

# A CONTRIBUTION TO THE CHEMISTRY OF ORGANOTRANSITION METAL HALIDES

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## ABSTRACT

Transition metal halides are often converted into more or less well-defined reduction products by Grignard reagents, organolithium and organoaluminium compounds. By means of less polar alkylating or arylating agents, such as zinc dialkyls, tin tetraalkyls and boron trialkyls, definite organotransition metal halides can be obtained. Alkyl and aryltitanium trihalides, alkyltungsten pentachlorides and complexes of alkylzirconium trihalides, dialkylzirconium dihalides and dialkylvanadium dichlorides, prepared in this way, are described and discussed.

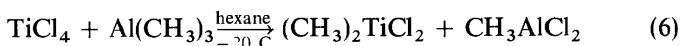
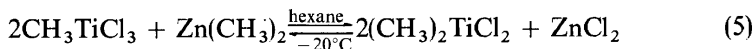
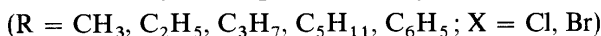
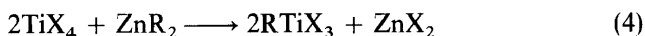
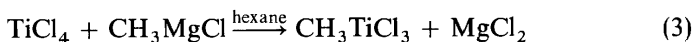
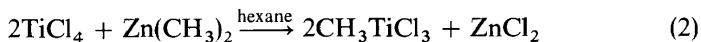
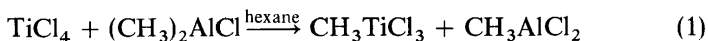
The chemistry of  $\sigma$ -transition metal compounds has been greatly developed in the last 10–15 years. The new compounds of this class of substances are predominantly such in which, besides  $\sigma$ -bonded organo-groups, ligands capable of forming  $\pi$ -bonds, such as carbon monoxide molecules or cyclopentadienyl groups are attached to the metal atoms. In this case, the  $\pi$ -bonded ligands ordinarily cause a rise in the stability of the  $\sigma$ -metal-carbon bonds.

According to the kind of reflection, the conditions of the bonds at the transition metal atoms are more simple or more complicated if, except for the  $\sigma$ -bonded alkyl or aryl groups, only halogen atoms are attached to the metal atoms. However, it is not yet possible to give universal statements concerning this part of the chemistry of organotransition metals since the number of known and more precisely characterized organotransition metal halides is still very small. This is still a very undeveloped area of organometallic chemistry, the treatment of which, however, requires a considerable amount of experimental work.

Experiments to alkylate or arylate different transition metal halides were carried out even in the second half of the last century. Zinc and mercury dialkyls or aryls and Grignard reagents and later organolithium compounds, were used predominantly, as alkylating agents. In many of these experiments the sensitivity of the expected compounds to air and moisture was not sufficiently taken into account. However, more important in all these former experiments was the fact that the small thermal stability of many organotransition metal compounds, which is well known today, was not expected at that time, and therefore, only more or less well-defined reduction products of the transition metal halides were obtained. However, the decomposition temperature of the desired organotransition metal halides

is not the only criterion involved, as will be exemplified later. The polarity of the metal-carbon bonds in the alkylating agents used for the alkylation of transition metal halides is much more significant than is frequently assumed. Considerable differences in the course of the reaction may occur even at rather small differences of polarity. Therefore, it is not very surprising that the preparation of compounds of the type  $R_nMX_m$  was more successful when anaerobic techniques were reliably mastered and when the reactions of transition metal halides with alkylating agents of small polarity, such as zinc and mercury dialkyls, boron and aluminium trialkyls as well as tetraalkyls of tin and lead, were carried out at low temperatures. Some exceptions are to be found in the case of certain alkyl compounds of gold and platinum as well as of some organochromium compounds. However, these will not be treated further here; this report will be mainly concerned with the preparation of some organotransition metal halides of titanium, zirconium, vanadium, tungsten and molybdenum and some of their properties.

In recent years methyltitanium trichloride has been studied intensively. The thorough investigation of this substance is, among others, a consequence of the importance of alkyltitanium trichlorides in Ziegler-Natta polymerization catalysts. The most important reactions by which methyltitanium trichloride can be prepared are represented by the following equations.



After Beermann and Bestian<sup>1</sup> had given the first report about the preparation of methyltitanium trichloride from titanium tetrachloride and diethylaluminium chloride in 1959, another method of the preparation, the reaction of titanium tetrachloride with dimethylzinc, was found in 1961 by de Vries<sup>2</sup>. Furthermore, the methyl compound can be prepared in a relatively simple way by the reaction of titanium tetrachloride with an ether-free suspension of methylmagnesium chloride in hexane solvent<sup>3</sup>. The reaction represented by equation 2 is universally suitable for the preparation of alkyltitanium trihalides. In this way, according to equation 4 besides the methyl compound, ethyl, propyl, n-pentyl and especially phenyltitanium trichloride as well as methyl and phenyltitanium tribromide can be obtained either in the pure state or in the form of complexes<sup>4</sup>. In such reactions, it is important that the molar ratios of the reactants, given by equation 4, are strictly obeyed. In the case of the methyl compound it could be proved that an excess of dimethyl-

zinc leads to the formation of dimethyltitanium dichloride. However, contrary to the reaction of titanium tetrachloride with trimethylaluminium already described<sup>1</sup> no quantitative reaction in the sense of equation 5 takes place. Dialkyltitanium dichlorides are considerably less stable than the monoalkyl compounds and therefore an excess, or too quick an addition of the dialkylzinc, leads to a considerable decrease in the yield of the monoalkyl compound.

Alkyltitanium trihalides are interesting from different aspects, and they still offer some unsolved problems. For instance, the conditions of structure, especially in the solid state of these substances, are not yet sufficiently clear. Without exception, the solid compounds form crystals of a deep-violet colour which changes into an intensive yellow when dissolved in aliphatic hydrocarbons, the molecules of which are not able to fully interact with the molecules of the alkyltitanium trichlorides. Furthermore, a comparison of the methyl and the phenyl compounds is of great interest. Whilst methyltitanium trichloride can be distilled in vacuo between 30 and 40°C without decomposition, the phenyl compound decomposes in the solid state as well as in solution above  $-5^{\circ}\text{C}$ . Specimens of the solid substance explode at this temperature. These observations which demonstrate considerable differences in the thermal stability of both compounds are directly opposed to the stability rules for organotitanium compounds established by Herman and Nelson<sup>5,6</sup> about 15 years ago. These rules are frequently cited and used in the literature, and therefore it is necessary to warn against a universal application. These remarks do not imply any doubt in the experimental results of these authors, but it is important to state that the mentioned results are not derived from isolated substances. Furthermore, the term 'thermal stability' is not defined exactly enough and is not used uniformly. The irreversible cleavage of metal-carbon bonds occurring above a certain temperature is dependent on many factors and therefore cannot be used for exact comparisons.

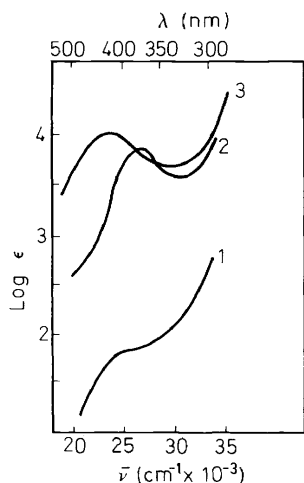


Figure 1. U.v. spectra of methyltitanium trichloride (1), phenyltitanium trichloride (2) and phenylvanadium oxydichloride (3) in *n*-hexane at 22°C

In connection with the stability of methyl and phenyltitanium trichlorides, a comparison of the absorption spectra of both compounds is very interesting (*Figure 1*). Methyltitanium trichloride shows an absorption band at  $26300\text{ cm}^{-1}$ . According to the results of Dijkgraaf and Rousseau<sup>7</sup> which are probably more exact, this peak occurs at  $25000\text{ cm}^{-1}$ . The corresponding  $\epsilon$ -value was found to be 75. The absorption band observed is due to a  $n\text{-}\sigma^*$  transition, i.e. an electron transfer from the Ti—C bond to a d-orbital of the titanium atom located in an energetically favourable position. In the spectrum of phenyltitanium trichloride, a strong band is found at nearly the same wave number of  $27000\text{ cm}^{-1}$ . This band may be attributed, as a metal reduction band, to an analogous electron transfer. The  $\epsilon$ -value of 5500 which is considerably higher corresponds to a greater probability of this transition and is in accord with the smaller strength of the titanium—carbon bond. This fact also corresponds with the observed thermal behaviour of the phenyl compound. For comparison, the spectrum of phenylvanadium oxydichloride is included in *Figure 1*; the compound itself is discussed below. The spectrum shows a sharp absorption band at  $23400\text{ cm}^{-1}$  with an extinction coefficient of 8450. It may be supposed that this band is also produced by a  $n\text{-}\sigma^*$  transition in the diamagnetic phenylvanadium oxydichloride.

Another problem which obviously is not yet sufficiently clear is the behaviour of  $\sigma$ -organotitanium compounds with donor molecules. Tetramethyl titanium which in its pure form decomposes above  $-60^\circ\text{C}$  can be stabilized considerably by ethers, tertiary aliphatic and aromatic amines, and tertiary phosphines<sup>8</sup> (*Table 1*).

Table 1. Complexes of tetramethyltitanium

Complex	Properties
$(\text{CH}_3)_4\text{Ti}\cdot\text{C}_4\text{H}_8\text{O}_2$	yellow needles, decomp. at $-20^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot\text{N}(\text{CH}_3)_3$	yellow crystals, spontaneous decomp. below $0^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot\text{NC}_5\text{H}_5$	yellow crystals, decomp. at $0^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot\text{P}(\text{CH}_3)_3$	yellow crystals, decomp. below $0^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot 2\text{P}(\text{CH}_3)_3$	orange needles, spontaneous decomp. at $20^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot 2\text{NC}_5\text{H}_5$	red crystals, decomp. at $25^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot\text{bipyridyl}$	red crystals, decomp. at $30^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}\cdot(\text{CH}_3)_2\text{P}(\text{CH}_2)_2\text{P}(\text{CH}_3)_2$	yellow plates, stable at room temperature
$(\text{CH}_3)_4\text{Ti}\cdot n(\text{C}_2\text{H}_5)_2\text{O}$ (solution)	decomp. at $-30^\circ\text{C}$
$(\text{CH}_3)_4\text{Ti}$ (solid)	decomp. at $-60^\circ\text{C}$

In this respect, typical examples are complexes with dioxane, trimethylamine, pyridine, bipyridyl, and tetramethylethylene diphosphine. Thereby it was possible to obtain a relationship between the thermal stability of the complexes and their thermodynamic stability, the first being characterized by the temperature at which a visible rapid decomposition of the compounds takes place, accompanied by a blackening of the substances. The strength of the bond between tetramethyltitanium, as the acceptor molecule, and the donor molecules increases distinctly with decreasing orbital electronegativity of the donor atoms of the ligands. A partly different behaviour is shown by organotitanium trihalides in the formation of complexes. With

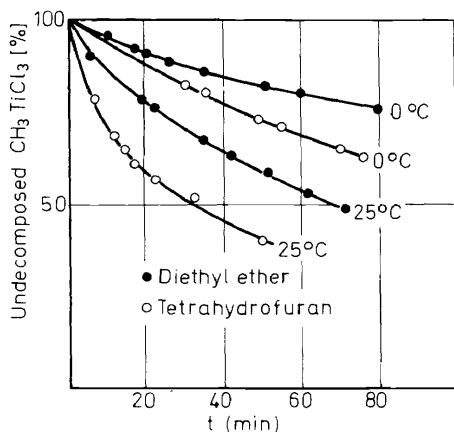
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ligands capable of forming chelate complexes, they form adducts which in general are rather stable. In this respect, a very detailed investigation of the complexes of methyltitanium trichloride was made by Clark and McAllees<sup>9</sup>. Other alkyltitanium trichlorides are also stabilized by some donor molecules, such as bipyridyl. Some of these complexes are shown in *Table 2*.

*Table 2.* Complexes of methyl and phenyltitanium trichloride

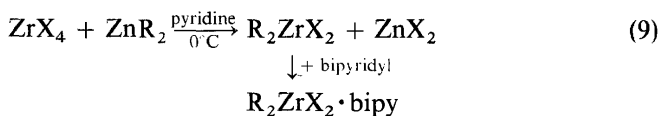
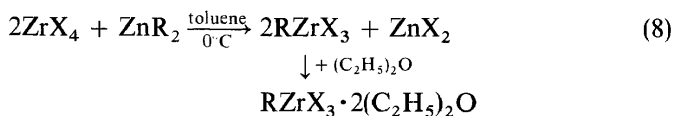
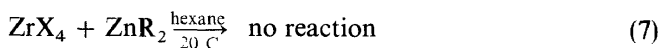
Complex	Colour	Decomp. temperature, °C
$\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$	pink-violet	98 <sup>99</sup>
$\text{CH}_3\text{TiCl}_3 \cdot (\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$	maroon	103–105 <sup>99</sup>
$\text{CH}_3\text{TiCl}_3 \cdot \text{bipyridyl}$	red-violet	c 180 <sup>3</sup>
$\text{C}_6\text{H}_5\text{TiCl}_3 \cdot 2\text{NC}_5\text{H}_5$	brown	c 30 <sup>24</sup>
$\text{C}_6\text{H}_5\text{TiCl}_3 \cdot \text{bipyridyl}$	wine-red	130 <sup>24</sup>
$\text{CH}_3\text{TiCl}_3$	violet	c 40 <sup>1</sup>
$\text{C}_6\text{H}_5\text{TiCl}_3$	black-violet	-5 <sup>1</sup>
$\text{CH}_3\text{TiCl}_3$ (in ether solution)	red	> 0 <sup>1</sup>
$\text{CH}_3\text{TiCl}_3$ (in THF solution)	red	> -20 <sup>1</sup>

However, it is also apparent from this table that methyltitanium trichloride is quite considerably destabilized by diethyl ether, tetrahydrofuran or triethylamine. Whilst the decomposition by triethylamine is observed by an immediate decolorization of the solution within a few seconds even at -20°C, the conditions could be better observed in ether or tetrahydrofuran solvents (*Figure 2*). The concentration of the methyltitanium trichloride in ether solution decreases, at a temperature of 25°C within an hour, to approximately one half of its original value. As expected, the decomposition proceeds with less speed at a lower temperature. In tetrahydrofuran, which is a stronger donor, an acceleration of the decomposition is observed. The decomposition of methyltitanium trichloride is preceded by the formation of defined charge transfer complexes which show characteristic absorption spectra with typical CT-bands at temperatures below 25°C.



*Figure 2.* Decomposition of methyltitanium trichloride in diethyl ether and tetrahydrofuran

The conditions found in organotitanium compounds may be partially transferred to the organo-compounds of other transition metals. It was reasonable to first consider the problem of alkylation of zirconium tetrahalides. A few years ago, it was demonstrated that at low temperatures zirconium tetrachloride in ether solution may be converted into tetramethylzirconium which is extremely reactive and very unstable<sup>10</sup>. The preparation of alkylzirconium halides, on the other hand, is very difficult. This is due to the fact that unlike titanium tetrahalides which are miscible with polar and non-polar solvents, zirconium tetrachloride and bromide are almost insoluble in hydrocarbons and ethers. Now it can be demonstrated that under certain reaction conditions the alkylzirconium halides  $RZrX_3$  and  $R_2ZrX_2$  are formed. An isolation of these substances, however, was only possible in the form of complexes with diethyl ether or with bipyridyl. Zinc dialkyls once more proved to be suitable alkylating reagents. Details are given in the following equations.



According to equation 8, methylzirconium trichloride and tribromide are obtained in the form of etherates. These are orange-red coloured substances which are very sensitive to air and which decompose at temperatures above 50°C. It is not possible to split off the ether molecules without destroying the compounds. Pyridine which is a stronger polar solvent first forms deep-blue solutions, according to equation 9, from which bipyridyl complexes of dimethyl, diethyl, dipropyl, and dibutylzirconium dichloride as well as dimethyl and diethylzirconium dibromide (which also show a deep-blue colour) can be separated. These compounds can be stored for some time at room temperature in the absence of air (*Table 3*).

The alkylzirconium halides without attached donor molecules are still unknown. They could possibly be prepared by the reaction of solutions of tetramethylzirconium with dry hydrohalogenic acids at low temperatures. This method was used with success recently by Giannini<sup>11</sup> in the preparation of benzylzirconium halides from tetrabenzylzirconium. It must be stated, however, that benzylzirconium compounds are much more stable than compounds with alkyl groups attached to the zirconium atom.

Some years ago, Juvinal<sup>12</sup> reported the preparation of trimethylniobium and trimethyltantalum dichlorides, the first alkylmetal halides of Group VB elements, from the corresponding pentachlorides and dimethylzinc. A considerably more difficult problem, however, is the preparation of alkyl or arylvanadium halides. Although this problem has been investigated for some

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Table 3. Complexes of alkylzirconium halides

Complex	Properties
$\text{CH}_3\text{ZrCl}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$	red microcrystalline powders very sensitive to air (ignition) and moisture insoluble in hydrocarbons, ether, tetrahydrofuran
$\text{CH}_3\text{ZrBr}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$	hydrolysis $\rightarrow$ methane decomp. temp. about 80°C
$\text{R}_2\text{ZrCl}_2 \cdot \text{bipyridyl}$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , C <sub>3</sub> H <sub>7</sub> , C <sub>4</sub> H <sub>9</sub> )	deep-blue crystals only weakly air sensitive soluble in pyridine; insoluble in benzene and tetrahydrofuran
$\text{R}_2\text{ZrBr}_2 \cdot \text{bipyridyl}$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> )	hydrolysis $\rightarrow$ methane decomp. temp. about 120–150°C

years, only incomplete results can be reported at present. Moreover, some of these results are contradictory or difficult to interpret.

Carrick and Reichle<sup>13, 14</sup> claimed the existence of phenylvanadium oxydichloride (mentioned earlier in another connection) some years ago and recently proved it was well defined in solutions. Large quantities of the substance can be prepared at lower temperatures in a crystalline form from vanadium oxytrichloride and diphenylzinc or diphenylmercury in liquid propane or in pentane solvents. The dark-red compound, the most important characteristics of which are listed in Table 4, bears some resemblance to phenyltitanium trichloride.

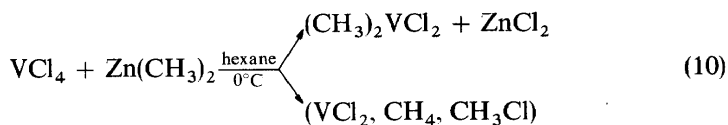
Table 4. Properties of phenylvanadium oxydichloride

$\text{C}_6\text{H}_5\text{VOCl}_2$ forms deep-red diamagnetic crystals
m.p. = 8–10°C (decomposition)
soluble in hydrocarbons, $\text{CCl}_4$ , $\text{CHCl}_3$
decomposition in diethyl ether at about –40°C
hydrolysis $\rightarrow$ $\text{C}_6\text{H}_6$ , ( $\text{C}_6\text{H}_5\text{---C}_6\text{H}_5$ , $\text{C}_6\text{H}_5\text{Cl}$ )
thermal decomposition $\rightarrow$ $\text{C}_6\text{H}_5\text{---C}_6\text{H}_5$ , $\text{C}_6\text{H}_5\text{Cl}$ , ( $\text{C}_6\text{H}_6$ )
reaction with bipyridyl $\rightarrow$ $\text{C}_6\text{H}_5\text{VOCl}_2 \cdot \text{bipy}$ (deep-blue, decomp. temp. = 14°C)
u.v. spectrum: $\lambda_{\text{max}} = 425 \text{ nm}$ ( $\epsilon = 8450$ )
i.r. spectrum: $\nu(\text{V=O})$ 1038 $\text{cm}^{-1}$
$\nu_{\text{as}}(\text{V---Cl})$ 508 $\text{cm}^{-1}$ ; $\nu_{\text{sym}}(\text{V---Cl})$ 405 $\text{cm}^{-1}$
$\nu(\text{V---C})$ 545 $\text{cm}^{-1}$ (?)

For instance, the diamagnetic compound which forms deep-red crystals melts with decomposition at 8–10°C; greater quantities decompose very violently with explosion. The products of the thermal decomposition were biphenyl, chlorobenzene and a small amount of benzene. Benzene is formed almost quantitatively on hydrolysis. The phenyl compound which is soluble in hydrocarbons and carbon tetrachloride with a dark-red colour is destroyed by ether at –40°C. At low temperatures, it is possible to obtain a blue bipyridyl complex which decomposes at 14°C. In the u.v. spectrum the strong band at 425 nm can be attributed to an electron transfer from the vanadium–carbon bond to a d-orbital of the metal atom. Nearly all bands

of the i.r. spectrum obtained at low temperatures can be allocated without error. Concerning the  $\nu(\text{V}-\text{C})$  bands, there are some doubts which are chiefly due to the fact that there are no other vanadium compounds with which a comparison can be made.

The results obtained in the experiments on the alkylation of vanadium tetrachloride are less well defined. If vanadium tetrachloride is allowed to react with boron trialkyls in ether solution, it is reduced to vanadium trichloride which crystallizes from the resulting deep-blue solution with two or three molecules of ether according to the temperature. The nature of the organic groups attached to the boron atom seems to have no influence on the course of the reaction since etherates of vanadium trichloride are formed with triethylboron as well as with tribenzyl and triallylboron. Quite similar conditions are observed in the reaction of tin tetraalkyls with vanadium tetrachloride by which etherates of vanadium trichloride are also formed. In order to exclude a destabilization of the vanadium-carbon bonds by the donor effect of the ether molecules, the reaction of vanadium tetrachloride with triethylboron in hexane solvent was repeated at  $-50^\circ\text{C}$ . The result was a violet reaction product with an effective magnetic moment of 2.6 B.M., the analytical composition of which was very similar to that of vanadium trichloride. A quite different reaction takes place in the case of the reaction of dimethylzinc with vanadium tetrachloride. The course of this reaction can be described approximately by equation 10.



Besides the alkylation of the vanadium tetrachloride, however, a partial reduction of the vanadium halide always takes place resulting predominantly in the formation of vanadium dichloride. Consequently it is possible to detect certain amounts of methane and methyl chloride in the reaction mixture. The solid product of the reaction is not sensitive to diethyl ether. On the contrary, most of the zinc chloride can be removed from the solid reaction product by extraction with boiling ether without any decomposition of the vanadium compound. The result is a violet substance which is very sensitive to air and is thermally stable up to  $120^\circ\text{C}$ . It retains persistently a small part of the zinc chloride and contains a small quantity of ether which cannot be removed even in vacuo. The composition of this substance comes near to that of dimethylvanadium dichloride. Hydrolysis results in the formation of methane and a smaller quantity of ethane. The magnetic moment was found at 2.3 B.M. which is due to the content of low valency vanadium compounds. If the substance is treated with tetrahydrofuran, these impurities remain, for the most part, undissolved. The dimethylvanadium dichloride which in the solid state is probably a coordination polymer, is soluble in the form of a tetrahydrofuran complex and may be precipitated as a green-coloured complex compound in the crystalline form. By addition of suitable donors to the tetrahydrofuran solution, the complex compounds listed in *Table 5* can be obtained in a pure and partly in the crystalline form.



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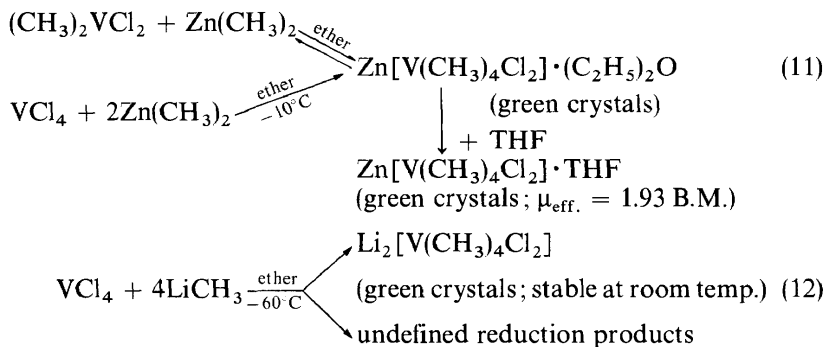
Table 5. Complexes of dimethylvanadium dichloride

Complex	Properties
$(\text{CH}_3)_2\text{VCl}_2 \cdot 1.66 \text{ THF}$	green crystals, $\mu_{\text{eff.}} = 1.72 \text{ B.M.}$ , decomp. temp. $110^\circ\text{C}$
$(\text{CH}_3)_2\text{VCl}_2 \cdot 2\text{NC}_5\text{H}_5$	violet crystals, m.p. = $188^\circ\text{C}$
$(\text{CH}_3)_2\text{VCl}_2 \cdot \text{TEEDA}^*$	dark-violet substance, decomp. temp. $100^\circ\text{C}$ , $\mu_{\text{eff.}} = 1.93 \text{ B.M.}$
$(\text{CH}_3)_2\text{VCl}_2 \cdot \text{phenanthroline}$	dark-blue substance, decomp. temp. $189^\circ\text{C}$ , $\mu_{\text{eff.}} = 1.77 \text{ B.M.}$
$(\text{C}_2\text{H}_5)_2\text{VCl}_2 \cdot \text{THF}$	green crystals, $\mu_{\text{eff.}} = 1.98 \text{ B.M.}$
$(\text{C}_2\text{H}_5)_2\text{VCl}_2 \cdot \text{bipyridyl}$	dark-blue substance, decomp. temp. $100^\circ\text{C}$

\* TEEDA = tetraethylethylenediamine.

As the magnetic moments of these complexes show, the valency state of the vanadium is not changed by the alkylating reaction.

Dimethylvanadium dichloride is distinguished by a remarkable stability. Experiments were carried out, therefore, to test this compound as a starting material for preparing tetraalkyl compounds of vanadium. However, this intention could not be realized, as is shown by the following equations.

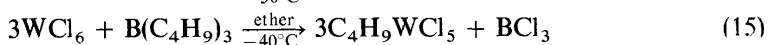
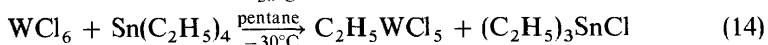
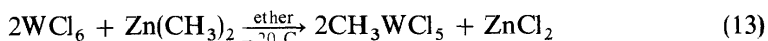


Dimethylvanadium dichloride reacts with an excess of dimethylzinc, according to equation 11, to form a green addition compound which contains ether. However, no definite statements concerning the nature of the structure and the bonds in this compound can be made. If the compound is separated from the solvent, it decomposes into the original components at room temperature. The same substance can be obtained directly by the action of an excess of dimethylzinc on vanadium tetrachloride in ether solution. By means of tetrahydrofuran the etherate can be converted into the tetrahydrofuran adduct which shows a greater thermal stability. The tetravalency of the vanadium is indicated by the measured magnetic moment of 1.93 B.M.

Vanadium tetrachloride and dimethylvanadium dichloride are reduced by methyl lithium. Thereby, the formation of different gases even at low temperatures is observed. By a very careful procedure, however, it was possible to prepare an addition compound of dimethylvanadium dichloride with methyl lithium, analogous to the dimethylzinc complex. A more precise characterization of these compounds is still required.

Finally, the behaviour of tungsten hexachloride and molybdenum pentachloride with weak alkylating agents will be briefly discussed. All experiments

to convert molybdenum pentachloride to alkylmolybdenum tetrachlorides by means of boron trialkyls, tin tetraalkyls and zinc dialkyls failed. In ether as well as in aliphatic hydrocarbon solvents, only a reduction to molybdenum tetrachloride or molybdenum trichloride took place. These compounds can be isolated partly in the form of etherates. The preparation of tungsten compounds, however, did not present any particular difficulties. The conditions for the preparation of alkyltungsten pentachlorides are illustrated more precisely by the following equations.



According to equation 13, crystalline green-coloured methyltungsten pentachloride precipitates from a solution of tungsten hexachloride in diethyl ether on the addition of dimethylzinc. The tungsten compound decomposes rapidly at room temperature, but it may be stabilized thermally by conversion into complexes with pyridine or bipyridyl. A reaction, according to equation 13, with diethylzinc or other zinc dialkyls with longer alkyl groups could not be accomplished. This is probably caused by the increased reducing effect of these compounds but not by a too small stability of the tungsten compounds searched for. By the action of tin tetraalkyls which are less polar alkylating agents and, strikingly, by boron trialkyls, it is possible to prepare alkyltungsten pentachlorides with longer alkyl groups (equations 14 and 15). The behaviour of these compounds is very similar to that of the methyl compound. Thermal decomposition, however, starts above  $-15^\circ\text{C}$ . It is a remarkable fact that in all reactions, which, for different reasons, lead to a reduction of the tungsten hexachloride, tungsten tetrachloride or its complexes were always found as reduction products. Tungsten pentachloride was never observed.

From the results already obtained it is possible to throw some light on the field of organotransition metal halides. However, there are still many unsolved problems. Among others there is the question of whether mono-alkyl transition metal halides of  $d^1$ -elements are especially unstable since compounds of the type  $\text{RTiX}_2$ ,  $\text{RVX}_3$ ,  $\text{RMOX}_4$ , and  $\text{RWX}_4$  have not been found until now or have proved to be especially unstable. Further investigations will be needed, therefore, to gain a more comprehensive knowledge of the chemistry of the organotransition metal halides.

## REFERENCES

- 1 C. Beermann and H. Bestian, *Angew. Chem.* **71**, 618 (1959).
- 2 H. de Vries, *Rec. Trav. Chim.* **80**, 866 (1961).
- 3 K.-H. Thiele and K. Jacob, *Ž. Anorg. Allgem. Chem.* **356**, 195 (1968).
- 4 K.-H. Thiele, P. Zdunneck and D. Baumgart, *Z. Anorg. Allgem. Chem.* **378**, 62 (1970).
- 5 D. F. Herman and W. K. Nelson, *J. Am. Chem. Soc.* **75**, 3882 (1953).
- 6 D. F. Herman, *Adv. Chem. Ser.* **23**, 265 (1959).
- 7 C. Dijkgraaf and J. P. G. Rosseau, *Spectrochim. Acta.* **25**, 1455 (1969).
- 8 J. Müller and K. H. Thiele, *Z. Anorg. Allgem. Chem.* **362**, 120 (1968).

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- <sup>9</sup> R. J. H. Clark and A. J. McAllees, *J. Chem. Soc. (A)*, 2026 (1970).  
<sup>10</sup> H. J. Berthold and G. Groh, *Z. Anorg. Allgem. Chem.* **319**, 230 (1963).  
<sup>11</sup> U. Zucchini, E. Albizzati and U. Giannini, *J. Organomet. Chem.* **26**, 357 (1970).  
<sup>12</sup> G. L. Juvinall, *J. Am. Chem. Soc.* **86**, 4202 (1964).  
<sup>13</sup> W. L. Carrick, W. T. Reichle, F. Panella and J. J. Smith, *J. Am. Chem. Soc.* **82**, 3887 (1966).  
<sup>14</sup> W. T. Reichle and W. L. Carrick, *J. Organomet. Chem.* **24**, 419 (1970).