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Dinuclear Metallocenes

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Data on the methods of synthesis and chemical reactions of bismetallocene complexes of Group IV-VI transition elements are analysed. Attention is concentrated on the determination of the general characteristics of the structure and reactions of dinuclear metallocenes and also on the analysis of the discrepancies frequently arising in studies of these compounds. The bibliography includes 117 references.

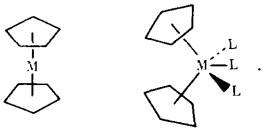
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I. INTRODUCTION

Since the discovery of ferrocene and the synthesis of its closest analogues, the modern stage of the development of the organic chemistry of transition and non-transition elements has begun. The synthesis of new unusual structures has sharply stimulated research into the theory of the chemical bond, studies on the synthesis of a wide variety of skeletal structures, regardless of the elements constituting them, and a vigorous development of virtually all the physical research methods, for which these new compounds have been an extremely rewarding object of study.

Among the entire wide variety of transition metal complexes with organic ligands obtained at the present time, the carbonyl and biscyclopentadienyl compounds continue to retain their leading position. This is caused mainly by the strength of the binding of the ligands in these complexes to the transition metal atoms, which makes it possible to carry out a wide range of reactions of these complexes in most cases without risk of a complete and unpredictable rearrangement of the entire ligand sphere of the metal. The wide variety of the chemical properties and the high stability of the metallocene (Cp_2M)† analogues of ferrocene in terms of the Group and Period permitted the hypothesis, put forward in the early stage of these studies, that the sandwich structure (I) with a parallel arrangement of the Cp rings is universally applicable to the complexes of all transition metals.



(I) (II)

Numerous attempts have therefore been made to obtain such compounds for all transition metals. However, it was found that the synthesis of mononuclear homoligand metallocenes (I) is not easy for transition elements located at the beginning and end of the long Periods; this is manifested particularly strikingly in the second and third transition series. The phenomenon is caused by the inconsistency, as regards these elements, between the coordinating capacity of the Cp ligand and the coordination requirements of the metal atom and also by the very markedly unfavourable character of the filling of the bonding and antibonding orbitals of the metal–ring bond. This results in a decrease of the overall metal–ring bond order, which facilitates the distortion of the sandwich and its conversion into wedge-shaped derivatives of the type Cp_2ML_{1-3} or into the monocyclopentadienyl complexes $CpML_n$.

This review deals with compounds of the Group IV, V, and VI elements at the beginning of the large Periods. Such differentiation of the objects of study is natural and easily attainable, since the majority of the transition metals in these Groups form compounds having similar structures; in addition, the methods of synthesis (of the complexes) and the reactions undergone by these derivatives are also similar. The very first and most general structural feature which it is appropriate to identify already at this stage is the tendency of these elements to form heteroligand wedge-shaped derivatives $Cp_2M(L)_{1-3}$ (II) in which the additional groups L are located in the bisector plane of the wedge-shaped sandwich.

Among all the nine elements of the above Groups, stable compounds, whose molecules consist of regular sandwiches of type (I), have been isolated only for vanadium and chromium (vanadocene and chromocene).[1,2] The relatively small size of the vanadium and chromium atoms enables the cyclopentadienyl ligands to exhaust to a large extent the coordinating capacity of the metal atoms in the regular sandwich structures, virtually isolating them from the possibility of attack by external reagents. Although the instances of the expansion of the coordination sphere of these elements above the formal hexacoordinate sphere in Cp_2M are feasible and known,[1,2] nevertheless the Cp_2V and Cp_2Cr molecules are kinetically fairly inert in many reaction mixtures, which makes it possible to isolate these complexes as individual crystalline products. As regards the remaining seven elements (Ti, Zr, Hf, Nb, Ta, Mo, and W), the structure of their biscyclopentadienyl complexes proved to be much more complex and the problem has not been yet fully elucidated. None of the early mentions of the synthesis of monomeric metallocenes of these elements were subsequently confirmed. The history of the development of the research into titanocene, the representation of the formula of which by $(C_5H_5)_2Ti$ can be encountered in the early communications by very many investigators together with claims that all operations have been carried out with an individual compound having precisely this structure, is most interesting and instructive.

Only in the very recent years has direct experimental confirmation been obtained for the existence of the extremely

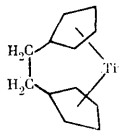
†Here and henceforth the symbol Cp has been adopted for the η^5-cyclopentadienyl ligand.

reactive mononuclear complexes of niobium (Cp_2Nb) [3] and molybdenum and tungsten (Cp_2Mo and Cp_2W) [4] with structure (I) analogous to that of ferrocene, as well as the titanium compound $(Me_5C_5)_2Ti$. [5,6] However, the experimental details quoted in the above studies[3–6] show that there is virtually no hope of isolating pure crystalline specimens of these complexes, since at room temperature they undergo either rapid dimerisation (the Nb, Mo, and W complexes) or the sandwich structures isomerise (the Ti complex). We may predict with a considerable degree of confidence that in the case of the mononuclear metallocenes of other Group IV–VI elements the situation will be entirely analogous, i.e. that direct experimental confirmation of their existence also will be obtained in the next few years. On the other hand, the set of data available at present allows virtually no doubt as to the formation of mononuclear compounds of type (I) as intermediate species in various chemical reactions of derivatives of these elements.

A series of theoretical studies have been made on the stereochemical and electronic structures of mononuclear metallocenes as a function of the position of the central metal atom in the transition series; the complete list of references can be found in a series of communications.[7–10] Analysis of the variation of the energies of three frontier molecular orbitals (MO) of the sandwich systems as a function of the angle θ characterising the distortion of the metallocene fragments has led to the conclusion that the regular sandwich structure (θ = 180°) and not the wedge-shaped sandwich is preferable for the monomeric homoligand species.



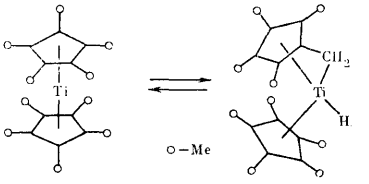
(III)



(IV)

The energies of these frontier MO, which are located in the bisector plane of the wedge-shaped sandwich and are predominantly the *d* orbitals (70–80%) of the metal, increase appreciably with decrease of θ. The energies of the deeper Cp–M bonding MO should also increase appreciably with decrease of θ. Consequently the distortion of the sandwiches requires a definite energy expenditure. The structures of all the known monomeric transition metal metallocenes, including the complexes Cp_2Mo, Cp_2W, and Cp_2Nb which have been detected only at a low temperature, are consistent with this conclusion.

On the other hand, the mononuclear metallocenes of Group IV–VI elements should remain distinctly carbene-like (carbenoid) complexes, since the frontier MO (in the regular sandwich these are two degenerate e_2 orbitals and the a_1 orbital having a similar energy) are only partly filled by electrons. The carbenoid character of many metallocene derivatives of these elements has been confirmed chemically by the ease of oxidative addition and ligand addition reactions. In conformity with the Jahn–Teller theorem, a distortion of the regular sandwich structure may be expected only for the elements of the titanium subgroup, but this would not alter the carbenoid character of the molecules, while an increase of the accessibility of the metallic centre, which occurs because the angle θ ceases to be 180°, increases still further the likelihood of the formation of wedge-shaped derivatives having the composition Cp_2MX_{1-2}. Experimental data permitting at least approximate inferences about the stereochemical configuration of the mononuclear metallocenes in the titanium subgroup are at present lacking. The greatest hopes are with further studies of decamethyltitanocene,[5,6,11,12] whose existence as a homoligand complex has been demonstrated but only in equilibrium with the isomeric cyclopentadienylfulvenetitanium hydride compound:



The search for methods of synthesis of titanocenophane (IV) with a fairly short bridge is also promising. The first study[13] on these lines demonstrated that the reactions which proceed readily for unsubstituted titanocene derivatives and which proceed preferentially via the homoligand complex $(C_5H_5)_2Ti^{II}$ cannot be achieved for the complex with a bridging ligand. The first stage of the reaction, namely the reduction of titanium (IV) or titanium (III) to titanium (II) with formation of the complex (IV) as a kinetically independent species, is then unsuccessful.

The carbenoid character and coordination accessibility of the central metal atom to attack by external reagents are the main causes responsible for the vanishingly low stability of the homoligand monomeric metallocenes of type (I) formed by Group IV–VI metals. The complexes Cp_2V and Cp_2Cr (see above), containing metals with the smallest atomic radii, are an exception. However, these complexes too are highly reactive and are readily converted into the wedge-shaped structures Cp_2ML_n and are unstable when acted upon by atmospheric oxygen and moisture. For all the remaining metals of these Groups, the complexes Cp_2ML_n are virtually the only form of the compounds in which the metallocene fragment is present.

The spontaneous formation of dinuclear compounds in reactions where the formation of monomeric metallocenes of type (I) would be expected constitutes perhaps the most striking confirmation of the preferred formation of wedge-shaped structures where metal atoms are bound not only to the η^5-cyclopentadienyl ligands but also to other groups. The vast majority of bismetallocene structures obtained at the present time for the Group IV–VI elements are formed as a result of the insertion of one carbene-like metallocene fragment in the C–H bonds of the ligands of a second analogous fragment.

The first hypothesis that the metallocenes of Ti, Zr, Hf, Nb, Ta, Mo, and W are associated was put forward a fairly long time ago, almost immediately after the first attempts to synthesise these compounds in the middle 1950's. However, it was not until more than 15 years had elapsed that the first studies demonstrating the structure of the bismetallocene molecules have been published. The fact that studies in this field using unusually sophisticated experimental techniques began has played a decisive role. Low-valence metallocene complexes of the above elements are extremely sensitive to atmospheric oxygen and moisture and sometimes to molecular nitrogen. In view of the high M–O bond energy, the range of organic solvents which can be used in experiments with these compounds is extremely narrow. It is virtually necessary to confine oneself to saturated and aromatic hydrocarbons and solvents of the ether type. The employment of chromatographic methods of purification with carriers such as alumina, silica gel, and similar substances is not permissible.

The composition of the bismetallocenes obtained at the present time, derivatives of Group IV–VI elements, as a rule corresponds to the formula $(C_{10}H_{10}M)_2$ or differs from it by one, two, or more hydrogen atoms. The data concerning

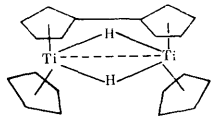
bismetallocenes presented below are arranged in terms of Groups of elements.

II. BISMETALLOCENE COMPLEXES OF GROUP IV ELEMENTS

1. Titanium Compounds

The development of the chemistry of titanocene has been extremely non-uniform and has been distinguished by the publication of a large number of inconsistent results obtained by different investigators. The isolation of the dark-green diamagnetic titanocene $(C_5H_5)_2Ti$ was first reported by Fischer and Wilkinson[14] in 1956. Somewhat later, other investigators[15] who attempted to reproduce this synthesis were unable to isolate the complex of this composition and they therefore raised serious doubts concerning the existence of titanocene. The attempts to synthesise this metallocene were frequently resumed, but the monomeric complex was never obtained. At the present time at least five different bistitanocenes have been described. With serious stipulations, an attempt may be made to regard some of them as identical but the number of undoubtedly different bistitanocenes is even then reduced only to as many as three.

The most thermally stable form of titanocene is the fulvalenetitanium hydride complex μ-(η^5:η^5-$C_{10}H_8$)-μ-(H_2)-(η^5-$C_5H_5)_2Ti_2$:



(V)

The possibility of the formation of this structure was first suggested in 1970.[16] Analysis of the mass spectra[16,17] and infrared spectra[17,18] has played an important role in demonstrating its existence. The infrared spectrum of the complex is characterised by an intense absorption at 1230 cm^{-1} due to the metal–hydride vibration. Important information has also been obtained from an X-ray diffraction study of certain products of the chemical transformation of the stable bistitanocene. However, a study of the ^{13}C NMR spectra in 1974 was of decisive importance.[19]

Thus more than 15 years elapsed between the first publication about the synthesis of titanocene and the elucidation of its structure. Approximately the same period was required to determine the necessary experimental conditions for its successful synthesis. In particular, prolonged heating of the reaction mixture or, better, sublimation of the reaction product at temperatures of ~200–220 °C is essential. When this requirement is met, bistitanocene (V) can be synthesised by reducing titanocene dichloride by various reducing agents and also by the thermal decomposition of titanium hydride complexes.

The bistitanocene (V) has been obtained on reducing Cp_2TiCl_2 with sodium in toluene with the system heated to 50 °C; the completion of the reaction requires 4 days.[18] Titanocene dichloride is rapidly reduced by sodium in the presence of catalytic[20] or equimolar[21] amounts of naphthalene. Studies have recently been published[17,22] in which $LiAlH_4$ was used as the reducing agent. The stable bistitanocene is formed when the reaction is carried out above 100 °C in cyclo-olefins or aromatic solvents:

$$Cp_2TiCl_2 \xrightarrow{Na,\ or\ Na\text{-}C_{10}H_8,\ or\ LiAlH_4} (V)$$

The stable bistitanocene is also obtained on heating the titanocene hydride $(Cp_2TiH)_2$ [28] above 170 °C or on hydrogenating the dimethyl derivative of titanocene in solution:[24]

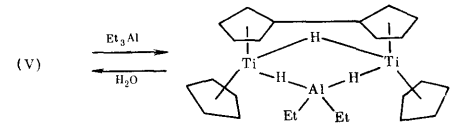
$$(Cp_2TiH)_2 \rightarrow H_2 + Cp_2Ti_2(H)_2\ (\eta^5\text{:}\ \eta^5\text{-}C_{10}H_8);$$

$$Cp_2Ti(Me)_2 + H_2 \rightarrow Cp_2Ti_2(H)_2\ (\eta^5\text{:}\ \eta^5\text{-}C_{10}H_8).$$

The second reaction apparently proceeds via the intermediate formation of the hydride complex $(Cp_2TiH)_2$, which decomposes under the reaction conditions to form the stable bistitanocene; however, the result depends greatly on the reaction conditions (see below).

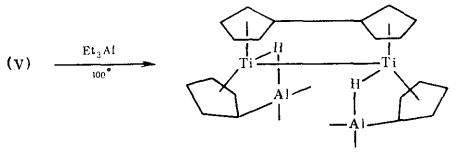
The chemical properties of the bistitanocene (V) have been studied in fair detail. The structures of the products of its reactions with HCl, H_2O, and Et_3Al have been established by X-ray diffraction. In all these reactions the dinuclear fulvalene structure is retained.

The interaction of the stable bistitanocene with triethylaluminium under mild conditions (25 °C) yielded the fulvalenetitanium hydride complex,[25] whose hydrolysis under mild conditions regenerates the bistitanocene (V):



(A) $R(Ti\text{–}Ti) = 3.374$ Å

When the reaction was carried out under more severe conditions (100 °C), another fulvalene complex was obtained:[25–27]



(B) $R(Ti\text{–}Ti) = 2.910$ Å

The large difference between the Ti–Ti distances in the structures of compounds (A) and (B) obtained, which are derived from the same initial complex (V), is somewhat unexpected. However, the difference is almost wholly a consequence of the fact that the stereochemical requirements of the Ti–H–Al–C_{Cp} and Ti–H–Al–H–Ti bridging groups are different in the two complexes. The presence of the bridging hydride hydrogen atom in the first structure (A) does not imply the absence of direct Ti–Ti bonding. The three AO in the three-atom system M–H–M (one for each atom) form a single strongly bonding three-centre orbital or two antibonding combinations.[28,29]

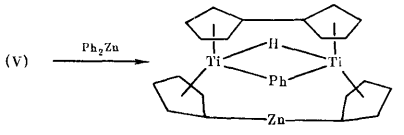
When the system contains only two electrons, only the bonding orbital is filled. In this case the two metal atoms and hydrogen should be located at the corners of a non-equilaterial triangle. The addition of a pair of electrons fills one of the antibonding orbitals, i.e. leads formally to the formation of a four-electron three-centre bond. Either the linear configuration (M–H–M) or dissociation of the system with formation of M–H and M is preferable in such a situation. The presence of the direct M–M overlap in the bridging metal hydride complexes has been frequently emphasised in the literature.[28–31]

As already stated, the stable bistitanocene reacts with water[14,21,32] and hydrogen chloride.[14,17,18,21] The products of these reactions, namely $Cp_2Ti_2(\mu\text{-}OH)_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ [32] and $Cp_2Ti_2(\mu\text{-}Cl)_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$,[33] have the structure of dinuclear fulvalene complexes with bridging hydroxy-groups or with bridging chlorine atoms; the structure has been established by X-ray diffraction. It has been noted that,

on interaction of the stable bistitanocene with HCl, the replacement of bridging hydrogen atoms by bridging chlorine atoms takes place consecutively.[17] The reactions of the fulvalene bistitanocene with HCl and H_2O, in which the fulvalene structure is retained and only the bridging hydrogen atoms are replaced by the μ-Cl or μ-OH ligands, are as a whole analogous to the thoroughly investigated reactions of the mononuclear complexes Cp_2TiX_2 and Cp_2TiX with nucleophiles.[34]

When the bistitanocene (V) reacts with HCl, the mononuclear complex Cp_2TiCl_2 is not formed. This conclusion is important: the metastable titanocene dimers, which are frequently obtained together with the stable isomer, give rise to a high yield of Cp_2TiCl_2 in their reactions with HCl, in contrast to the stable isomer. The reaction with hydrogen chloride is therefore a qualitative test for the absence of an admixture of metastable titanocenes in the stable bistitanocene.

Together with the reactions of the stable bistitanocenes examined above, in which the structure of the products has been reliably established, studies have been made where the structure of the products of the reactions of compound (V) cannot be regarded as established. The interaction of the bistitanocene (V) with diphenylzinc yielded the unusual compound [μ-(η^5:η^5-$C_{10}H_8$)-μ-(η^5-C_5H_4Zn-η^5-C_5H_4)(μ-H)(μ-Ph)Ti_2], whose structure has been proposed on the basis of the study of the products of its decomposition by heating or by treatment with various chemical reagents.[35] There is no doubt that the proposed structure should be very strained.



When the stable bistitanocene reacts with nitrogen (at a nitrogen pressure of 4 atm) in benzene at room temperature, a nitrogen complex having the composition $C_{20}H_{20}Ti_2(N_2)_2$, whose structure has also not been established, is formed slowly (over a period of three weeks).[36] On reduction with sodionaphthalene and subsequent hydrolysis, the nitrogen complex gives rise to ammonia.[36]

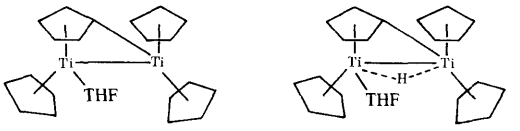
Doubts as to whether the complex is really formed from the molecule of the stable bistitanocene have been raised.[37] One must note that in the first communication concerning the fixation of nitrogen under mild conditions it was already noted that the Cp_2TiCl_2–reductant system combined with molecular nitrogen.[38] Later such nitrogen-fixing systems were investigated in many studies (see, for example, Refs. 36–41). In these systems nitrogen is fixed rapidly even at low temperatures and atmospheric nitrogen pressure, while the formation of a complex of the stable bistitanocene and nitrogen is very slow (if it occurs at all).[37] The stable isomer of bistitanocene is chemically fairly inert in the reaction with nitrogen and is apparently not the compound responsible for the effective activation of nitrogen in the Cp_2TiCl_2–reductant system.

The stable fulvalene bistitanocene, the synthesis and chemical properties of which were examined above, is the least reactive form of titanocenes. Together with the stable bistitanocene, there exist several highly reactive, so-called "metastable" bistitanocenes. The metastable forms of titanocenes exist at temperatures not exceeding 90 °C; on heating to 100–110 °C, the metastable titanocenes are converted into the stable isomer (V). The properties of the metastable titanocenes are similar but not identical. Nor can one rule out the possibility that in the future, after appropriate checks of the data obtained previously, the number of compounds treated as individual will be reduced.

At least four different metastable isomers of bistitanocene are known: (1) the "low-temperature titanocene" $(C_5H_5)_3$.$(\mu\text{-}C_5H_4)Ti_2$; (2) the "active titanocene" $[(C_5H_5)_2Ti]_{1-2}$; (3) the metastable titanocene" $[(C_5H_5)_2Ti]_2$; (4) the "black titanocene" $(C_{10}H_{10}Ti)_n$ or $(C_{10}H_{9-10}Ti)_n$. Rigorous evidence for the structure is available only for the first of these compounds, obtained in 1976 by the low-temperature reduction of Cp_2TiCl_2.[42] Henceforth we shall refer to this form of titanocene as "low-temperature titanocene".

$$Cp_2TiCl_2 + C_{10}H_8\cdot K \xrightarrow{-80^\circ} Cp_3Ti_2\,(\eta^5{:}\ \eta^1\text{-}C_5H_4)\,.$$

The complex obtained is stable in an atmosphere of argon at 20 °C for several days but decomposes in solution, the decomposition being particularly rapid in tetrahydrofuran (THF). The structure of the complex with a THF solvate molecule has been established by X-ray diffraction:[42]



(VIa) R(Ti–Ti) = 3.336 Å (VIb)

In the molecule of compound (VIa) there are two types of titanium atoms—bivalent and tervalent titanium. The Cp_2Ti^{II} species is stabilised by the formation of a Ti–Ti bond and by coordination to the THF molecule. A characteristic feature of this molecule is a high degree of electron unsaturation (a 31-electron complex) and the accessibility of the Ti^{II} atom and the Ti–Ti bond to attack by various reagents. These factors are responsible for the high reactivity of the low-temperature titanocene (VIa) compared with the fulvalene titanocene (V).

The chemical properties of the low-temperature titanocene have been investigated in fair detail. In the majority of reactions the structure of the low-temperature titanocene decomposes with formation of mononuclear biscyclopentadienyltitanium complexes or fulvalene complexes. The THF solvate molecule can be removed by evacuating solutions of the complex in octane. On the basis of infrared spectroscopic data, it is believed that the structure of the complex is then retained. According to Pez,[42] the ease of formation of the non-solvated complex is one of the causes which can explain its high reactivity in relation to compounds such as CO, N_2, H_2, olefins, etc.

On heating to 110 °C, the low-temperature titanocene is slowly converted into the fulvalene complex (V) in 40% yield:[43]

$$(VI) \xrightarrow[\Delta]{} (V)\,.$$

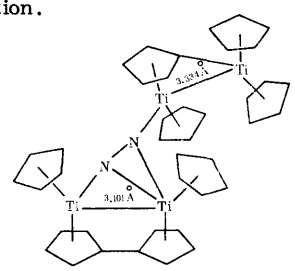
The reactions of compound (VI) with hydrogen chloride, carbon monoxide, ammonia, and hydrogen take place readily and with high yields:[43,44]

$$(VI) \begin{cases} \xrightarrow{HCl} Cp_2TiCl_2 + Cp_2TiCl\,; \\ \xrightarrow{CO} Cp_2Ti(CO)_2\,; \\ \xrightarrow{NH_3} (Cp_2TiNH)_2H\,; \\ \xrightarrow{H_2} (Cp_2TiH)_n\,. \end{cases}$$

In contrast to the stable bistitanocene (V), the low-temperature titanocene (VI) is active in the hydrogenation and isomerisation reactions of unsaturated compounds. Thus compound (VI) catalyses the conversion of ethylene into ethane and buta-1,3-diene.[45]

The high reactivity of the low-temperature titanocene compared with the stable bistitanocene is manifested particularly strikingly in the reaction with molecular nitrogen.

The low-temperature titanocene (VI) reacts with nitrogen even at −80 °C to form a tetranuclear complex with a bridging N_2 molecule;[46] its structure has been established by X-ray diffraction.



It is striking that two different bistitanocene fragments are linked by the nitrogen bridge in this molecule: one resembles the low-temperature dimer, while the other is analogous to the molecule of the stable bistitanocene. In discussing the infrared spectrum of this complex and in comparing it with data for other complexes with molecular nitrogen, the authors[46] put forward the interesting idea that the unusually pronounced decrease of the vibration frequency of the N–N bond in some of these complexes, including the compound considered, where $\nu(^{14}N^{14}N) = 1282\ cm^{-1}$ or $\nu(^{15}N^{15}N) = 1240\ cm^{-1}$, is due to the coordination of a nitrogen molecule in these complexes to three metal atoms simultaneously.

It is essential to note a further two significant facts. Firstly, when the N–N bonding [R(N–N) = 1.302 Å] is retained in the dinuclear fulvalene fragment of the molecule, the Ti–N and Ti–Ti bonds are unable to be located in a single plane close to the bisector plane of the wedge-shaped sandwiches, as required by the theory and the stereochemical features of the structure of the wedge-shaped sandwiches. Thus the above molecular fragment must be greatly strained. Secondly, the exceptional ease of the transformation of the structure of the low-temperature titanocene with the bridging μ-($\eta^5:\eta^1$-C_5H_4) ligand into a structure of the fulvalene type is significantly non-trivial, particularly in view of the fact, mentioned above, that the $Ti(N_2)Ti$ fragment is strained and also the fact that, in the absence of the N_2 molecule, the conversion of the low-temperature titanocene (VI) into the fulvalene isomer (V) requires much more severe conditions (temperature ~100 °C) and proceeds at a much lower rate.

The phenomenon of the preferential transformation of the dinuclear metallocene structures with the bridging μ-($\eta^5:\eta^1$-C_5H_4) ligands into dinuclear structures with the μ-($\eta^5:\eta^5$-$C_{10}H_8$) bridging fulvalene ligand has been studied in detail in relation to niobocene systems (see below). Regardless of the mechanism of these reactions, the above structural transformations of the dinuclear complexes are always accompanied by the substitution of the metal hydride atoms by other elements capable of playing a much more effective role as bridging ligands; in the first place these are halogen, sulphur, oxygen, nitrogen, etc. atoms. One of the driving forces of these reactions is undoubtedly the energy gain associated with the formation of the M–E–M bridge bonds (where E = halogen, O, S, N, etc.).

In conclusion of the discussion of the available data concerning the structure and properties of the low-temperature titanocene, we shall consider a few more facts. Although for a number of reasons the proposed structure (VIa) is preferable, it is not possible to reject fully the possible presence in the molecule of yet another bridging atom–the hydride hydrogen atom (the location of the hydrogen atoms was not established in the X-ray diffraction study), i.e. the formation of the structure (VIb).

It was established that the interaction of the low-temperature titanocene with HD yields a mixture of gases (H_2 + HD + D_2), while the reaction with methyl iodide affords methane.[43] In addition there are discrepancies between various spectroscopic properties of the low-temperature titanocene. The hypothesis of the existence of the bridging hydrogen atom agrees with the finding that the infrared spectra of even very pure specimens of the low-temperature dimer always contain an intense absorption at 1230 cm^{-1}. The presence of this band cannot be explained (as suggested by Pez[42]) by the presence of an admixture of stable bistitanocene, since according to other estimates its amount cannot exceed several per cent. It may be that the bridging hydrogen atom is present in the molecule of compound (VI) itself. On the other hand, the paramagnetism of the low-temperature bistitanocene agrees well with the structure without a bridging hydrogen atom. However, the conclusion that the complex is paramagnetic is not based on the study of the EPR spectra or a direct measurement of the magnetic moment and was reached only from the change in the positions of the signals of the cyclopentadienyl rings in the ^1H NMR spectra as the temperature was altered.[42]

We shall proceed to the consideration of other metastable bistitanocenes. In contrast to compound (VI), obtained by Pez,[42] attempts to establish their exact structure has not been reported.

Van Tamelen et al.[47] investigated the multistage reduction of Cp_2TiCl_2 by sodium in toluene, the process being followed by visible and infrared spectroscopy. It was established that different products, which can be isolated, are formed in succession; one of these the authors regard as the "active titanocene":[47] #

$$Cp_2TiCl_2 + 2Na \xrightarrow{20^\circ} [Cp_2Ti]_{1-2}.$$

The results of elemental analysis are not available for this complex, the criteria of its purity and individuality have not been specified, and reactions, sufficiently refined to help in the elucidation of its structure, have not been found. Nevertheless, it has been demonstrated that the complex $[Cp_2Ti]_{1-2}$ is metastable and is converted into the stable bistitanocene on prolonged stirring in solutions with sodium or on heating to 100 °C. Its properties have been described extremely briefly.[47] Thus it has been reported that the reaction with HCl leads to Cp_2TiCl_2, while the reaction with CO yields $Cp_2Ti(CO)_2$. The complex catalyses the hydrogenation of olefins at atmospheric hydrogen pressure and is capable of forming a complex with nitrogen having the tentative composition $Cp_2Ti{-}N{=}N{-}TiCp_2$.

A highly reactive titanocene complex, called "metastable titanocene", was obtained in 1971 as a result of the slow spontaneous decomposition of a suspension of the grey-green polymeric hydride $(Cp_2TiH)_x$ § in toluene.[11,23] The process proceeds with evolution of hydrogen:

$$Cp_2Ti(Me)_2 \xrightarrow[0^\circ]{H_2} (Cp_2TiH)_n \rightarrow (C_5H_5Ti)_2 + H_2.$$

The complex has an intense dark colour with a greenish tint; measurement of its molecular weight showed that it is dimeric and has the tentative composition $C_{20}H_{20}Ti_2$. Measurement

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#The reduction of Cp_2TiCl_2 by sodium amalgam and the Na/K alloy has been mentioned;[48–51] the structures of the products of these reactions have not been established.

§The polymeric hydride $(Cp_2TiH)_x$ is characterised by an intense Ti–H absorption at 1140 cm^{-1}, in contrast to the dimeric hydride $(Cp_2TiH)_2$, in the spectrum of which the Ti–H absorption band is at 1450 cm^{-1}.[12,23]

of its magnetic susceptibility demonstrated that it is paramagnetic. The complex could not be isolated from solution in the crystalline state and its elemental composition was not therefore analysed; it is not known whether one or several compounds are present in solution. We may note that conclusive evidence concerning the structure and individuality of the polymeric hydride $(Cp_2TiH)_n$ is not available either.

The chemical properties of this bistitanocene have been investigated in fair detail; all the reactions quoted below take place readily and with high yields:[11,23,52]

$$\begin{array}{l} (Cp_2Ti)_2O \xleftarrow{N_2O} \\ (Cp_2TiH)_n \xleftrightarrow{H_2} \\ Cp_2Ti(CO)_2 \xleftarrow{CO} \end{array} \Bigg| \longleftarrow [(C_5H_5)_2Ti]_2 \longrightarrow \Bigg| \begin{array}{l} \xrightleftharpoons{N_2} (Cp_2Ti)_2N_2; \\ \xrightarrow{HCl} Cp_2TiCl_2; \\ \xrightarrow{PPh_3} C_{10}H_{10}TiPPh_3. \end{array}$$

It is striking that the reactions of all the metastable titanocenes described above with HCl and CO proceed in the same way. The so-called "black titanocene", obtained by the photolysis of dimethyltitanocene,[53] i.e.

$$Cp_2Ti(Me)_2 \xrightarrow[\text{solvent}]{h\nu} (C_{10}H_{10}Ti)_n + CH_3^{\cdot},$$

also reacts analogously with the above reagents.

The authors themselves[53] initially suggested that the "black titanocene" which they obtained is analogous to the metastable titanocene synthesised previously.[11,23] However, in contrast to the latter the "black titanocene" is diamagnetic and the ^1H NMR spectra of its solutions contain signals due to the Cp protons (albeit broadened). The structure of the complex has not been discussed in detail and there is also uncertainty as regards its composition: $[C_{10}H_{10}Ti]_2$ or $[C_{10}H_{9-10}Ti]_2$. The complex is much less volatile than the stable bistitanocene. It was found unexpectedly that its interaction with molecular nitrogen leads to the formation of a dark-red compound. In a later investigation[54] the same workers reported the isolation of a very similar but not identical compound on photochemical decomposition of Cp_2TiPh_2.[54] However, it was suggested almost simultaneously[55] that the "black titanocene" is in essence the polymeric compound $[Cp_2TiH]_n$.

All four metastable titanocenes described above are reactive towards molecular nitrogen. Complexes of different compositions have been described and it has been established that treatment of these complexes with reducing agents and subsequent hydrolysis lead to the evolution of ammonia or hydrazine. These investigations have been analysed in detail in a communication[37] whose authors have been actively engaged in this field recently.¶ Only those data are important to us which make it possible to compare the metastable titanocenes with one another. In particular the "metastable titanocene"[11,23] has properties resembling those of the "low-temperature titanocene".[42] Their reactions with H_2, N_2, HCl, and CO are also similar; their infrared spectra and the spectra of the products of their reactions with H_2 and N_2 are likewise similar but not identical. Both compounds form adducts with THF.[12,42,43] One can also assume that the "active titanocene" is identical with the "low-temperature titanocene".[47] The infrared and ultraviolet spectroscopic characteristics of both the initial complex and of its compounds with nitrogen are similar. On the other hand, in terms of a series of other characteristics discussed above, these compounds are not identical or cannot be compared. The greatest uncertainty concerns the "black titanocene".[53] All its reported characteristics differ from those of the other isomers of bistitanocene.

In conclusion, it is appropriate to mention yet again that the metastable bistitanocenes are highly reactive compounds and that in many cases this might have led to methodological errors in the formulation of the experiments and hence to an incorrect interpretation of some of the results.

Titanocenes whose nature is close to that of the metastable complexes discussed above have also been obtained in studies of the thermal decomposition of titanocene derivatives of the type Cp_2TiR_2, where R is an organic or organoelemental group. Depending on the substituents, the decomposition of the complexes Cp_2TiR_2 is carried out at room temperature (R = CH_2Ph,[56] $SnEt_3$, $GeEt_3$, or $SiEt_3$ [57]) or on heating to 70–90 °C (R = Me or Ph [58,59]). It was assumed that initially the thermolysis proceeds in the same way in all cases:

$$Cp_2TiR_2 \rightarrow (C_{10}H_{10}Ti)_n + R^{\cdot},$$

The reactions result in the formation of highly reactive titanocenes sometimes containing THF solvate molecules. The possible structures of the complexes have not been discussed and the formulae of the compounds (Cp_2Ti and Cp_2Ti. .THF) were proposed mainly on the basis of the microanalytical determination of their metal content.

The following reactions have been achieved for the titanocenes obtained in this way:[58–62]

$$(C_{10}H_{10}Ti)_n \Bigg| \begin{array}{ll} \xrightarrow{PhCH_2Cl} Cp_2TiCl_2; & \text{(Ref.58)} \\ \xrightarrow{HCl} Cp_2TiCl_2; & \text{(Ref.59)} \\ \xrightarrow{RCCl_3} Cp_2TiCl_2; & \text{(Ref.59)} \\ \xrightarrow{(PhCOO)_2} Cp_2Ti(OCOPh)_2; & \text{(Ref.60)} \\ \xrightarrow{H_2CCl_2} Cp_2TiCl_2; & \text{(Ref.61)} \\ \xrightarrow{Ph_3CCl} Cp_2TiCl_2 + CpTi(Cl)CPh_3. & \text{(Ref.62)} \end{array}$$

All these reactions with reagents tending to interact via the oxidative addition mechanism proceed readily; they all result in the formation of isotypical mononuclear titanocene derivatives and the yields of the products are frequently high.

Later investigations of the thermal decomposition reactions of the titanocene derivatives Cp_2TiR_2 showed, however, that the abstraction of the groups R from the Cp_2TiR_2 molecules is followed by a hydride shift from the cyclopentadienyl ring to the titanium atom;[63] thus, the structure of the reaction products is undoubtedly more complex than Cp_2Ti or Cp_2Ti. .THF, although it has not yet been established.

The reactions of titanocenes obtained by reducing Cp_2TiCl_2 with boron disulphides, diselenides,[64] and halides[65] have also been achieved:

$$(C_{10}H_{10}Ti)_n \Bigg| \begin{array}{l} \xrightarrow{RS-SR} Cp_2Ti(SR)_2, \\ \xrightarrow{YBX_2} Cp_2Ti(Y)BX_2. \end{array}$$

Unfortunately the relevant communications contain no information which would make it possible to determine the type and quality of the titanocenes with which the authors worked; one cannot rule out the possibility that they dealt with a mixture of isomers.

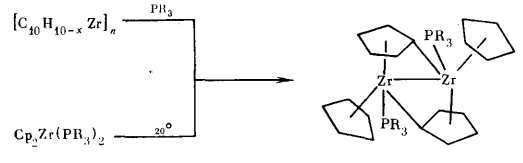
¶ We may point out that the majority of the nitrogen-containing complexes of titanocene and their derivatives, whose structure has been established fairly reliably in one way or another, are dinuclear compounds. However, the dinuclear nature of the structures arises precisely and solely as a result of the 1,2-bidentate nature of the N_2 ligand, which entails the formation of the long Ti–N–N–Ti bridge. Examination of this mode of formation of the dinuclear structures is outside the framework of this review, but the synthesis is nevertheless almost always based on mononuclear titanium compounds. Such structures differ little from other bridged structures with long bidentate or polydentate ligands of the type M–L–L–M.

2. Compounds of Zirconium and Hafnium

Zirconium and hafnium bismetallocenes have been investigated to a much lesser extent than the corresponding titanium derivatives. The increase of the atomic radius on passing from titanium (1.45 Å) to zirconium and hafnium (~1.60 Å), while the structures of the outer electronic levels are the same (d^2s^2 or d^4), leads to an increase of coordinating capacity on passing from Ti to Zr and Hf; the ionisation potentials of the atoms diminish in the same sequence. Accordingly, compounds of the type Cp_2MX_2 are more stable for the heavy elements. It has also been noted that the dialkyl and diaryl derivatives of zirconocene and hafnocene Cp_2MR_2, where R = alkyl or aryl, are thermally more stable than the corresponding titanium compounds.[66]

The methods used to synthesise the zirconium and hafnium metallocenes are on the whole analogous to those employed for the synthesis of bistitanocenes. The reduction reactions of the dihalides Cp_2MCl_2,[20,25,67,68] the thermal decomposition reactions of the dialkyl compounds $Cp_2M(Alk)_2$ and the alkyl hydride complexes,[53,69,70] as well as the reduction reactions involving the cleavage of the dimethylmetallocenes $Cp_2M(Me)_2$ by triethyltin and triethylgermanium hydrides[71] have been investigated. All the reactions led to similar but not identical compounds. The attempts to obtain crystals suitable for X-ray diffraction studies were unsuccessful. The hypothesis that the zirconocene and hafnocene structures are identical with the structure of the stable bistitanocene has not received serious confirmation.

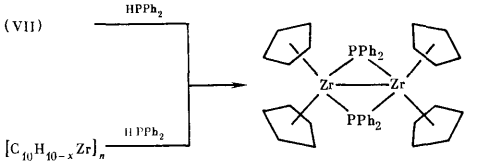
The majority of the investigations have been carried out with zirconium derivatives. However, the data available at present are insufficient to attribute a specific structure to these compounds with adequate confidence. There are also no reliable grounds for the assumption that these compounds are chemically individual (although it is quite natural that, in the analysis of their reactions, the discussion is conducted from the standpoint of their individuality). The presence of an intense absorption band in the infrared spectra of the zirconocenes isolated in the range 1250–1300 cm^{-1}, which disappears after only brief contact of the compounds with air, has been noted. The band occurs in the region characteristic of the Zr–H–Zr bridging fragments.[70,72] Its great width is most probably due to the indeterminate oligomeric character of the structures, which leads to the non-equivalence of the crystal-chemical environments of the hydride atoms. In solution, the zirconium compounds are unstable and give rise slowly to insoluble polymers. It has been found[70,73,74] that the zirconocenes obtained by different methods react with phosphines (PMe_2Ph and PPh_2Me) at 50–60 °C to form the dinuclear zirconocene complexes $[Cp_2.(\mu\text{-}C_5H_4)_2Zr(PR_3)_2]$ in 30–50% yields; the processes are accompanied by the evolution of hydrogen. This readily occurring reaction constitutes in fact the main objection to the hypothesis that the zirconocene has a structure analogous to that of the stable bistitanocene (V).



(VII)

The thermal decomposition of the mononuclear zirconocene–phosphine complexes $Cp_2Zr(PR_3)_2$ leads to the same biszirconocene–bisphosphine product in a high yield.[73,74] The structure of the complex (VII) has been postulated on the basis of the study of its NMR spectra. It is shown below that this complex can be regarded as a kind of structural and electronic analogue of the bisniobocene (XIV).

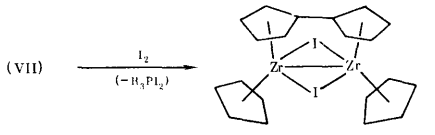
Treatment of compound (VII) with diphenylphosphine (Ph_2PH), which contains a mobile hydrogen atom, results in a very ready cleavage of the Zr–C σ-bonds and the formation of the dinuclear phosphide complex (VIII), whose cyclopentadienyl ligands contain only hydrogen atoms as substituents.[74] However, this reaction is not unambiguous, since the complex $[(C_5H_4)_2Cp_2Zr_2(PHPh_2)_2]_n$ is formed in addition to compound (VIII).



(VIII)

The complex (VIII)† is also formed when oligomeric zirconocenes are treated with Ph_2PH.

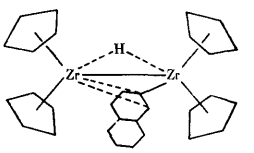
The only example of a dinuclear fulvalene derivative of zirconocene is compound (IX) obtained by treating compound (VII) with iodine at a temperature below −50 °C. The complex (VIII) is diamagnetic, is weakly associated in solution, and, according to ^1H and ^{13}C NMR spectra, has a structure analogous to the fulvalene bistitanocene (V):[74]



(IX)

It must be assumed that, as in compound (V), a direct metal–metal bond should be present in the complex (IX).

In conclusion of this Section, we may mention a recently published study[76] in which an attempt was made to synthesize monomeric zirconocene by the low-temperature reduction of Cp_2ZrCl_2 with potassionaphthalene in THF at −80 °C. The reaction led to the unexpected dinuclear complex (X) with a bridging β-naphthyl group and hydride hydrogen:



(X) $R(Zr\text{-}Zr) = 3.307$ Å

The presence of hydride hydrogen was demonstrated by ^1H NMR and by chemical methods. At room temperature the complex (X) decomposes slowly, giving rise to unknown products. Treatment of the complex with HCl produces Cp_2ZrCl_2 and a mixture of hydrogenated naphthalenes ($C_{10}H_{10}$, $C_{10}H_{12}$, and $C_{10}H_8$). Comparison of the properties of compound (X) and the "low-temperature" bistitanocene as hydrogenation catalysts showed that the effectiveness of compound (X) in this reaction is incomparably lower.[76]

As regards the chemistry of the bismetallocene complexes of Group IV elements, one should also note than an increasing number of studies of the reactions of compounds contain-

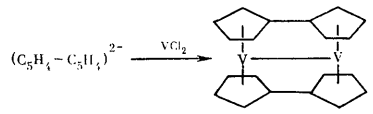
†Such complexes had been obtained earlier from Cp_2ZrCl_2 and $LiPR_2$.[75]

ing the η-C_5Me_5 ligands instead of the η-C_5H_5 ligands have been published in recent years. It has been established that the hydrogen atoms of the methyl groups are directly involved in many reactions of these metallocene derivatives, but the compounds formed are as a rule mononuclear and their structures have nothing in common with those discussed above. For this reason, we have in fact not considered these data; most of such studies have been surveyed in another review.[37]

III. BISMETALLOCENE COMPLEXES OF GROUP V ELEMENTS

Numerous dinuclear metallocene derivatives can be obtained comparatively readily for heavy Group V elements—niobium and tantalum. On the other hand, the formation of bismetallocene complexes, resulting from the combination of mononuclear molecules, has not so far been observed for vanadium. Simple vanadium compounds such as Cp_2V,[1,77] Cp_2VR,[1,78,79] Cp_2VX,[1,80] and Cp_2VR_2[1,81] are monomeric both in solution and in the crystalline state and are not converted into dinuclear structures even under severe conditions. One of the most important causes of this is the marked coordination shielding of the small vanadium atom. All reactions whose mechanisms involve a stage in which there is a significant expansion of the coordination sphere of the metal are apparently extremely energetically unfavourable. Reactions which do not incorporate such a stage proceed readily and lead to complexes with coordination numbers typical for vanadium.

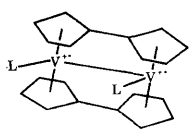
There has been only one study devoted to the synthesis of bismetallocene derivatives of vanadium.[82,83] The key compound in this investigation was difulvalenedivanadium, which has been synthesised in a high yield from the vanadium salt VCl_2 and the fulvalene dianion $(C_5H_4-C_5H_4)^{2-}$:



(XI)

As for the monovanadocene complexes, the coordinating capacity of the metal atom in this compound has been to a significant extent exhausted. Accordingly, the chemical properties of the complex (XI) have nothing in common with those observed for compounds of the Ti, Zr, and Hf series.

Difulvalenedivanadium (XI) and its dicarbonyl derivative $(C_{10}H_8)_2V_2(CO)_2$ are diamagnetic,[83] and in contrast to the related complexes of monomeric vanadocene. The mono- and di-cationic compounds $[(C_{10}H_8)_2V_2]^{n+}$, where $n = 1$ or 2, and $[(C_{10}H_8)_2V_2L_2]^{n+}$, where $n = 1$ or 2 and L = CO or $NCCH_3$, obtained from them are also either diamagnetic or their magnetic susceptibility is low, which distinguishes them sharply from the related derivatives of mononuclear vanadocene. The dicationic adduct $[(C_{10}H_8)_2V_2(NCCH_3)_2]^{2+}(PF_6^-)_2$,[82] i.e.



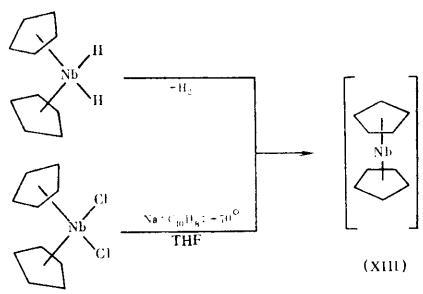
(XII) $R(V-V)=3.329$ Å

has been studied by X-ray diffraction. Crystallographic data for compound (XII) as well as analysis[83] of the electronic absorption spectra and the magnetic behaviour of other dinuclear complexes are consistent with the occurrence of a direct bonding interaction between the vanadium atoms.

Analogous difulvalene compounds of the elements in the second and third transition series are unknown for both Group V and Group IV elements examined above.

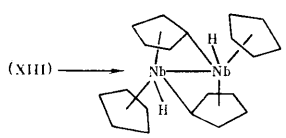
A different picture has been observed for niobium derivatives (there are very few data on the tantalum compounds[84]). There are numerous elements of similarity in the structure and characteristic features of the reactions of the bismetallocene compounds of Ti, Zr, Hf, Nb, and Ta (and, as will be shown below, also Mo and W). However, the first characteristic which draws attention is the fact that the dinuclear compounds are readily formed when attempts are made to synthesise the mononuclear metallocenes. The observed structural and chemical differences between the isoligand dinuclear complexes of different metals are fairly simply and unambiguously related to the electronic configuration of the atoms of these metals, which have different numbers of intrinsic valence electrons depending on the Group.

Like the Group IV elements, niobium and tantalum do not form homoligand mononuclear metallocenes of the type Cp_2M which are stable at room temperature. However, at low temperatures a niobium complex having this particular composition can in fact be detected in solution by EPR.[85-87] It may be that this fact manifests objectively the lower reactivity of the mononuclear metallocenes of the Group V metals caused by their lower electron deficiency.



(XIII)

The monomeric niobocene (XIII) is comparatively stable at temperatures below −60 °C; an increase of temperature entails its rapid and easy conversion into the bisniobocene (XIV):[85,86]



(XIV) $R(Nb-Nb)=3.105$ Å

This reaction is of second order with respect to the monomeric complex and is so far the only known example confirming directly the possibility of the formation of bismetallocenes considered via the dimerisation of the monomeric homoligand metallocenes $(\eta\text{-Cp})_2M$.[86] In essence this is an oxidative addition reaction involving the C–H bonds of another niobocene fragment.# Furthermore the Nb–Nb bond is formed in compound (XIV) despite the fact that the resulting structure is sterically very strained. Overall, the effective atomic number rule holds for the niobium atoms in compound (XIV) and these atoms thus make use of their coordinating and valence capacities in bonding.

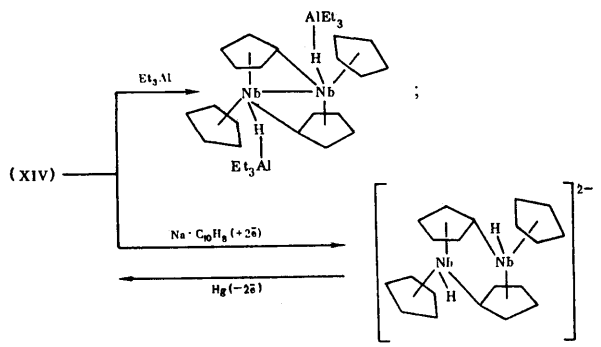
#We may note that other oxidative addition reactions are also known for compound (XII), which, however, have no bearing on the subject of this review.[3]

We may note that the bisniobocene (XIV) was the first compound among the dinuclear metallocene complexes of Group IV–VI elements whose structure and dinuclear nature have been established by direct investigation.[88,89] It was in fact after these publications that all the early studies where the formation of coordination- and electron-deficient mononuclear complexes had been unjustifiably postulated for Group IV–VI elements were re-examined and retested.

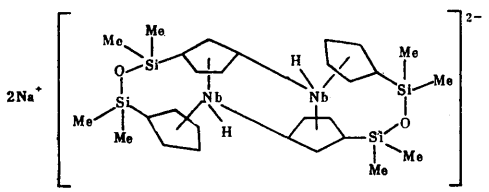
The structure of the bisniobocene (XIV) has different elements of similarity with the "low-temperature" bistitanocene (VI). However, in contrast to the latter, the bisniobocene (XIV) is thermally entirely stable and does not isomerise to a complex with the fulvalene ligand analogous to compound (V) even after prolonged heating to 200–250 °C. The explanation of this difference in the behaviour of compounds (VI) and (XIV) is that the direct thermal rearrangement to the fulvalene dimer $[(Cp)_2(C_5H_4{-}C_5H_4)Nb_2(H)_2]$ is unfavourable for the bisniobocene (XIV) as a consequence of the overall loss of bonding energy. However, we showed in our later studies (see the appendix at the end of the review) that the indirect two-stage conversion of compound (XIV) into a fulvalene complex of this kind takes place readily; it entails the intermediate synthesis of a dinuclear halogeno-derivative.

The majority of the reactions of the bisniobocene (XIV), like those of the titanium subgroup derivatives, are many-centre processes and involve the entire system of σ-bonds (i.e. the M–M, M–C, and M–H σ-bonds) in the central fragment of this compound. On the whole, this is not surprising, since such molecular fragments are none other than heteronuclear clusters in which the simultaneous rearrangement of a large number of chemical bonds constitutes a common phenomenon. The local transformations involving one atom or one bond are not then ruled out, but the range of reagents capable of effecting such reactions is sharply reduced.

It has been noted for only two reactions of the bisniobocene (XIV) that the nature of the ligand groups does not change. Thus the interaction of compound (XIV) with Et_3Al involves only the Nb–H hydride atoms and converts them into the Nb–H–Al bridge group.[90] On the other hand, treatment of compound (XIV) with strong electron donors leads to the formation of dianionic complexes.[91] In the latter case the reverse reaction also takes place quantitatively.



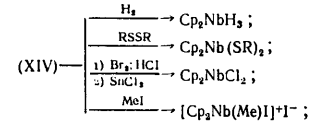
The disodium salt of silylbisniobocene has been investigated by X-ray diffraction.[91]



(XV) $R(Nb{-}Nb) = 3.932$ Å

Compared with the neutral bisniobocene, the corresponding dianionic complexes (XV) are characterised by significantly greater interatomic distances M...M, which can no longer be regarded as metal–metal bonds. As a consequence, there is virtually no steric strain in the structure of the dianions. The additional electrons are thus transferred to the antibonding σ^*_{MM} molecular orbital. This conclusion has been confirmed unambiguously by a study of the electronic spectra of the neutral and anionic complexes.[91]

One of the most characteristic many-centre reactions of the bisniobocene (XIV) is its ready decomposition to the mononuclear derivatives Cp_2NbX_2. These reactions are rapid and smooth and the yields of the final products are extremely high.[3,84]

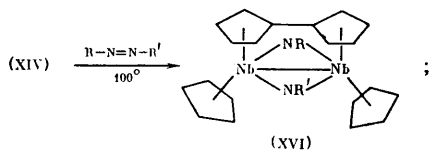


Cp_2NbH_3; $Cp_2Nb(SR)_2$; Cp_2NbCl_2; $[Cp_2Nb(Me)I]^+I^-$;

R = aryl or ferrocenyl.

It should be specially noted that the products of these reactions contain no substituents in the cyclopentadienyl rings other than hydrogen. We have already encountered a similar fact in relation to the individual reactions of the complexes (VI) and (VII), but, in view of the small number of available observations and the low yields of the final products, great importance could not be attributed to such reactions. The results obtained for bisniobocene show that these reactions occur consistently, but their mechanism is at present unknown. The main feature which must be established is whether individual stages of these processes can be discovered and then carried out as independent reactions (see the appendix below).

Another type of many-centre reactions of bisniobocene comprises those which lead to dinuclear complexes with the fulvalene ligand. As noted above in the discussion of the complexes of titanocenes with molecular nitrogen, such rearrangements are very strongly promoted by the presence in the coordination sphere of the metal of atoms capable of acting as effective bridging ligands; these are usually halogen, oxygen, sulphur, and nitrogen atoms. This approach has been specifically and widely used in the synthesis of fulvalene derivatives of niobium. Thus the interaction of compound (XIV) with aromatic azo-compounds led to fulvalene complexes with two bridging nitrene ligands:[92]



(XVI)

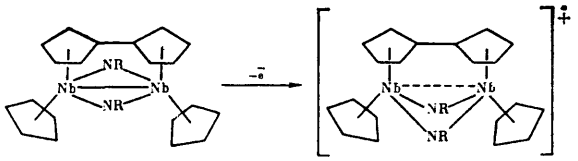
(a) $R = R' = Ph, C_6H_4Me, C_6H_4OMe$;

(b) $R = Ph$, $R' = C_6H_4NMe_2$.

The use of an asymmetric azo-derivative made it possible to obtain a compound with two different nitrene ligands.

The complexes (XVI) proved to be very interesting subjects for spectroscopic, structural, and chemical studies.[93,94] The presence of the direct metal–metal bond and the stereochemical and electronic saturation of the coordination spheres of the metal atoms determine all the characteristic features of their structure and behaviour. Among all the dinuclear metallocene complexes examined in the present review, these are the only compounds which are entirely stable in air even at elevated temperatures (250 °C). They withstand chromatographic purification on Al_2O_3 and readily sublime *in vacuo*.

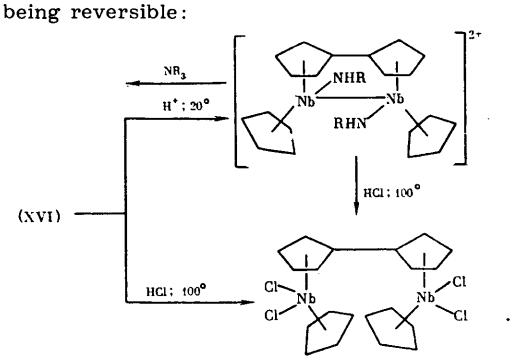
The one-electron oxidation of the fulvalenenitreneniobium complexes (XVI) by ferrocenium salts, mercury and silver salts, and atmospheric oxygen in an acid medium takes place quantitatively.[94] This has led to the synthesis of a whole series of salts of the complex radical-cations (XVII) which are stable in air.



(XVIa) $R(Nb-Nb)=2.834$ Å (XVII) $R(Nb-Nb)=2.921$ Å

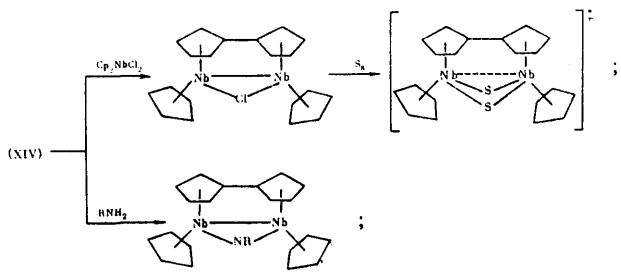
Comparison of the structures and the electronic spectra of the complexes (XVI) and (XVII) established that the electron is eliminated from the metal–metal bond.[94]

Protonation of compound (XVI) by dilute solutions of strong acids under mild conditions converts them into dicationic complexes with terminal nitrogen-containing ligands, the process being reversible:



Under severe conditions (~100 °C) in the presence of an excess of acid and anions which are powerful nucleophiles the nitrene ligands are split off irreversibly.[93]

Another series of dinuclear fulvalene complexes have been obtained from the bisniobocene (XIV), namely compounds with a single bridging heteroligand. Two types of such compounds have been obtained: diamagnetic with a single bridging nitrene two-electron-donating ligand[95] and paramagnetic with a bridging halogen atom—a three-electron-donating ligand:[96,97]



R = Ph, C_6H_4Me, $C_6H_4N_2Ph$.

The chlorine-containing single-bridge complex is converted by elemental sulphur into a disulphide radical-cation complex, which is an analogue of the radical-cation dinitrene compound (XVII).[98]

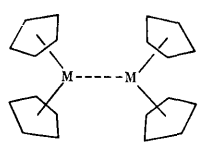
Comparison of the overall data on the bismetallocenes of Group IV and V elements shows that throughout the period of the development of the research into the Group IV elements, most effort has been directed to the determination of the structures of the key compounds. In the case of the Group V compounds the situation is different; the structure of the compounds was established comparatively rapidly and investigations were concentrated mainly on the characteristic features of their chemical reactions.

IV. BISMETALLOCENE COMPLEXES OF GROUP VI ELEMENTS

The first bismetallocene compounds of Group VI metals were synthesised approximately 10 years ago and the most intense research has been prosecuted during the last five years. As for the Group V compounds, among the derivatives of the Group VI elements dinuclear complexes with a wide variety of structures are formed readily only by the heavy elements—molybdenum and tungsten. On the other hand, as in the case of vanadium,[1] the formation of bismetallocene compounds is altogether uncharacteristic of chromium.[2] The only exception is difulvalenedichromium,[99] which is discussed below after the monofulvalene derivatives; data on the difulvalenedimolybdenum compounds are also presented.[100]

The monomeric homoligand molybdenocene and tungstocene were obtained in 1979 by the low-temperature photolysis of Cp_2MH_2 and $Cp_2M(CO)$ and have been detected spectroscopically (on the basis of infrared spectroscopic data) in an argon matrix at 10 K.[4] The claims concerning the formation of derivatives having the composition $C_{10}H_{10}M$ prior to the above study refer, as is now clear, to compounds having a more complex structure; the monomeric compounds $C_{10}H_{10}M$ are indeed formed but only as extremely labile intermediates which cannot be detected by physical methods. It has been found that, on raising the temperature, the monomeric molybdenocene and tungstocene undergo irreversible association to form complexes $(Cp_2M)_x$ of unknown structure—tentatively dimers.[101,102] It may be that these compounds are identical with complexes having the same composition and obtained previously by the reduction of Cp_2MCl_2 with sodium amalgam.[103,104] In the mass spectra of the complexes $(Cp_2M)_x$, obtained by reducing metallocene dihalides, the $C_{20}H_{20}M_2^+$ ion is heaviest, while the ^1H NMR spectra of solutions of these compounds exhibit only one signal due to the protons of the unsubstituted cyclopentadienyl rings.[104]

For a long time, the above derivatives were the only bismetallocene complexes whose association was tentatively assumed to occur only as a result of metal–metal bonding. Analogous evidence has now been obtained also for rheniocene (see the appendix below).



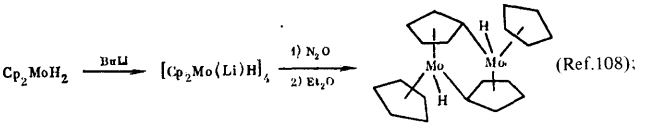
(XVIII)

The chemical behaviour of the complexes (XVIII) is characterised by an extremely ready conversion into mononuclear derivatives on interaction with a wide variety of compounds in which they behave as carbene-like species.[103–107] The reaction products are complexes of the type $Cp_2M(L)_n$ (n = 1 when L is a two-electron-donating ligand and n = 2 when L is a one-electron-donating group).

Attention has been drawn to the fact[105,107] that the rearrangement of these associated species to other bismetallocenes, whose structures include bridging $\eta^5:\eta^1$-C_5H_4 and $\eta^5:\eta^5$-C_5H_4-C_5H_4 ligands, does not take place. This is surprising because many compounds with such bridging groups are known for both molybdenum and tungsten and the latter complexes readily undergo interconversions.

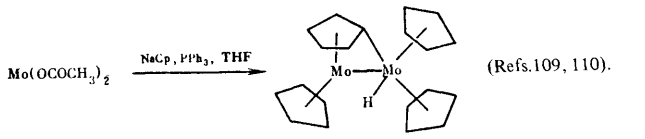
The bismetallocenes of molybdenum and tungsten with the $\eta^5:\eta^1$-C_5H_4 and $\eta^5:\eta^5$-C_5H_4–C_5H_4 ligands have now been investigated in fair detail. Their structure and interconversions follow the same rules, as regards their most fundamental aspects, which were manifested in the behaviour of the isoligand complexes of Group IV and V metals.

Two reactions, which make it possible to obtain dinuclear compounds with bridging $\eta^5:\eta^1$-C_5H_4 ligands, are known for molybdenocene derivatives:



(Ref.108);

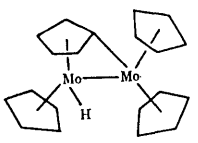
(XIX)



(Refs.109, 110).

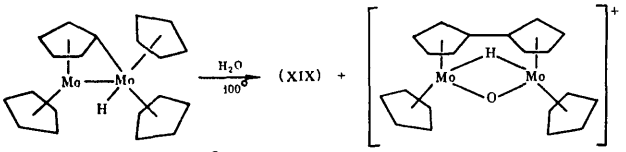
(XXa)

The bismolybdenum complex (XIX) resembles the bisniobocene (XIV), while the other compound (XXa) is similar to the "low-temperature" isomer of the bistitanocene (V). Compound (XXa) has also been converted into the complex (XIX) by heating a suspension of compound (XX) in water at 100 °C.[110]



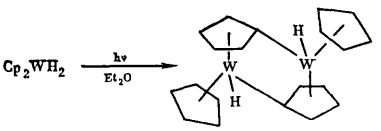
(XXb)

As shown below, the process leads to a mixture of two products. Compound (XXa) is apparently converted into compound (XIX) directly in the crystal phase, while the second compound is formed on interaction of compound (XX) with water. The structures of the complexes were determined from infrared spectroscopic, NMR, and mass spectrometric data and for compound (XXa) an X-ray diffraction study was carried out in addition.[109,110] However, the locations of the hydrogen atoms could not be determined in the course of the structural study. The association of the hydride hydrogen with the molybdenum atom can therefore be regarded merely as being most probable on the basis of a set of spectroscopic and stereochemical considerations but has been by no means finally demonstrated. The structure (XXb) is possible as an alternative.



(XXa) R(Mo–Mo)=3.189 Å

The bistungstocene (XXI) has been obtained by the photolysis of tungstocene dihydride in ether and also by its thermolysis in cyclohexane.[111,112] The structure of the product has been demonstrated by X-ray diffraction:[101]



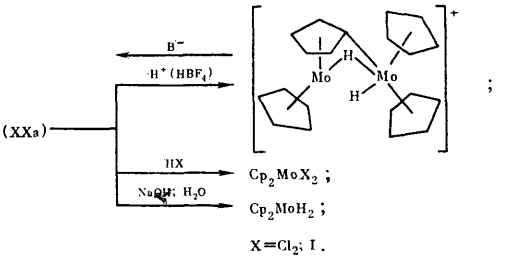
(XXI) R(W–W)=3.81 Å

Its photolysis or thermolysis in the presence of tetramethylsilane led to the synthesis of the related *cis*- and *trans*-isomeric products $(C_5H_5)(Me_3SiCH_2)W(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)_2W(H)\cdot(C_5H_5)$.[101,111] The methyl analogue $(C_5H_5)MeW(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)_2W(C_2H_5)(H)$ has also been obtained by the thermolysis of $Cp_2WH(Me)$.[112]

In discussing the mechanisms of these reactions, it has been suggested[111,112] that they all include a stage involving the formation of the free metallocenes $(\eta^5\text{-}C_5H_5)_2M$, because otherwise the complexes (XIX), (XX), and (XXI) should have been readily obtained from the monomeric molybdenocene and tungstocene, whose existence has been demonstrated. It has been postulated[101,108–112] that the dimers (XIX)–(XXI) listed above arise not from the free mononuclear metallocenes but from their highly reactive adducts (having a wedge-shaped structure) with molecular nitrogen [in the synthesis of compound (XIX)], with triphenylphosphine [in the formation of compound (XXI)], or, finally, with solvent molecules [in the formation of compound (XXI)]. However, there is no reliable experimental confirmation of these hypotheses.

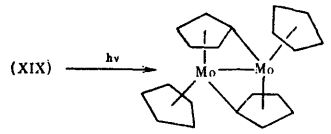
Further chemical reactions of the dinuclear compounds with bridging η^5-C_5H_4 ligands resemble the familiar reactions of the corresponding bistitanocene and bisniobocene complexes. The differences observed in these reactions are due to the increase of the number of intrinsic electrons in each metal atom in the series of derivatives of Group IV, V, and VI elements or, in other words, to the decrease of the electron deficiency of the metallic centre. In the molybdenum and tungsten compounds this is responsible for the resulting decrease of the maximum number of possible chemical bonds. Such a decrease entails a smaller steric strain in virtually all the dinuclear derivatives of molybdenum and tungsten compared with the analogous isoligand complexes of Group IV and V metals. A second characteristic feature, an overall appreciable decrease of the reactivity of the bismetallocene compounds on passing to derivatives of Group VI elements and also a significant decrease of the proportion of many-centre reactions of such compounds, is directly related to the first feature described above. Thus molybdenum and tungsten complexes are as a rule fairly resistant to reaction with water and acids (even at elevated temperatures), while the decomposition of the titanium, zirconium, hafnium, niobium, and tantalum compounds proceeds very readily and is frequently accompanied by the loss of cyclopentadienyl ligands. Reactions involving individual bonds, in the first place M–M and M–H bonds, can be achieved much more readily having molybdenum and tungsten complexes.

The complex (XXa) is readily and reversibly protonated. On the other hand, when acids whose anions are powerful nucleophiles are used for the protonation, the dinuclear structure is completely cleaved:[109,110]



Treatment of compound (XXa) with aqueous alkali unexpectedly led to the formation of the mononuclear molybdenocene dihydride.[110] In relation to the metal atoms, this is in essence a disproportionation reaction, although the nature of the metal-containing products has not been established.

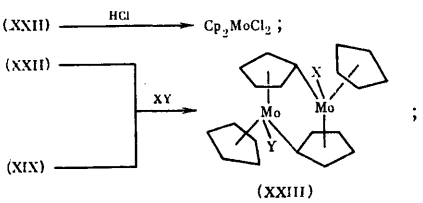
The structures of the complexes (XIX) and (XXI) are analogous to that of the dianionic bisniobocene derivative (XV). This is not surprising, since all these compounds contain identical ligand groups and are isoelectronic. On the other hand, the oxidised dicationic derivatives of the bismolybdenocene (XIX) and the bistungstocene (XXI) should apparently be isoelectronic and apparently isostructural with the neutral bisniobocenes (XIV). However, the oxidation reactions of molybdenocene and tungstocene have not been investigated. At the same time, the photochemical dehydrogenation of compound (XIX) has been achieved.[102,110,113]



(XXII) $R(Mo-Mo)=2.886$ Å

The structure of compound (XXII) isolated in this reaction, which the authors called "dehydromolybdenocene", has been established by X-ray diffraction. This structure does indeed resemble that of the bisniobocene (XIV) and differs from it by the absence of two hydride hydrogen atoms, whose place in the molecule of compound (XXII) is taken by three electron pairs. The same compound has been obtained also from other isomeric bismolybdenocenes by their photochemical dehydrogenation.[111,113] It was found that all the reactions leading to compound (XXII) are extremely sensitive to a series of factors and their successful occurrence is strongly influenced by the temperature, the nature of the solvent, and the presence of specific nucleophilic additives (organic phosphines, etc.).

Two types of reactions have been carried out for the dehydromolybdenocene (XXII)—the complete cleavage of the dinuclear structure and oxidative degradation of the Mo–Mo σ-bond.[112-113] The latter reaction leads to the dinuclear complexes (XXIII), which are analogues of bismolybdenocene (XIX). It has been shown that the same compounds (XXIII) can be obtained directly from the molybdenocene (XIX) by treatment with the appropriate reagents under mild conditions:[108]



XY=MeBr; MeI; I_2.

The complex (XXIII), in which the neopentyl substituents CH_2CMe_3 are σ-bound by the Mo–X and Mo–Y groups, was unexpectedly obtained by the reaction of Cp_2MoCl_2 with $LiCH_2CMe_3$.[114]

We shall now consider data on the dinuclear fulvalene complexes. As happens for the derivatives of Group IV and V metals, the bismolybdenocenes (XIX) and (XX) with the bridging $\eta^5:\eta^1$-C_5H_4 ligands enter comparatively readily into thermal reactions, rearranging under these conditions into bimetallic fulvalene derivatives. The simultaneous replacement of hydride hydrogen atoms by other more electronegative atoms accelerates these reactions significantly, enabling many of them to take place rapidly even at room temperature.

It has been noted that two types of bismolybdenocene complexes are formed.[101,106,108,110-112,115,116] Compounds of the first type [(X)(Y)CpMo(η^5-C_5H_4-η^5-C_5H_4)MoCp(Y)(X)] (XXIV) are usually produced. The corresponding monometallocene analogues Cp_2Mo (X)(Y) are known and have been thoroughly investigated for all the complexes (XXIV) synthesised. The chemical and physical properties of the mononuclear and dinuclear complexes are extremely similar owing to the absence of the mutual influence of the two metallic centres in compound (XXIV). In view of the foregoing, there is no point in considering in detail the reactions of compound (XXV). Another situation arises as regards the fulvalene bismolybdenocene complexes of the second type—compounds (XXV). These complexes have no direct analogues among the mononuclear derivatives. A distinctive structural characteristic of the molecule of compound (XXV) is the presence of the direct metal–metal bond, as a consequence of which the number of σ-bound groups is reduced by two in these compounds compared with compound (XXIV). The schematic formula (X)CpMo(η^5-C_5H_4-η^5-C_5H_4)MoCp(X) corresponds to compounds (XXV); the groups X always occupy the terminal positions and cannot pass to the bridging positions owing to the electronic and coordination saturation of the metallic centres.

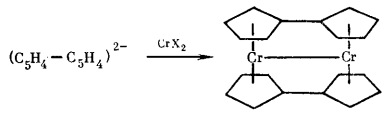
Certain reactions involving the Mo–Mo σ-bonds in the complexes (XXV) have been investigated and it has been shown that these reactions do not differ essentially from those which occur normally for different dinuclear complexes of other transition metals of the type L_nM-ML_n without bridging groups. All the reactions in which compounds (XIX) and (XX) are converted into the fulvalene derivatives (XXIV) (XXV) and the principal reactions of the latter are indicated in the Scheme below.

The photochemical reactions of the fulvalenebismolybdenocenes, which permit the reverse conversion of the fulvalene complexes into compounds with bridging $\eta^5:\eta^1$-C_5H_4 ligands, are much more important and interesting. Such reactions have not been investigated at all for other dinuclear metallocene compounds.

It has been established that the photolysis of the fulvalene derivative (XXV) takes place rapidly in toluene in the presence of small amounts of added tri-n-propylphosphine, which results in a mixture of the *cis*- and *trans*-isomeric complexes (XIX).[113] It has also been observed that, in the presence of free phosphine, compounds (XXV) and (XIX) are virtually unable to be converted into the "dehydromolybdenocene" (XXII). At the same time the complex (XXII) is readily formed from both compound (XXV) and compound (XIX) by their photolysis in the absence of phosphine in the reaction mixture.[112] The mechanisms of these reactions are at present obscure. It has been suggested that intermediates containing both hydride hydrogen atoms at one metal atom, i.e. incorporating the MoH_2 fragment, lead to the "dehydromolybdenocene" (XXII). On the other hand, the role of phosphine in this process reduces to the fact that, by occupying coordination sites at the Mo atoms (and possibly also by converting some of the η^5-Cp ligands into η^3-bound ligands), it prevents the transfer of hydride atoms and the formation of intermediates with MoH_2 fragments.[112,113]

In conclusion we shall consider the very small amount of data on compounds containing two fulvalene ligands. As for vanadium (see above), the presence of two rigid polydentate ligands sharply restricts the capacity of such compounds for chemical reactions. The only bismetallocene complex of chromium, namely difulvalenedichromium, has been obtained by direct synthesis from the fulvalene ligand and a chromium

salt:[99]

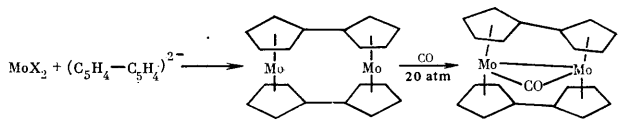


(XXVI)

Only one reaction of the complex (XXVI) has been achieved, namely oxidation leading to the formation of the corresponding monocation and dication.

The magnetic and spectroscopic characteristics of compound (XXVI) agree with the hypothesis of the direct overlap of the AO of the metal atoms, which results in the complete pairing of the electron spins in the ground state (even at temperatures below −50 °C). On the other hand, with increase of temperature, the excited paramagnetic states of the molecule are populated.[99]

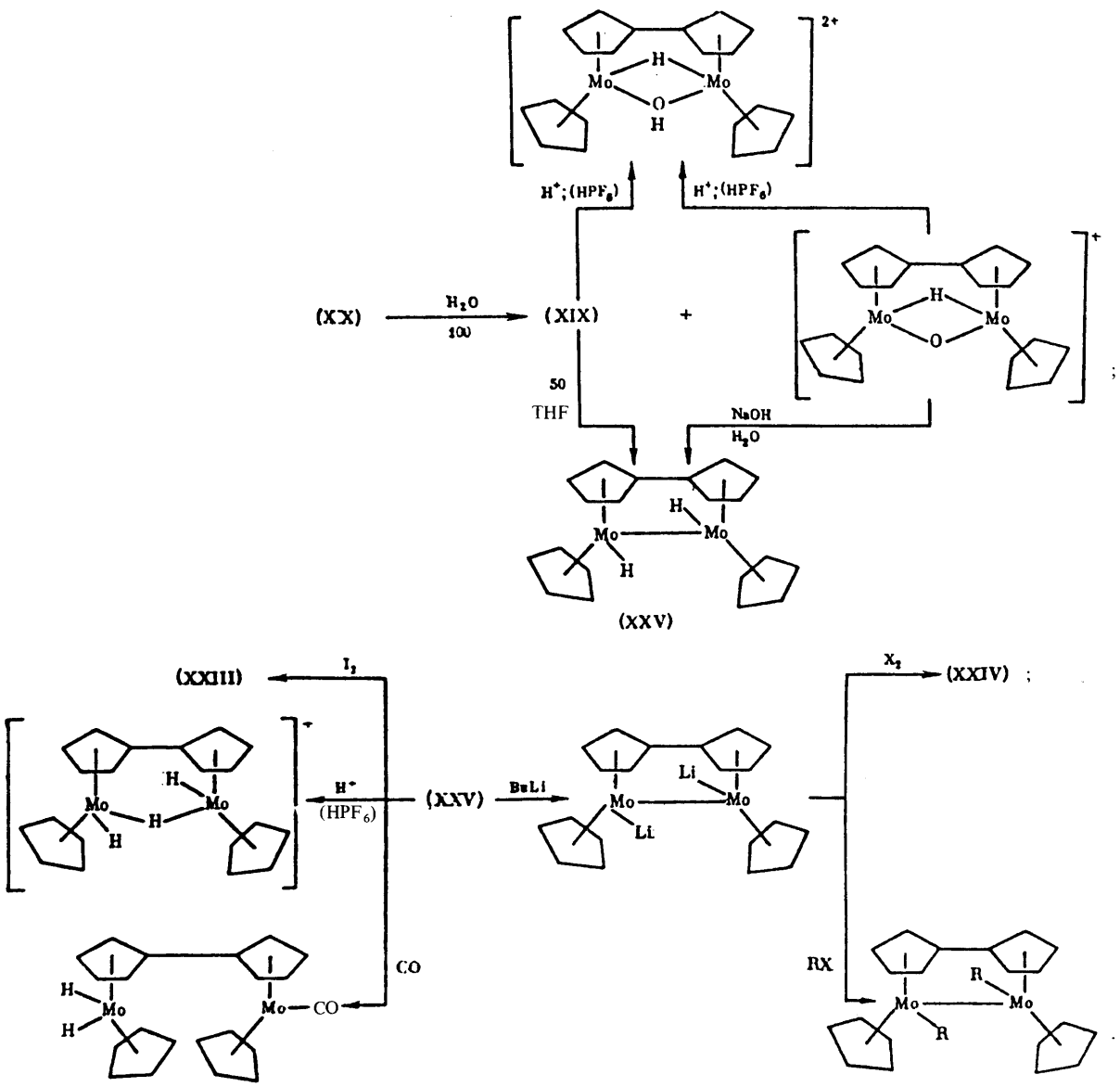
An analogous difulvalene complex has been synthesised for molybdenum [compound (XXVII)]; this is so far the only difulvalene derivative obtained for metals of the second transition series:[100]



(XXVII) (XXVIII)

The ready addition of carbon monoxide to compound (XXVII), which results in the formation of compound (XXVIII), can be easily explained by taking into account the coordination capacity of molybdenum and the entire data presented above. The question of metal–metal interaction in compounds (XXVII) and (XXVIII) has not been analysed in detail, but one cannot rule out the possibility that a multiple

Scheme



metal–metal bond exists in the molecule of compound (XXVII), since in the related complex tetraallyldimolybdenum a quadruple metal–metal bond is believed to be produced.[117]

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During the preparation of the manuscript for the press, one of the authors of this review obtained new data on the structure and reactions of the bisniobocene and bistitanocene complexes.[118–121] It was established that the replacement of one of the terminal hydride atoms in the bisniobocene (XIV) under mild conditions by a halogen atom entails the formation of thermally extremely unstable derivatives having apparently the structure $Cp(H)Nb(\mu\text{-}C_5H_4)_2NbCp(Hal)$. These intermediates rapidly rearrange to the thermally stable fulvalene hydride halide complexes $\mu\text{-}(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Cp_2Nb_2(\mu\text{-}H)(\mu\text{-}Hal)$ (XXIX), such rearrangements being both thermodynamically and kinetically allowed.[118,119] The bridging halogen atom in compound (XXIX) can be readily substituted by nucleophiles. The alkoxide hydride complexes $\mu\text{-}(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Cp_2Nb_2(\mu\text{-}H)(\mu\text{-}OR)$ (XXX), where R = Me or Et, and the dihydride complex $\mu\text{-}(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Cp_2Nb_2(\mu\text{-}H)_2$ (XXXI) have been obtained in this way. The latter is an isomer of the bisniobocene (XIV). One cannot rule out the possibility that the majority of the syntheses of the stable isomer bistitanocene (V) described in the literature also proceed via the hydride halide fulvalene complex $\mu\text{-}(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Cp_2Ti_2(\mu\text{-}H)(\mu\text{-}Hal)$ (XXXII), by-passing the stage involving the formation of the metastable bistitanocenes. This conclusion agrees with the finding that the metastable bistitanocenes are converted into compound (V) usually under more severe conditions and that the yields of compound (V) are far from quantitative.

Compounds (XXX, R = Et) and (XXXII) have been studied by X-ray diffraction. Despite the different electronic configurations of the metal atoms, the structures of the two complexes are almost identical; the metal–metal distances are respectively R(Nb–Nb) = 3.136 Å and R(Ti–Ti) = 3.126 Å.[120]

The temperature variation of the ^{1}H NMR spectra of compounds (V) and (XXXI) have been investigated.[121] The complex (XXXI) is diamagnetic, while the complex (V) is also diamagnetic at a low temperature (–60 °C) but at higher temperatures its excited triplet state is appreciably populated, which is manifested by the corresponding shift of the signals and broadening of the lines.

Mention should also be made of the study[122] of the rheniocene dimers. $(Cp_2Re)_2$ was obtained by oxidising Cp_2ReLi with benzaldehyde. This complex gives rise to a single signal in the ^{1}H NMR spectrum and is apparently associated only via a direct metal–metal bond. A disproportionation reaction is induced when it is heated in acetonitrile, which entails the formation of a mixture of Cp_2ReH and $\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4)_2Cp_2Re_2$. The photolysis of $(Cp_2Re)_2$ leads to the formation of $\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4)CpRe(\eta^4\text{-}C_5H_6)ReCp$.

In conclusion of the review, we may say that the studies of recent years have led to the discovery of a large new field of bismetallocene complexes of the elements at the beginning of the transition series, the complexes having specific structures. Interesting many-centre rearrangements and certain unusual reactions have been observed for these complexes. The very fact of the formation of bismetallocenes demonstrates that the labile intermediates arising in the course of the reactions activate the C–H bonds of the organic ligands very effectively. On the other hand, the determination of the characteristic features of the electronic structures of the bismetallocenes already makes it possible not only to explain the experimental results but also to plan specific syntheses of quite definite new compounds.

However, it is evident that the point on which research is concentrated is beginning to shift. In the next few years there will probably be an appreciable expansion of research into the chemical properties of bismetallocenes and among them compounds of interest for practical applications will be found. The synthesis of mixed metallic complexes, whose chemistry is richer still, is also in the pipeline.

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