl \rightarrow 2\,CO + Ti(C_5H_5)_2(COR)Cl \quad (10)$$

$(R = CH_3, C_6H_5)$

or by carbonylation of $Ti(C_5H_5)_2(CH_3)Cl$ and $Ti(C_5H_5)_2(CH_2C_6H_5)Cl$ with carbon monoxide[32]:

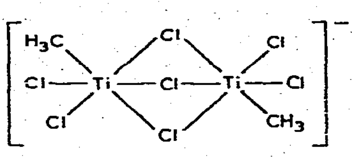
$$Ti(C_5H_5)_2(R)Cl + CO \rightarrow Ti(C_5H_5)_2(COR)Cl \quad (11)$$

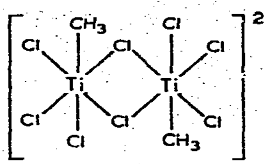
$(R = CH_2C_6H_5)$

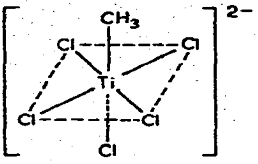
It is important noting that reactions (10) and (11) yielded the first acyl derivatives of titanium reported in the literature.

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

Confirming the generally accepted view that saturation of coordination sites increases the stability of alkyltitanium derivatives, thermally stable adducts of $TiCH_3Cl_3$ have been reported[33,34,35]. The reactions of the methyltitanium(IV) derivative with halide ions have been studied[33,34]. Anionic dimeric and monomeric products were obtained; structural assignments were mainly based on infrared measurements. The reactions were carried out in dichloromethane at 0°.


(VI)


(VII)


(VIII)

The colours of the compounds are: (VI) dark violet, (VII) light brown, (VIII) deep blue.

Results complementary to those obtained earlier by Clark and McAlees[36] and by Thiele and coworkers[37] were reported by Fowles and coworkers[35]. Methyltrichlorotitanium(IV) yields 1/1 adducts and 1/2 adducts with a number of oxygen-, sulfur-, nitrogen-, and phosphorous-donor ligands. In general, adducts were formed in which the central metal atom has six coordination. On the other hand, with tetrahydrofuran, α-picoline and triphenylphosphine, 1/1 adducts were also isolated of formula $TiCH_3Cl_3 \cdot L$ and cryoscopic measurements have shown that these compounds are monomeric in benzene solution. Thus, pentacoordinate titanium(IV) was suggested in these cases. This is consistent with the similar results obtained[38] with $TiCl_4$. The 1/1 adducts of the tetrachloride with PMe_2Ph and $P\text{-}n\text{-}Bu_3$ ($Me = CH_3$) were found to be monomeric in benzene. Of course, this does not exclude that the compounds might be dimeric in the solid state.

The kinetics of the thermal decompositions of the dicyclopentadienyl derivatives $Ti(C_5H_5)_2(R)Cl$ were reported[39]. The decompositions were found to be first-order and accordingly a monomolecular mechanism was suggested involving the formation of an active species suggested to be radical in character; however, no free radicals as such were believed to be formed. It is interesting noting that the benzyl derivative is the least stable of the compounds studied. This contrasts with the behaviour of $Ti(C_5H_5)_2(CH_2C_6H_5)_2$ and $Ti(CH_2C_6H_5)_4$: it was suggested that in the case of the less sterically hindered derivatives of the type $Ti(C_5H_5)_2(R)Cl$ a π-allyl type of intermediate would form more readily. This explanation is, however, scarcely convincing because exactly the same argument may be proposed to explain an increased thermal stability.

D. Allyl derivatives of titanium(IV)

Dialkylamido-allyl derivatives of titanium(IV) were obtained[40] by Grignard reactions, such as, for example, the following:

$$TiBr(NEt_2)_3 + MgBrC_3H_5 \xrightarrow{(C_2H_5)_2O} MgBr_2 + TiC_3H_5(NEt_2)_3 \qquad (12)$$

2-Methylallyl and 3-methylallyl derivatives were similarly obtained. It is interesting noting that the infrared spectra suggest the presence of σ-bonded allyl groups; on the other hand, the ^1H NMR spectra are suggestive of fluxional behaviour in solution.

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

Titanocene diazide was prepared[41] by the following reactions:

$$\mathrm{Ti(C_5H_5)_2Cl_2 + 2NaN_3 \xrightarrow{H_2O} 2\,NaCl + Ti(C_5H_5)_2(N_3)_2} \qquad (13)$$

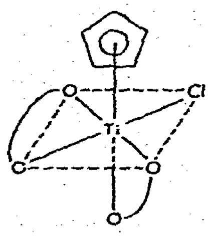
$$\mathrm{Ti(C_5H_5)_2Cl_2 + 2NaN_3 \xrightarrow{THF} 2\,NaCl + Ti(C_5H_5)_2(N_3)_2} \qquad (14)$$

Only by reaction (14), in the presence of trace amounts of $AlCl_3$, the diazide could be obtained in a pure form. The diazido complex had a surprisingly high thermal stability: it could be sublimed *in vacuo* at 200°.

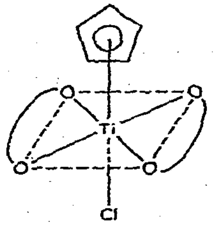
The reactions of dicyclopentadienyl derivatives of the type $Ti(C_5H_5)_2X_2$ (especially with X = Cl) with potentially chelating substances containing active protons have been investigated. $Ti(C_5H_5)_2Cl_2$ reacts[42] with acetylacetone in the presence of triethylamine giving a bis(acetylacetonato) complex and simultaneous elimination of one cyclopentadienyl group as cyclopentadiene. The reaction is the following:

$$\mathrm{Ti(C_5H_5)_2Cl_2 + Et_3N + 2\,C_5H_8O_2 \rightarrow C_5H_6 + NEt_3HCl + Ti(C_5H_5)Cl(C_5H_7O_2)_2} \quad (15)$$

A similar reaction was also carried out with benzoylacetone, thus obtaining a product having the same composition, $Ti(C_5H_5)Cl(Chelate)_2$. These titanium chelates are nonelectrolytes and, by analogy with similar zirconium compounds to be discussed later, were assumed to be monomeric. From the ^1H NMR spectra at variable temperatures, suggestions about the stereochemistry of these compounds were made. Considering the cyclopentadienyl ring as a monodentate ligand, the compounds were regarded, to a first approximation, as containing hexacoordinate titanium. Two geometrical isomers (IX) and (X), respectively *cis* and *trans*, may then be considered. The titanium-acetylacetonato complex was found to consist of a mixture of the two isomers at low temperatures (below −20°) and further, isomerization and ligand interchange were observed by ^1H NMR measurements at variable temperatures.



(IX)



(X)

Also the reactions of $Ti(C_5H_5)_2X_2$ (X = F, Cl, Br) with 8-hydroxyquinoline were investigated[43]:

$$\mathrm{Ti(C_5H_5)_2F_2 + 2\,C_9H_7NO \rightarrow 2\,C_5H_6 + TiF_2(C_9H_6NO)_2} \qquad (16)$$

$$Ti(C_5H_5)_2Cl_2 + 3\,C_9H_7NO \rightarrow C_9H_7NO{\cdot}HCl + C_5H_6 + Ti(C_5H_5)Cl(C_9H_6NO)_2 \quad (17)$$

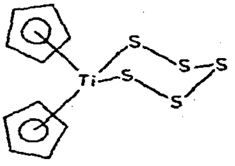
$$Ti(C_5H_5)_2Br_2 + 3\,C_9H_7NO \rightarrow C_9H_7NO{\cdot}HBr + C_5H_6 + Ti(C_5H_5)Br(C_9H_6NO)_2 \quad (18)$$

The reactions were carried out in acetonitrile as solvent at room temperature and resulted in very good yields of the products. The chloro derivative had been obtained earlier by different routes. The ^1H NMR spectra did not show any change in the temperature range from +40° to −60° which was taken as indication of non-fluxional behaviour of the cyclopentadienyl ring.

The occurrence of reactions (15)–(18) suggests that cleavage of the titanium–cyclopentadienyl bond can occur in the presence of proton active substances. This is confirmed by results obtained recently by Nogina and coworkers[44]. A series of monocyclopentadienyl compounds of the type $Ti(C_5H_5)(OC_6H_4R)_3$ were prepared. These compounds would undergo cleavage of the titanium–cyclopentadienyl bond with formation of C_5H_6 in the presence of water or alcohol.

A detailed ^1H and ^{19}F NMR study of several monocyclopentadienyl derivatives of types $Ti(C_5H_5)(OC_6H_4R)_3$ and $Ti(C_5Me_5)(OC_6H_4R)_3$ has appeared[45]. In general it was found that the resonance of the cyclopentadienyl ring protons (including the methyl groups of the pentamethylcyclopentadienyl derivatives) is little sensitive to the presence of *meta-* or *para-*substituents in the aromatic ring. The influence of the solvent on the ^{19}F NMR spectra has been studied.

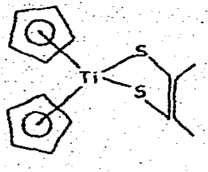
Full details concerning the X-ray structure of $Ti(C_5H_5)_2S_5$ have been published[46]. A preliminary note of this work had appeared last year[47]. The molecular structure is (XI) and consists of two symmetrically bonded cyclopentadienyl rings and a TiS_5 six-membered ring. In the solid state the TiS_5 ring has a chair conformation.



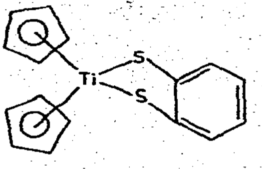
(XI)

^1H NMR spectra at variable temperatures of dithiolato complexes (XII), (XIII) and (XIV) have been measured[48]. These molecules, as judged from the observation of the resonances due to the cyclopentadienyl protons, were found to be non-rigid in a certain temperature range. Thus, for example, compound (XII) exhibits two distinct singlets at −50°, which is in agreement with the presence of non-equivalent cyclopentadienyl ligands in view of the conformation of the TiS_2C_2 ring. The separation between the two singlests is 38 cps. At higher temperature, however, signal broadening occurred and finally a single resonance for the cyclopentadienyl rings was observed at room temperature (36°). The coalescence temperature was +10°.

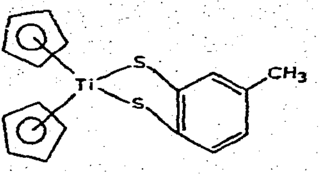
The molecular structure of a titanocene dichloro derivative in which the two cyclopen-



(XII)



(XIII)



(XIV)

tadienyl rings are connected by a $-CH_2-CH_2-CH_2-$ chain has been solved by X-ray diffraction methods at room temperature[49]. This molecule was chosen in order to minimize the intramolecular motions of the cyclopentadienyl rings. The compound was $Ti[C_5H_4(CH_2)_3C_5H_4]Cl_2$ and its structure is schematically drawn in Fig. 5. Contrary to what had been found[46] for $Ti(C_5H_5)_2S_5$, the C–C distances in the two cyclopentadienyl rings were found to be equal within experimental error with an average value of 1.399 Å. It was therefore concluded that the differences found for $Ti(C_5H_5)_2S_5$ were due to an artifact related to the librational motion of the rings.

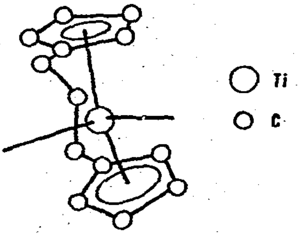


Fig. 5. Molecular structure of $TiCl_2[C_5H_4(CH_2)_3C_5H_4]$. (Adapted from B.R. Davis and I. Bernal, *J. Organometal. Chem.*, 30 (1971) 75.)

^{13}C NMR measurements have been carried out on a vast class of organometallic compounds of transition elements including, for titanium, $Ti(C_5H_5)_2Cl_2$ and $Ti(C_5H_5)_2(C_6H_5)_2$[50]. The shifts were observed over a wide range, thus making it possible to foresee that this technique should be very useful for structural assignments in organometallic chemistry.

F. Titanium(III) derivatives with one-electron donors

Following some earlier work[51] aimed at the preparation of $Ti(CH_2C_6H_5)_3$, Schäfer and Thiele have reacted $TiCl_3$ with several classical alkylating agents[52]. Chemical evidence for the existence of $Ti(CH_3)_3$ and some triaryltitanium(III) in solution was obtained. However, the high thermal instability of these compounds prevented their isolation in an analytically pure form. Diphenylchlorotitanium(III), obtained by the following reaction, was isolated as its etherate:

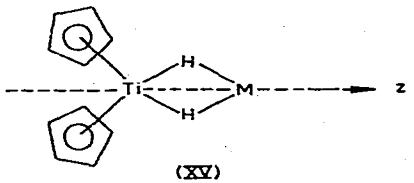
$$TiCl_3{\cdot}3THF + 2\ LiC_6H_5 \rightarrow 2\ LiCl + 3THF + TiCl(C_6H_5)_2 \qquad (19)$$

Subsequent crystallization from diethyl ether yielded the final product, $TiCl(C_6H_5)_2{\cdot}3\ O(C_2H_5)_2$, in an analytically pure form. The compound is deep red and decomposes around −40°.

The preparation of methyldichlorotitanium(III) free from additional electron donors has been reported, although only in a preliminary note[53]. The compound was obtained by the following reaction:

$$2\,\mathrm{TiC_3(CH_3)} + \mathrm{Hg[Si(CH_3)_3]_2} \rightarrow \mathrm{Hg} + 2\,\mathrm{TiCl_2(CH_3)} + 2\,\mathrm{SiCl(CH_3)_3} \qquad (20)$$

ESR measurements on hydrido complexes of titanium(III) have been reported[4]. These are complexes of formula $Ti(C_5H_5)_2H_2M$ (M = Li, Na, MgBr, $AlCl_2$, AlH_2) and they are believed to have the general structure (XV), although in the case of the lithium and sodium derivatives the ionic character is considered to be predominant. The results were interpreted as suggesting the localization of the unpaired electron in these d^1 systems mainly in the d_{z^2} orbital.



(XV)

G. *Organometallic derivatives of titanium(III) with carbon, nitrogen, phosphorous, oxygen, sulfur and halogen lone-pair donors*

ESR measurements have been published[54] on several dicyclopentadienyl derivatives of titanium(III). The compuonds had nitrogen, phosphorous, arsenic, germanium, tin, lead, chlorine, carbon and hydrido donors beside the cyclopentadienyl rings. The compounds were not isolated, and the ESR measurements were carried out on their frozen tetrahydrofuran solutions. The formulae assigned to the complexes were the following:

$[Ti(C_5H_5)_2(NHPh)_2]^-$, $[Ti(C_5H_5)_2(NCH{=}CHCH{=}CH)_2]^-$, $Ti(C_5H_5)_2PbPh_3$,

$Ti(C_5H_5)_2Cl$, $Ti(C_5H_5)_2H_2{\cdot}MgCl$, $Ti(C_5H_5)_2H(PPh_3)$, $[Ti(C_5H_5)_2(CH_2Ph)_2]^-$,

$[Ti(C_5H_5)_2(ER_2)_2]^-$, $[Ti(C_5H_5)_2(ER_3)_2]^-$ (For ER_2: E = P, R = Me, Ph ;

E = As, R = Ph. For ER_3: E = Ge, Sn, R = Ph).

Four-coordinate titanium was assumed for all these complexes. Thus, for the apparently three-coordinate compounds, the fourth coordination position was suggested to be occupied by a solvent molecule. As for the case of the analogous hydrido complexes discussed above, the experimental parameters were accommodated by a model in which the unpaired electron was largely localized in the d_{z^2} orbital.

Alkylamidocyclopentadienyl derivatives of titanium(III) have been reported[55]. The compounds obtained were bis[dicyclopentadienyldimethylamidotitanium(III)] and bis[cyclopentadienylbis(dimethylamido)titanium(III)]. They were prepared by the following reactions:

$$[Ti(C_5H_5)_2Cl]_2 + 2\,LiNMe_2 \xrightarrow{THF} 2\,LiCl + \underset{(XVI)}{[Ti(C_5H_5)_2NMe_2]_2} \qquad (21)$$

$$[Ti(NMe_2)_3]_2 + 2\,C_5H_6 \xrightarrow{benzene} 2\,NHMe_2 + [Ti(C_5H_5)(NMe_2)_2]_2 \qquad (22)$$

Preliminary results concerning these compounds had been reported earlier[56]. Evidence for the formation of a monomeric tetrahydrofuran adduct of (XVI) was obtained.

The dimethylamido groups bonded to titanium(III) can be split off by protic reagents[57] The following reactions were carried out:

$$[Ti(C_5H_5)(NMe_2)_2]_2 + 4\,C_2H_5OH \rightarrow [Ti(C_5H_5)(OC_2H_5)_2]_2 + 4\,NHMe_2 \qquad (23)$$

$$[Ti(C_5H_5)_2(NMe_2)]_2 + 2\,C_6H_5OH \rightarrow [Ti(C_5H_5)_2(OC_6H_5)]_2 + 2\,NHMe_2 \qquad (24)$$

$$[Ti(C_5H_5)_2(NMe_2)]_2 + 2\,C_6H_5SH \rightarrow [Ti(C_5H_5)_2(SC_6H_5)]_2 + 2\,NHMe_2 \qquad (25)$$

The same paper[57] reports the preparation of dicyclopentadienylethoxytitanium(III) obtained by a metathetical reaction from the corresponding chloro derivative:

$$[Ti(C_5H_5)_2Cl]_2 + 2\,LiOC_2H_5 \rightarrow 2\,LiCl + \underset{(XVII)}{[Ti(C_5H_5)_2(OC_2H_5)]_2} \qquad (26)$$

Compound (XVII) was suggested to be an ethoxy-bridged dimer, in the solid state in agreement with the low magnetic moment (1.3 BM at 21°); no molecular weight measurements were carried out on this compound because of its low solubility. Also interesting were the insertion reactions into the titanium–nitrogen bonds of $[Ti(C_5H_5)(NMe_2)_2]_2$ and $[Ti(C_5H_5)_2(NMe_2)]_2$, such as for example:

(27)

The dimethyldithiocarbamato complex obtained by reaction (27) was isolated at its CS_2-adduct. The unsolvated product had been prepared earlier by a different route[57a].

Monocyclopentadienyl derivatives of titanium(III) have been reported[58,59]. The general procedure used for the preparation of these compounds was the reduction of the corresponding titanium(IV) derivatives with zinc at room temperature in tetrahydrofuran. The following reactions were carried out:

$$2\,Ti(C_5H_5)X_3 + 2\,THF + Zn \xrightarrow{THF} ZnX_2 + 2\,Ti(C_5H_5)X_2(THF) \qquad (28)$$

(X = Cl, Br, I, OMe, OEt)

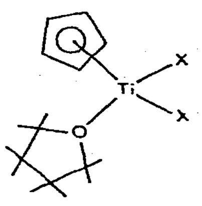
$$2\,Ti(C_5H_5)X_2(OR) + 2\,THF + Zn \xrightarrow{THF} ZnX_2 + 2\,Ti(C_5H_5)X(OR)(THF) \qquad (29)$$

(X = Cl, Br)

$$2\,Ti(C_5H_5)X_2(SR) + 2\,THF + Zn \xrightarrow{THF} ZnX_2 + 2\,Ti(C_5H_5)X(SR)(THF) \quad (30)$$

$(X = Cl, Br)$

The products obtained by reactions (28)–(30) with OR or OS ligands have a molecular complexity higher than that shown in the equations, even in tetrahydrofuran solution[58]. On the other hand, the compounds with halogen ligands only are monomeric by ebullioscopy in tetrahydrofuran and the pseudo-tetrahedral arrangement of ligands (XVIII) has been proposed[59] for them. This is also in agreement with the magnetic susceptibility measurements showing that the bromo derivative has a μ_{eff} substantially independent of temperature, as expected for a magnetically dilute substance. By heating at 120–150° *in vacuo*, the tetrahydrofuran adducts lose THF and the complexes $Ti(C_5H_5)X_2$ ($X = Cl, Br$) were obtained[59]. The analytical results for the iodo compound were not satisfactory, thus showing that partial decomposition had occurred during the process of THF elimination.



(XVIII)

Interestingly enough, the chloro and bromo derivatives have a somewhat unusual magnetic behaviour since the magnetic moments slightly increase at decreasing temperatures above 1.73 BM ($X = Cl$), which is the expected value for one unpaired spin. The increase was more pronounced for the bromo derivative. On the basis of these findings, tetracoordinate titanium for compounds $Ti(C_5H_5)X_2$ should be excluded. If these compounds were dimers with tetracoordinate titanium, one would have expected an antiferromagnetic behaviour, similar to what had been found[60] previously for $[Ti(C_5H_5)_2Cl]_2$.

H. Bimetallic derivatives of titanium

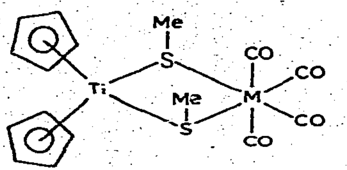
This section contains those compounds in which, beside titanium, a transition element is also present. It may be recalled that bimetallic derivatives of titanium[54] (containing non transition elements, such as lead and tin) have been discussed earlier at section G.

Bimetallic derivatives of formula $(C_5H_5)_2Ti(SR)_2M(CO)_4$ were prepared by the following general reaction[61]:

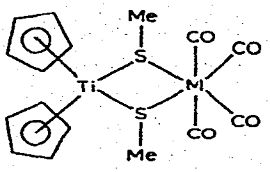
$$Ti(C_5H_5)_2(SR)_2 + M(CO)_4(\text{norbornadiene}) \rightarrow \text{norbornadiene} + (C_5H_5)_2Ti(SR)_2M(CO)_4 \quad (31)$$

$(R = Me, M = Cr, Mo, W; R = Ph, M = Mo, W)$

Previous work in this area has been reported[61a,61b]. The tetracarbonyl compounds were found to have four infrared CO stretching vibrations, thus suggesting a *cis* arrangement of the carbonyl groups. It has been found[61] that the ^1H NMR spectra at room temperature for the methyl derivatives $(C_5H_5)_2Ti(SMe)_2M(CO)_4$ (M = Cr, Mo, W) consist of three peaks for the cyclopentadienyl protons. This has been interpreted as being due to the presence of two different geometrical isomers in solution, namely the *cisoid* isomer (XIX) and the *transoid* isomer(XX), with the former being predominant.



(XIX)



(XX)

It will be recognized that the two cyclopentadienyl rings (which are to be considered freely rotating) are not equivalent in the *cisoid* form (XIX), thus giving rise to two different resonances in the NMR spectrum.

The conclusions drawn on the basis of the NMR and IR results[61] have been confirmed by the X-ray study[62] carried out on the methyl derivative $(C_5H_5)_2Ti(SMe)_2Mo(CO)_4$. The compound was found to have the *cisoid* form in the solid state. The molecular structure of the compound is schematically drawn in Fig. 6. It will be seen that the titanium—molybdenum distance is 3.32 Å. This distance is somewhat larger than usually found for metal—metal bonds. However, the M—S—M bond angle is 83° and this was taken as good indication of titanium—molybdenum interaction in this compound.

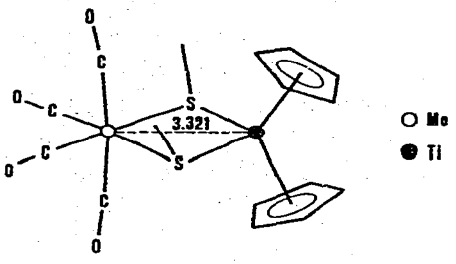


Fig. 6. Molecular structure of $(C_5H_5)_2Ti(SMe)_2Mo(CO)_4$ schematically drawn. (From G.R. Davies and B.T. Kilbourn, *J. Chem. Soc. A*, (1971) 87.)

Vibrational and electronic spectra of compounds $(C_5H_5)_2W(SPh)_2M(CO)_4$ (M = Cr, Mo, W) have been analyzed[63] in comparison with those of $(C_5H_5)_2Ti(SR)_2Mo(CO)_4$ (R = Me, Ph). The Ti—Mo compounds have unusually high CO stretching vibrations suggesting a transfer of charge from molybdenum to titanium.

Titanium—copper complexes of formula $[(C_5H_5)_2Ti(SR)_2CuX]_n$ (R = Ph, X = Cl; R = Me, Ph, X = Br) were prepared[64] by the following general reaction:

$$Ti(C_5H_5)_2(SR)_2 + CuX(COD) \rightarrow COD + \frac{1}{n}[(C_5H_5)_2Ti(SR)_2CuX]_n \qquad (32)$$

(COD = 1,5-cyclooctadiene)

The electronic spectra of the bimetallic complexes show a low-energy band between 15300 and 17300 cm^{-1}, depending on the nature of the groups R and X, which may be interpreted as a charge-transfer band Cu → Ti. As a consequence, a certain amount of titanium–copper interaction has been suggested in these compounds.

A bimetallic derivative of titanium and molybdenum was obtained[67] by the following reactions:

$$[Ti(C_5H_5)_2Cl]_2 + 2\,Na[Mo(C_5H_5)(CO)_3] \rightarrow 2\,NaCl + (C_5H_5)_2TiMo(CO)_3(C_5H_5) \quad (33)$$

$$[Ti(C_5H_5)_2(NMe)_2]_2 + 2\,Mo(C_5H_5)H(CO)_3 \rightarrow 2NHMe_2 + 2(C_5H_5)_2TiMo(CO)_3(C_5H_5) \quad (34)$$

The compound is paramagnetic with $\mu_{eff} = 1.74$ BM corresponding to one unpaired electron per molecule.

I. Organometallic derivatives of titanium(II) and titanium(0)

The controversy still existing about the structure of the so-called "titanocene dimer" has been discussed earlier when dealing with the problem of nitrogen fixation. It was also mentioned earlier that a metastable form of the titanocene dimer could be obtained[7] which had a reactivity towards H_2, CO and N_2 much more pronounced than that of the more frequently encountered titanocene dimer. Support to the existence of the metastable form of the dimer was found[65] in the successful preparation of the corresponding pentamethyl derivative. The following sequence of reactions was carried out:

$$Ti(C_5Me_5)_2Cl_2 + 2\,LiCH_3 \rightarrow 2\,LiCl + Ti(C_5Me_5)_2(CH_3)_2 \quad (35)$$

$$Ti(C_5Me_5)_2(CH_3)_2 \xrightarrow[\text{toluene}]{100^\circ} TiCH_2(C_{10}Me_{10}) + CH_4 \quad (36)$$

$$TiCH_2(C_{10}Me_{10}) + H_2 \xrightarrow[\text{hexane}]{0^\circ} Ti(C_5Me_5)_2 + CH_4 \quad (37)$$

The nature of the product of formula $TiCH_2(C_{10}Me_{10})$ obtained by reaction (36) was not completely clarified. On the basis of NMR results, the decamethyltitanocene complex resulting from reaction (37) was believed to exist in solution in a dimer–monomer equilibrium:

$$2\,Ti(C_5Me_5)_2 \rightleftharpoons [Ti(C_5Me_5)_2]_2 \quad (38)$$

Decamethyltitanocene reacts rapidly with CO in toluene solution yielding the corresponding dicarbonyl derivative:

$$Ti(C_5Me_5)_2 + 2\,CO \rightarrow Ti(C_5Me_5)_2(CO)_2 \quad (39)$$

The dicarbonyl compound has two bands in the infrared at 1930 and 1850 cm^{-1}, *i.e.*, at wavenumbers lower than those found for $Ti(C_5H_5)_2(CO)_2$ (1975 and 1897 cm^{-1}). This is consistent with the electron-pushing properties of the methyl groups promoting transmission of negative charge into the carbonyl groups. Reversible additions of hydrogen and nitrogen were observed with decamethyltitanocene. With nitrogen, the following reaction was found:

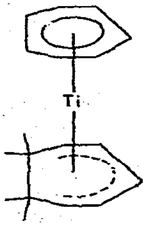
$$2\,Ti(C_5Me_5)_2 + N_2 \rightleftharpoons (C_5Me_5)_2TiNNTi(C_5Me_5)_2 \qquad (40)$$

Thermochemical measurements[66] have been carried out on the "titanocene dimer", as prepared by sodium amalgam reduction of $Ti(C_5H_5)_2Cl_2$. From combustion data, the average $Ti-C_5H_5$ dissociation energy was calculated to be 108 kcal/mole. This is much higher than the corresponding energy for the $V-C_5H_5$ bond which is 88 kcal/mole[66]. Of course, it has to be recalled that we are dealing with two compounds having most probably a completely different structure. In particular, the titanium derivative is dimeric, whereas the vanadium compound is a monomer.

A compound with two seven-membered rings bonded to formally zerovalent titanium has been prepared[67] by the reaction of $TiCl_3$ with the isopropyl Grignard reagent in the presence of cycloheptatriene:

$$TiCl_3 + i\text{-}C_3H_7MgBr + C_7H_8 \xrightarrow[-78^\circ]{(C_2H_5)_2O} Ti(C_7H_7)(C_7H_9) + \text{products} \qquad (41)$$

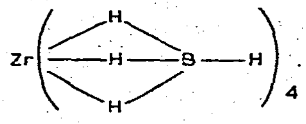
The formula of the compound was established by elemental analysis and by the observation of the parent peak at *m/e* 232 in the mass spectrum. The compound is diamagnetic and, on the basis of the ^1H NMR results, structure (XXI) was assigned to it with a planar C_7H_7 ring and a C_7H_9 ring in which only five of the carbon atoms would be involved in the bonding to titanium.



(XXI)

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

An electron-diffraction study of $Zr(BH_4)_4$ had appeared[68]. It is to be recalled that an earlier X-ray diffraction study[69] for the solid compound at −160° had shown that the molecule has the structure (XXII), *i.e.*, with the three-hydrogen bridge between zirconium and boron. It was therefore of interest to see whether this structure would persist also in the gas phase. The electron-diffraction study has concluded that structure (XXII) is the correct one also in the gas phase. Thus, the results of another electron-diffraction study[70] were confirmed, apart from some differences in bond distances.



(XXII)

The zirconium borohydride is a unique molecule since it contains the three-hydrogen bridge. This explains the earlier difficulties[71] in interpreting its infrared spectrum. The Raman spectrum of $Zr(BH_4)_4$ has now been measured in benzene solution[72]; it was found to be consistent with the tetrahedral arrangement of the ZrB_4 skeleton suggested by the X-ray diffraction and by the electron-diffraction studies mentioned above.

The mass spectrum of $Zr(BH_4)_4$ has been measured[73]. The molecular ion was detected and the predominant peaks were found to be those corresponding to $Zr(BH_4)_2^+$.

Some reactions of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ have been reported[74]. In particular, adducts with Lewis bases of the type $M(BH_4)_4L_n$ (M = Zr, Hf) were mentioned. $Zr(BH_4)_4$ in the presence of tetrahydrofuran was reported to give rise to the formation of $Zr(BH_4)_4 \cdot THF$. Adduct formation was also reported with triethylamine and pyridine.

Among tetraalkyl derivatives of zirconium and hafnium, the molecular structures of the tetrabenzyls are of considerable interest. As mentioned above, the X-ray diffraction study[20] of tetrabenzylzirconium(IV) has shown that the molecular structure (see Fig. 7) is similar to that of the corresponding titanium(IV) derivative. However, a remarkable difference is that the angles[18] at the methylene carbon atoms (88°, 92°, 93° and 101°) are even smaller than those of the titanium analogue. Further support to the suggestion that some kind of interaction exists between the aromatic ring carbon atom and empty *d* orbitals of the metal comes from the determination[18] of the angles at the methylene carbon atoms for $Sn(CH_2C_6H_5)_4$. In this case the angles are much closer to the tetrahedral value: 110°, 110°, 112° and 114°.

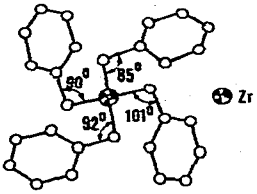


Fig. 7. Molecular structure of $Zr(CH_2C_6H_5)_4$ schematically drawn showing the angles at the methylene carbons. (From G.R. Davies, J.A.J. Jarvis, B.T. Kilbourn and A.J.P. Pioli, *Chem. Commun.* (1971) 677.)

The chemical shift difference[21] $\Delta\tau$ between *ortho* and *meta–para* ring protons is larger for $Zr(CH_2C_6H_5)_4$ ($\Delta\tau = 0.64$ ppm) than for the corresponding titanium analogue ($\Delta\tau = 0.50$ ppm) under comparable conditions. As in the case of titanium, tetrabenzylzirconium(IV) decomposes thermally giving rise to the formation of toluene: the latter was also in this case formed by a process of intramolecular hydrogen abstraction since in deuterated solvents no deuterated toluene was found.

The X-ray structure of $Zr(C_5H_5)_4$ had been reported last year[75] and described as containing one σ-bonded (*monohapto*) cyclopentadienyl ring and three symmetrically bonded (*pentahapto*) rings. However, Cotton and coworkers[24] have more recently argued that the data reported by Struchkov and coworkers for $Zr(C_5H_5)_4$ may be interpreted in a somewhat different way. Apart from the *monohapto* ring, of the other three rings only one would be symmetrically bonded as suggested by Struchkov and coworkers whereas the other two would probably resemble those highly dissymmetrical found in $Mo(C_5H_5)_3NO$[76].

The infrared and Raman spectra of $Zr(C_5H_5)_4$ and $Hf(C_5H_5)_4$ have been measured[77] in the solid state and in solution. It was concluded that the two compounds have a different structure and that for these compounds both symmetrically (*pentahapto*) and σ-bonded (*monohapto*) cyclopentadienyl rings could be suggested to be present. Of course, no definite conclusion could be drawn from this study about the details of bond arrangement for the non-monohapto rings.

Relatively few examples of zirconium—carbon σ-bonds have been reported in the literature. Thiele and Krüger have described[78] some reactions of ZrX_4 (X = Cl, Br) with zinc alkyls. Zirconium(IV) chloride and bromide react with $Zn(CH_3)_2$ in toluene to give monoalkylated zirconium(IV) derivatives:

$$2\,ZrX_4 + Zn(CH_3)_2 \xrightarrow[0^\circ]{\text{toluene}} ZnX_2 + 2\,ZrX_3(CH_3) \qquad (42)$$

$(X = Cl, Br)$

The monomethyl derivatives were isolated and analyzed as their diethyl ether adducts (XXI) and (XXII).

$ZrCl_3(CH_3)\cdot 2\,O(C_2H_5)_2$
(XXI)

$ZrBr_3(CH_3)\cdot 2\,O(C_2H_5)_2$
(XXII)

By using pyridine as solvent, two halogen atoms of the starting zirconium(IV) halide could be replaced:

$$ZrX_4 + ZnR_2 \xrightarrow[0^\circ]{\text{pyridine}} ZnX_2 + ZrX_2R_2 \qquad (43)$$

$(X = Cl, Br;\ R = CH_3, C_2H_5)$

The four dialkyl derivatives obtained by reaction (43) were isolated as their 2,2′-dipyridyl adducts. These are deep-blue substances, moderately stable to heat (they decompose at 110–120°), well soluble in pyridine.

The reactions of the zirconium(IV) hydrido derivatives, $Zr(C_5H_5)_2H(Cl)$ and $Zr(C_5H_5)_2H_2$, with mono- and disubstituted acetylenes have been reported[79]. These led to the preparation of σ-bonded alkenyl- and alkyl derivatives of zirconium(IV). Some of the compounds were liquid at room temperature and technical difficulties prevented the determination of their C—H content. Only those compounds for which satisfactory elemental analyses were reported are discussed here. $Zr(C_5H_5)_2H(Cl)$ reacted with diphenylacetylene to give a monomeric orange solid, for which structure (XXV) was suggested:

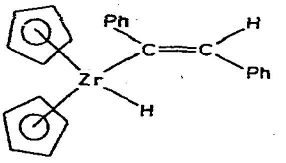
$$Zr(C_5H_5)_2H(Cl) + C_6H_5{-}C{\equiv}C{-}C_6H_5 \xrightarrow{\text{benzene reflux}} (XXV) \qquad (44)$$

Reactions with $Zr(C_5H_5)_2H_2$ were similarly carried out:

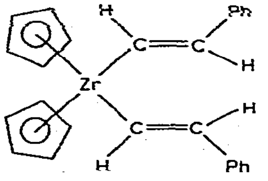
$$Zr(C_5H_5)_2H_2 + 2\ HC{\equiv}CC_6H_5 \rightarrow (XXVI) \qquad (45)$$

$$Zr(C_5H_5)_2H_2 + C_6H_5C{\equiv}CC_6H_5 \rightarrow (XXVII) \qquad (46)$$

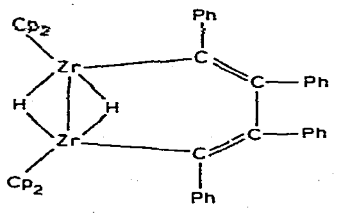
$$Zr(C_5H_5)_2H_2 + CH_3C_6H_4C{\equiv}CC_6H_4CH_3 \rightarrow (XXVIII) \qquad (47)$$



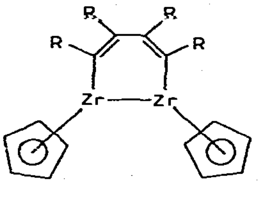
(XXV)



(XXVI)



(XXVII)



(XXVIII)

Structures (XXV)–(XXVIII) were assigned mainly on the basis of ^1H NMR spectra.

Some X-ray investigations of compounds containing metal–silicon bonds had revealed the presence of rather short metal–silicon bonds, *i.e.*, shorter than one would have expected on the basis of the sum of covalent radii. For example the rhodium–silicon distance in $RhH(Cl)(SiCl_3)(PPh_3)_2 \cdot SiHCl_3$ was reported[80] to be 2.203 Å and the iron–silicon distance in $Fe(C_5H_5)H(SiCl_3)_2(CO)$ was[81] 2.252 Å. Since we are dealing in these two cases with transition elements having a relatively high number of *d* electrons, the suggestion was made[81] that $d_\pi - d_\pi$ bond between filled *d* orbitals of the metal and empty *d* orbitals of silicon could be invoked in order to explain the small metal–silicon distance. It therefore appeared of interest to examine the X-ray structure[82] of a silyl derivative of a d^0 element for which such effect could not come into play. The compound chosen was $Zr(C_5H_5)_2Cl(SiPh_3)$. The molecular structure of the compound is schematically drawn in Fig. 8. The arrangement of the ligands around the metal and silicon is approximately tetrahedral. The most important feature is the distance Zr–Si which is 2.813 Å, this is a sur-

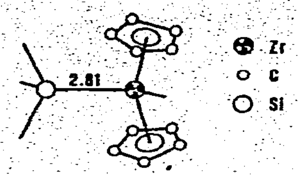


Fig. 8. Molecular structure of $Zr(C_5H_5)_2Cl(SiPh_3)$ schematically drawn, showing the zirconium—silicon distance (2.81 A). (From K.W. Muir, *J. Chem. Soc. A*, (1971) 2663.)

prisingly long distance and this data might thus be taken as a support for the $d_\pi - d_\pi$ bonding suggestion previously mentioned.

Dicyclopentadienyldiazidozirconium(IV) was obtained[41] by reacting under anhydrous conditions dicyclopentadienyldichlorozirconium(IV) with sodium azide in the presence of trace amounts of $AlCl_3$:

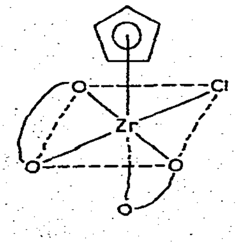
$$Zr(C_5H_5)_2Cl_2 + 2\,NaN_3 \xrightarrow{THF} 2\,NaCl + Ti(C_5H_5)_2(N_3)_2 \qquad (48)$$

The diazido complex was reported to be a pale yellow solid, of good thermal stability (it can be sublimed *in vacuo* at 140°), showing the parent peak in the mass spectrum.

Proton nuclear magnetic resonance spectra of compounds (XXIX), (XXX) and (XXXI) have been investigated[83]. The X-ray structure of $Zr(C_5H_5)Cl(C_5H_7O_2)_2$ is known[84] and it has now been shown[83] by X-ray powder diagrams that compounds

$Zr(C_5H_5)Cl(C_5H_7O_2)_2$ (XXIX) $Hf(C_5H_5)Cl(C_5H_7O_2)_2$ (XXX) $Zr(C_5H_5)Br(C_5H_7O_2)_2$ (XXXI)

(XXIX), (XXX) and (XXXI) are isomorphous. The structure of compound (XXIX) in the solid state can be, at least to a first approximation, described in terms of hexacoordinate zirconium (considering the cyclopentadienyl ring as a monodentate ligand), as shown below.



(XXIX)

It has been found that the ^1H NMR spectrum of (XXIX) can be accommodated by the approximate hexacoordinate model. In fact, four different resonances of equal intensity due to the methyl protons were observed together with two equally intense resonances *due to the methyne protons of the acetylacetonato ligand. This is true for the room tem*perature spectrum. As the temperature is increased above 70°, changes were observed[83], namely line broadenings and coalescence of the signals. This suggested a non-rigid behaviour of the molecule above 70° with interchange of the acetylacetonato ligands. The process was found to be first-order in the complex. Intramolecular interchange mechanisms were accordingly suggested.

^1H NMR and infrared data for compound (XXIX) and for the corresponding benzoylacetonato and dibenzoylmethanato complexes were also reported by Frazer and Newton[42].

Reactions of $Zr(C_5H_5)_2X_2$ ($X = Cl, Br$) and $Hf(C_5H_5)_2Cl_2$ with 8-hydroxyquinoline[43] in acetonitrile as solvent led to the formation of the monocyclopentadienyl-bis(chelate) complexes:

$$Zr(C_5H_5)_2X_2 + 3\,C_9H_7NO \xrightarrow{CH_3CN} C_9H_7NO{\cdot}HX + C_5H_6 + Zr(C_5H_5)X(C_9H_6NO)_2 \tag{49}$$

$$Hf(C_5H_5)_2Cl_2 + 3\,C_9H_7NO \xrightarrow{CH_3CN} C_9H_7NO{\cdot}HCl + C_5H_6 + Hf(C_5H_5)Cl(C_9H_6NO)_2 \tag{50}$$

Infrared and mass spectra of these complexes were studied, together with the reactions with proton-active substances, such as alcohols and hydrogen halides.

Dicyclopentadienyldichlorozirconium(IV) was found[85] to undergo reactions with alcohols giving rise to compounds of general formula $Zr(C_5H_5)_2(OR)_nCl_{2-n}$, such as for example:

$$Zr(C_5H_5)_2Cl_2 + CH_3OH + Et_3N \xrightarrow[\text{reflux}]{\text{THF}} Et_3N{\cdot}HCl + Zr(C_5H_5)_2(OCH_3)Cl \tag{51}$$

The crystal structures of $Zr(C_5H_5)_2F_2$ and $Zr(C_5H_5)_2I_2$ have been published[86]. The structure in both cases can be roughly described with a tetrahedral arrangement of the four ligands around the central metal atom. The C_5H_5–Zr–C_5H_5 and X–Zr–X bond angles are substantially insensitive to the nature of the halogen, as it can be seen from Fig. 9.

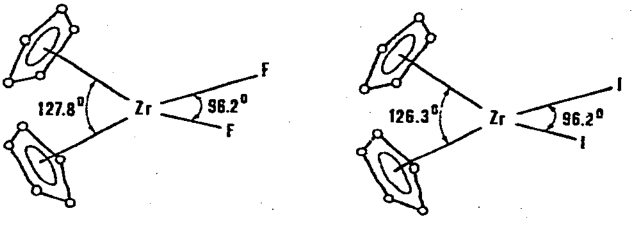


Fig. 9. Molecular structures of $Zr(C_5H_5)_2F_2$ and $Zr(C_5H_5)_2I_2$ showing the bond angles. (From M.A. Bush and G.A. Sim, *J. Chem. Soc. A*, (1971) 2225.)

K. Compounds of zirconium in oxidation states lower than IV

The chemistry of zirconium and hafnium in oxidation states III and II is relatively little known.

Wailes and Weigold have reported[87] some reductions of cyclopentadienyl derivatives of zirconium(IV) giving rise to zirconium(III) and zirconium(II) compounds. Dicyclopentadienyldichlorozirconium(IV) was treated with the 2,2'-dipyridyldisodium in tetrahydrofuran and the compound $Zr(C_5H_5)_2(C_{10}H_8N_2)$ was so obtained:

$$Zr(C_5H_5)_2Cl_2 + Na_2C_{10}H_8N_2 \rightarrow 2\,NaCl + Zr(C_5H_5)_2(C_{10}H_8N_2) \qquad (52)$$

The purple compound was reported to be substantially diamagnetic, the magnetic moment being $\mu_{eff} = 0.44$–0.34 in the temperature range 356–99 K. "Zirconocene", as obtained[88] by sodium naphthalene reduction of $Zr(C_5H_5)_2Cl_2$, was treated with 2,2'-dipyridyl in a sealed tube and, after extraction with benzene, the compound $Zr(C_5H_5)_2(C_{10}H_8N_2){\cdot}C_6H_6$ was isolated:

$$\frac{1}{n}[ZrC_{10}H_{10}]_n + C_{10}H_8N_2 \xrightarrow[\text{toluene}]{150^\circ} Zr(C_5H_5)_2(C_{10}H_8N_2) \qquad (53)$$

Two different dicyclopentadienyldichlorozirconium(III) compounds were isolated by the reaction of $Zr(C_5H_5)_2Cl_2$ with "zirconocene":

$$Zr(C_5H_5)_2Cl_2 + \frac{1}{n}[ZrC_{10}H_{10}]_n \rightarrow 2\,Zr(C_5H_5)_2Cl \qquad (54)$$

A green product was probably a polymeric substance $[Zr(C_5H_5)_2Cl]_n$; a benzene-soluble red solid was also isolated which was found to be dimeric in benzene solution. The latter compound in the solid state analyzed correctly for $[Zr(C_5H_5)_2Cl]_2{\cdot}C_6H_6$.

Detailed structural investigations of these compounds and of "zirconocene" would be highly desirable in view of the dispute still existing for the corresponding titanium complex.

L. Miscellaneous reactions including polymerizations in the presence of titanium and zirconium complexes

An improved preparation of $Mg(C_5H_5)_2$ has been reported[89] which consists of treating magnesium turnings with cyclopentadiene in the presence of catalytic amounts of $Ti(C_5H_5)Cl_3$:

$$Mg + 3C_5H_6 \xrightarrow[Ti(C_5H_5)Cl_3]{THF} Mg(C_5H_5)_2 + C_5H_8 \qquad (55)$$

No hydrogen was evolved and cyclopentene was quantitatively formed, which established the stoichiometry of reaction (55).

The reactions of alkyl halides with titanium films have been studied[90]. This work was undertaken in order to understand the fact that ball milling promotes the polymerization of ethylene by titanium metal. The polymerization is improved by adding alkyl halide. At 0° a clean titanium film reacts with R–X ($R = i\text{-}C_3H_7, C_2H_5$; $X = Cl, Br, I$) giving rise to the formation of hydrocarbons (alkenes and alkanes).

Styrene was reported[91] to be polymerized photochemically in toluene in the presence of $Zr(CH_2C_6H_5)_4$.

Isoprene was reported[92] to undergo oligomerization in the presence of a catalytic system consisting of $Zr(C_3H_5)_4$ and several alkylaluminium compounds.

Dicyclopentadienyl(1-methylallyl)titanium(III), after hydrogenation, is a convenient catalyst[93] for the hydrogenation of olefins and diolefins, for the polymerization of acetylene to *trans*-polyacetylene and for the isomerization of olefins and cyclic polyolefins.

ACKNOWLEDGMENT

The author wishes to thank Dr. M. Aglietto for the translation and the discussion of the Russian papers.

REFERENCES

1 H.H. Britzinger and J.E. Bercaw, *J. Amer. Chem. Soc.*, 92 (1970) 6182.
2 L.J. Guggenberger and F.N. Tebbe, *J. Amer. Chem. Soc.*, 93 (1971) 5924.
3 R. Hoxmeier, B. Deubzer and H.D. Kaesz, *J. Amer. Chem. Soc.*, 93 (1971) 536.
4 J.G. Kenworthy, J. Myatt and M.C.R. Symons, *J. Chem. Soc. A*, (1971) 1020.
5 J.J. Salzmann and P. Mosimann, *Helv. Chim. Acta*, 50 (1967) 1831, and references therein.
6 K. Clauss and H. Bestian, *Ann. Chem.*, 654 (1962) 8.
7 R.H. Marvich and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 93 (1971) 2046.
8 J.E. Bercaw and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 91 (1969) 7301.
9 E.E. van Tamelen, R.B. Fechter, S.W. Schneller, G. Boche, R.H. Greeley and B. Åkermark, *J. Amer. Chem. Soc.*, 91 (1969) 1551.
10 A.E. Shilov, A.K. Shilova, E.F. Kvashina and T.A. Vorontsova, *Chem. Commun.*, (1971) 1590.
11 J.H. Teuben and H.J. de Liefde Meijer, *Rec. Trav. Chim. Pays-Bas*, 90 (1971) 360.
12 See also AS 1970, *Organometal. Chem. Rev. B*, 9 (1972) 139.
13 M.E. Volpin, A.A. Belyi, V.B. Shur, Yu.I. Lyakhovetsky, R.V. Kudryavtsev and N.N. Bubnov, *J. Organometal. Chem.*, 27 (1971) C5; see also AS 1970, *Organometal. Chem. Rev. B*, 9 (1972) 137.
14 V.B. Shur, E.G. Berkovich and M.E. Volpin, *Izv. Akad. Nauk SSSR*, (1971) 2358.
15 I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya, G.G. Aleksandrov, Yu.T. Struchkov and M.E. Volpin, *Chem. Commun.*, (1971) 972.
16 E.E. van Tamelen, H. Rudler and C. Bjorklund, *J. Amer. Chem. Soc.*, 93 (1971) 3526.
17 E.E. van Tamelen, G. Boche, S.W. Ela and R.B. Fechter, *J. Amer. Chem. Soc.*, 89 (1967) 5707.
18 G.R. Davies, J.A.J. Jarvis and B.T. Kilbourn, *Chem. Commun.*, (1971) 1511.
19 I.W. Bassi, G. Allegra, R. Scordamaglia and G. Chioccola, *J. Amer. Chem. Soc.*, 93 (1971) 3787.
20 G.R. Davies, J.A.J. Jarvis, B.T. Kilbourn and A.J.P. Pioli, *Chem. Commun.*, (1971) 677.
21 U. Zucchini, E. Albizzati and U. Giannini, *J. Organometal. Chem.*, 26 (1971) 357.
22 W. Brüser, K.H. Thiele, P. Zdunneck and F. Brune, *J. Organometal. Chem.*, 32 (1971) 335.
23 N. Corsi, unpublished results.
24 J.L. Calderon, F.A. Cotton, B.G. DeBoer and J. Takats, *J. Amer. Chem. Soc.*, 93 (1971) 3592.
25 J.L. Calderon, F.A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, 93 (1971) 3587.
26 V. Kocman, J.C. Rucklidge, R.J. O'Brien and W. Santo, *Chem. Commun.*, (1971) 1340.
27 B. Wozniak, J.D. Ruddick and G. Wilkinson, *J. Chem. Soc. A*, (1971) 3116.
28 M.D. Rausch and L.P. Klemann, *Chem Commun.*, (1971) 354.
29 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, 33 (1971) 181.
30 G. Fachinetti and C. Floriani, *Chem. Commun.*, (1972) 654.

31 C. Floriani and G. Fachinetti, *Chem. Commun.*, (1972) 790.

32 C. Floriani and G. Fachinetti, *Proc. XIVth ICCC Toronto*, June 22–28, 1972.

33 R.J.H. Clark, M. Coles and A.J. McAlees, *Proc. Vth Intern. Conf. Organometal. Chem.*, Moscow, 1971, p. 626.

34 R.J.H. Clark and M. Coles, *Chem. Commun.*, (1971) 1587.

35 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, *J. Chem. Soc. A*, (1971) 1920.

36 R.J.H. Clark and J.A. McAlees, *J. Chem. Soc. A*, (1970) 2026.

37 K.H. Thiele, P. Zdunneck and D. Baumgart, *Z. Anorg. Allgem. Chem.*, 378 (1970) 62.

38 F. Calderazzo, S.A. Losi and B.P. Susz, *Helv. Chim. Acta*, 54 (1971) 1156.

39 J.A. Waters, V.V. Vickroy and G.A. Mortimer, *J. Organometal. Chem.*, 33 (1971) 41.

40 H.J. Neese and H. Bürger, *J. Organometal. Chem.*, 32 (1971) 213.

41 R.S.P. Coutts and P.C. Wailes, *Austr. J. Chem.*, 24 (1971) 1075.

42 M.J. Frazer and W.E. Newton, *Inorg. Chem.*, 10 (1971) 2137.

43 J. Charalambous, M.J. Frazer and W.E. Newton, *J. Chem. Soc. A*, (1971) 2487.

44 O.V. Nogina, N.A. Lazareva, V.A. Dubovitsky and B.A. Kvasov, *Proc. Vth Intern. Conf. Organometal. Chem. Moscow*, 1971, p. 357.

45 A.N. Nesmeyanov, O.V. Nigona, V.A. Dubovitsky, B.A. Kvasov, P.V. Petrovsky and N.A. Lazareva, *Izv. Akad. Nauk SSSR*, (1971) 2729.

46 E.F. Epstein and I. Bernal, *J. Organometal. Chem.*, 26 (1971) 229.

47 E.F. Epstein and I. Bernal, *Chem. Commun.*, (1970) 410; see As 1970, *Organometal. Chem. Rev. B*, 9 (1972) 144.

48 H. Köpf, *Angew. Chem.*, 83 (1971) 146.

49 B.R. Davis and I. Bernal, *J. Organometal. Chem.*, 30 (1971) 75.

50 L.F. Farnell, E.W. Randall and E. Rosenberg, *Chem. Commun.*, (1971) 1078.

51 K.H. Thiele and W. Schäfer, *Z. Anorg. Allgem. Chem.*, 379 (1970) 63.

52 W. Schäfer and K.H. Thiele, *Z. Anorg. Allgem. Chem.*, 381 (1971) 205.

53 K. Kühlein and K. Clauss, *Proc. Vth Intern. Conf. Organometal. Chem., Moscow*, 1971, p. 100.

54 J.G. Kenworthy, J. Myatt and M.C.R. Symons, *J. Chem. Soc. A*, (1971) 3428.

55 M.F. Lappert and A.R. Sanger, *J. Chem. Soc. A*, (1971) 874.

56 E.C. Alyea, D.C. Bradley, M.F. Lappert and A.R. Sanger, *Chem. Commun.*, (1969) 1064; see AS 1969, *Organometal. Chem. Rev. B*, 6 (1970) 1014.

57 M.F. Lappert and A.R. Sanger, *J. Chem. Soc. A*, (1971) 1314.

57 a. R.S.P. Coutts, P.C. Wailes and J.V. Kingston, *Chem. Commun.*, (1968) 1170; see also AS 1968, *Organometal. Chem. Rev. B*, 5 (1969) 556.

58 R.S.P. Coutts, R.L. Martin and P.C. Wailes, *Austr. J. Chem.*, 24 (1971) 1079.

59 R.S.P. Coutts, R.L. Martin and P.C. Wailes, *Austr. J. Chem.*, 24 (1971) 2533.

60 R.L. Martin and G. Winter, *J. Chem. Soc.*, (1965) 4709.

61 P.S. Braterman, V.A. Wilson and K.K. Joshi, *J. Chem. Soc. A*, (1971) 191.

61 a. H. Köpf and K.H. Räthlein, *Angew. Chem.*, 81 (1969) 1000; see AS 1969, *Organometal Chem. Rev. B*, 6 (1970) 1016.

61 b. K.K. Joshi, R. Wardle and V.A. Wilson, *Inorg. Nucl. Chem. Letters*, 6 (1970) 49.

62 G.R. Davies and B.T. Kilbourn, *J. Chem. Soc. A*, (1971) 87.

63 T.S. Cameron, C.K. Prout, G.V. Rees, M.L.H. Green, K.K. Joshi, G.R. Davies, B.T. Kilbourn, P.S. Braterman and V.A. Wilson, *Chem. Commun.*, (1971) 14.

64 P.S. Braterman and V.A. Wilson, *J. Organometal. Chem.*, 31 (1971) 131.

65 J.E. Bercaw and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 93 (1971) 2045.

66 V.I. Telnoi, I.B. Rabinovitch, V.N. Latyaeva and A.N. Linieva, *Dokl. Akad. Nauk SSSR*, 197 (1971) 1348.

67 H.O. van Oven and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 31 (1971) 71.

68 V. Plato and K. Hedberg, *Inorg. Chem.*, 10 (1971) 590.

69 P.H. Bird and M.R. Churchill, *Chem. Commun.*, (1967) 403.
70 V.P. Spiridonov and G.I. Mamawa, *Zh. Strukt. Khim.*, 10 (1969) 120.
71 B.D. James, R.K. Nanda and M.G.H. Wallbridge, *J. Chem. Soc. A*, (1966) 182.
72 B.E. Smith and B.D. James, *Inorg. Nucl. Chem. Letters*, 7 (1971) 857.
73 Yu.S. Khodeev and B.M. Kirin, *Zh. Strukt. Khim.*, 12 (1971) 531.
74 V.V. Volkov, K.G. Myakishev, V.A. Grigorev, G.I. Bagryantsev and I.S. Kalinina, *Proc. Vth Intern. Conf. Organometal. Chem., Moscow,* 1971, p. 189.
75 V.I. Kulishov, E.M. Brainina, N.G. Bokiy and Yu.T. Struchkov, *Chem. Commun.*, (1970) 475; see also AS 1970, *Organometal. Chem. Rev. B*, 9 (1972) 149.
76 J.L. Calderon, F.A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, 91 (1969) 2528.
77 B.V. Lokshin and E.M. Brainina, *Zh. Strukt. Khim.*, 12 (1971) 1001.
78 K.H. Thiele and J. Krüger, *Z. Anorg. Allgem. Chem.*, 383 (1971) 272.
79 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, 27 (1971) 373.
80 K.W. Muir and J.A. Ibers, *Inorg. Chem.*, 9 (1970) 440.
81 L. Manojlović-Muir, K.W. Muir and J.A. Ibers, *Inorg. Chem.*, 9 (1970) 447.
82 K.W. Muir, *J. Chem Soc. A*, (1971) 2663.
83 T.J. Pinnavaia and A.L. Lott, *Inorg. Chem.*, 10 (1971) 1388.
84 J.J. Stezowski and H.[illegible]. Eick, *J. Amer. Chem. Soc.*, 91 (1969) 2890; see also AS 1969, *Organometal. Chem. Rev. B*, 6 (1970) 1020.
85 D.R. Gray and C.H. Brubaker, *Inorg. Chem.*, 10 (1971) 2143.
86 M.A. Bush and G.A. Sim, *J. Chem. Soc. A*, (1971) 2225.
87 P.C. Wailes and H. Weigold, *J. Organometal. Chem.*, 28 (1971) 91.
88 G.W. Watt and F.O. Drummond, *J. Amer. Chem. Soc.*, 88 (1966) 5926.
89 T. Saito, *Chem. Commun.*, (1971) 1422.
90 J.F. Harrod and W.R. Summers, *J. Amer. Chem. Soc.*, 93 (1971) 5051.
91 D.G.H. Ballard and P.W. van Lienden, *Chem. Commun.*, (1971) 564.
92 Y. Uchida, K. Furuhata and S. Yoshida, *Bull. Chem. Soc. Japan*, 44 (1971) 1966.
93 H.A. Martin and R.O. de Jongh, *Rec. Trav. Chim. Pays-Bas*, 90 (1971) 713.