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SYNTHESIS AND PROPERTIES OF COVALENT TRI- AND TETRAVALENT VANADIUM

G.A. RAZUVAEV *, V.N. LATYAEVA, L.I. VYSHINSKAYA and V.V. DROBOTENKO
Institute of Chemistry, Academy of Sciences, Gorky (U.S.S.R.)

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Summary

Reactions of $VCl_3 \cdot 3$ THF with RMgX (R = Ph, CH_2SiMe_3, C_6F_5) in various ratios have been studied. The stable compounds $R_3V \cdot$ THF (R = CH_2SiMe_3, C_6F_5) were obtained. The chemical properties of $R_3V \cdot$ THF, $R_4V \cdot 2$ L (R = CH_2Ph, L = Et_2O; R = C_6F_5, L = THF) and $(Me_3SiCH_2)_4V$ were investigated. Cleavage of the vanadium—carbonium σ-bond occurs in reactions with H_2O, HCl and $HgCl_2$. The insertion of carbon dioxide into the vanadium—carbon σ-bond was investigated. A scheme for the derivatives of tri- and tetravalent vanadium is proposed. Oxidative addition to $(C_6F_5)_3V \cdot$ THF by Ph_3CCl and $VCl_3 \cdot 3$THF was also studied.

Introduction

At the present time it has been established on the basis of the study of the nature of the transition metal—carbon σ-bond that ligands which do not have a hydrogen atom in the β-position to the transition metal may favour the kinetic stabilization of this bond. Examples of such ligands are the benzyl, mesityl, neopentyl, trimethylsilylmethyl and pentafluorophenyl groups. In the last few years several stable covalent compounds of tri- and tetravalent vanadium with these ligands have been obtained [1—5]. In general, the data in the literature include the methods of preparation and a brief physicochemical characterization. The chemical properties of binary alkyls of vanadium have practically not been investigated. In this work we studied the possibility of preparing covalent compounds of the type R_nVCl_{3-n} ($n = 1, 2, 3$; R = CH_2Ph, CH_2SiMe_3, C_6F_5) and the chemical properties of stable derivatives of tri- and tetravalent vanadium, R_3V and R_4V.

Results and discussion

We have studied the exchange interaction of $VCl_3 \cdot 3$ THF (I) with RMgX (R = CH_2Ph, CH_2SiMe_3, C_6F_5), at various ratios (from 1 : 1 to 1 : 3) of initial

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components. All reactions were carried out in diethyl ether (Et_2O) or in tetrahydrofuran (THF) in the temperature range from —78 to —15°C. The colour change of the reaction solutions indicated that an exchange reaction had occurred. After termination of the reaction, dioxane was added to the reaction mixture to precipitate magnesium salts in dioxanate form. The quantitative yield of magnesium salts showed that the exchange reactions were complete.

The temperature of the solutions was increased from 0 to 20°C to isolate the vanadium-containing products. The attempts to isolate mono-substituted derivatives of vanadium, $RVCl_2$, were unsuccessful. The composition and yield of the reaction products (Table 1) indicate that the $RVCl_2$ compounds decompose at 0°C. Experiments to substitute tetrahydrofuran for pyridine were unsuccessful.

$$\begin{array}{l} VCl_3 \cdot 3\,THF + RMgX \xrightarrow[diox]{} [RVCl_2 \cdot n THF] + MgClX \cdot diox \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad [R\cdot] + VCl_2 \cdot 2\,THF \end{array} \tag{1}$$

An attempt to isolate the disubstituted derivatives of R_2VCl from the reaction solutions was also unsuccessful.

$$\begin{array}{l} VCl_3 \cdot 3\,THF + 2\,RMgCl \xrightarrow[diox]{Et_2O} [R_2VCl \cdot n THF] + 2\,MgCl_2 \cdot diox \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad \tfrac{1}{2} R_4V \cdot 2\,Et_2O + \tfrac{1}{2} VCl_2 \cdot 2\,THF \end{array}$$

The interaction of $VCl_3 \cdot 3$ THF with two moles of RMgCl gave the disproportionation products R_4V and VCl_2 (Table 2). Apart from the exchange interaction, another method of preparing R_2VCl was employed. The interaction of R_3V ($R = CH_2SiMe_3$, C_6F_5) with an equivalent quantity of hydrogen chloride was studied. These experiments also resulted in an equimolar mixture of R_4V and VCl_2.

The experimental data indicate that in the systems studied a redox reaction takes place. The redox processes in solution take place via the formation of a transitional complex, where the transfer of electrons or atoms from one reagent to another occurs. The formation of a binuclear intermediate complex with two bridges is usually postulated when the oxidation state of the metal ion changes by two units.

The products of the reactions studied indicate that in the intermediate com-

TABLE 1

REACTION PRODUCTS FROM $VCl_3 \cdot 3$ THF WITH RMgX (1 : 1) AT 0°C IN Et_2O

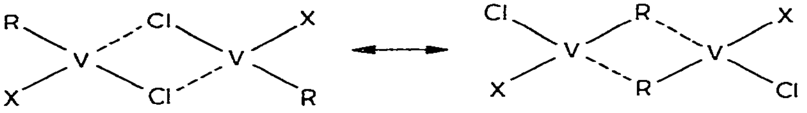
Initial RMgX	Products (mol per g atom V)		
	R—H	R—R	VCl_2 in form of $VCl_2 \cdot 4$ Py [10]
PhMgBr	traces	0.48	0.88
$PhCH_2MgCl$	none	0.49	0.99
Me_3SiCH_2MgCl	0.85	none	0.70
C_6F_5MgCl	0.86	0.07	0.98

TABLE 2

REACTION PRODUCTS FROM $VCl_3 \cdot 3$ THF WITH RMgCl (1 : 2) AT 0°C IN Et_2O

Initial RMgCl	Products (mol per g atom V)		
	R_4V	VCl_2 in the form of $VCl_2 \cdot 4$ Py [10]	$MgCl_2$
$PhCH_2MgCl$	0.42	0.45	1.98
Me_3SiCH_2MgCl	0.45	0.42	1.96
C_6F_5MgCl	0.43	0.46	1.97

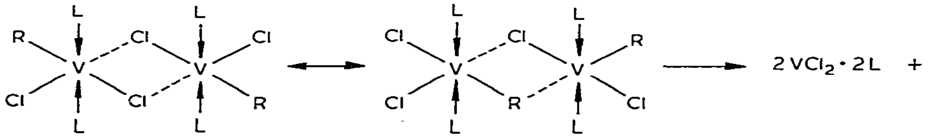
plexes exchange of chlorine atom for R groups takes place. The exchange is promoted by the electron-donor character of the solvent which coordinates to the



(X = Cl,R)

intermediate complex. The electron-donor ligands enhance the electron density on the vanadium ion, affecting the V—Cl bond. The bond becomes more labile and chlorine ion may be substituted for a less electronegative R group in the coordination sphere of the complex. The decomposition of the complexes depends upon their structure.

For complexes of monosubstituted $RVCl_2$ (type A), containing twice as many halogen atoms as R groups, reduction of the central metal ion with simultaneous elimination of R radicals generally takes place.



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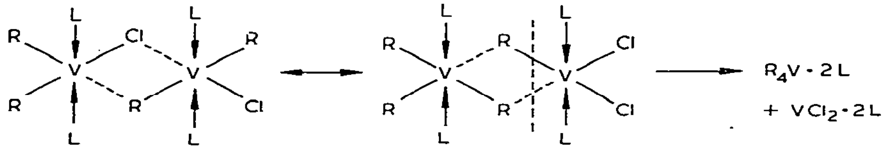
(A)



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(B)

The complexes of disubstituted R_2VCl (type B) undergo disproportionation to $R_4V \cdot 2$ L and $VCl_2 \cdot 2$ L. We observed this process during attempts to prepare the disubstituted vanadium acetylacetonates, R_2V(acac). It is likely that the formation of an intermediate complex with a chelate bridge takes place in the course of the reaction. Such complexes also decay with disproportionation [6].

Of the mixed trivalent vanadium derivatives only three stable compounds are known: $(2,6\text{-}Me_2C_6H_3)VCl_2 \cdot 2$ THF, $(2,4,6\text{-}Me_3C_6H_2)VCl_2 \cdot 2$ THF and $(Me_5C_6)VCl_2 \cdot 2$ THF [7]. Their stability may be accounted for by the fact that the large volume of the mesityl group and its analogues reduces the exchange rate of the ligands in the transitional octahedral complex and stabilizes the trigonal bipyramid configuration. It is likely that in order to prepare stable covalent vanadium halide compounds one should: i) make use of large ligands which stabilize the monomeric form, ii) eliminate the electron-donor ligands which increases the electronic density on the metal atom.

In contrast to the mixed derivatives $R_nV^{n+m}X_m$, for organometallic compounds of binary type, R_nM^n, the stability is determined by the availability of substituents not susceptible α- or β-elimination. The preparation of stable R_4V (R = CH_2Ph, CH_2SiMe_3, C_6F_5, Mes [1—4]) compounds confirms this fact. For trivalent vanadium only Mes_3V is known [5].

It was of interest to prepare R_3V (R = CH_2Ph, CH_2SiMe_3, C_6F_5), which according to theoretical prediction should be stable. Jacob reported in 1978 his unsuccessful attempts to obtain complete benzylation of $VCl_3 \cdot 3$ THF in Et_2O solution with $PhCH_2MgCl$ and $PhCH_2Li$ [8]. We were able to show that for successfully obtaining R_3V, the solvent and the strength of alkylation (arylation) agent play an important role. When employing Et_2O the reactions start only at —20° C and under these conditions the decomposition of intermediate $RVCl_2$ and R_2VCl proceeds more readily than the consequent exchange reaction. Employing THF and organolithium compounds provided a means of obtaining complete exchange at —60° C; i.e. under conditions ruling out decomposition of the mixed halide derivatives of vanadium.

We have studied the interaction of $VCl_3 \cdot 3$ THF with $PhCH_2Li$ in THF at —60° C. As a consequence of an exchange reaction a blue solution is formed containing a total vanadium oxidation state of +3. The ratio of toluene to vanadium after hydrolysis equals to 3 : 1. At 0° C $(PhCH_2)_3V$ decomposes, as can be seen by a distinct change of colour from blue to brown. In addition, a black solid precipitates, containing vanadium in lower oxidative states.

In contrast to the preparation of tribenzylvanadium, the exchange reaction of $VCl_3 \cdot 3$ THF with C_6F_5Li and Me_3SiCH_2MgCl in 1 : 3 ratio in THF gives the stable complexes $(C_6F_5)_3V \cdot$ THF (II) and $(Me_3SiCH_2)_3V \cdot$ THF (III):

$$\begin{array}{l} VCl_3 \cdot 3\,\text{THF} + 3\,\text{RMet} \xrightarrow{\text{THF}} R_3V \cdot \text{THF} + 3\,\text{MetCl} \\ \text{Met} = \text{Li},\ R = C_6F_5;\ \text{Met} = \text{MgCl},\ R = CH_2SiMe_3 \end{array} \qquad (5)$$

II and III are crystalline compounds soluble in ethers and aromatic hydrocarbons, but insoluble in aliphatic hydrocarbons. We obtained $(Me_3SiCH_2)_3V \cdot$ THF in the form of dark violet crystals, giving blue solutions at 0° C. This is inconsistent with data reported earlier by Bagdasarian et al. [9], who investigated the interaction of VCl_4 with 4 moles of Me_3SiCH_2Li in hexane solution at 20° C. On the basis of a determination of vanadium valency and the ratio of hydrolysis products $Me_4Si:V$ = 3.06 : 1, they concluded that the reaction mentioned gives $(Me_3SiCH_2)_3V$. The compound was not isolated in a pure form and only a green hexane solution was obtained. It was known from literature data that (Me$_3$-

$SiCH_2)_4V$ readily dissolves in hexane to form a green solution [2]. The crystalline tetrahydrofuranate III synthesized by us differed in colour and in solubility from that obtained by Bagdasarian et al. We reproduced the procedure described in ref. 9 and isolated dark green paramagnetic crystals of $(Me_3SiCH_2)_4V$ with $g_i = 1.968$ and $A_i^{51V} = -50{,}5\ e$ (yield 70%) by low temperature crystallization from the green solution. ESR isotropic spectral parameters, elemental analysis and melting temperature as consistent with tetravalent vanadium compounds. The results obtained suggest that a reliable and convenient synthesis of tris(trimethylsilylmethyl)vanadium is the exchange interaction of $VCl_3 \cdot 3\ THF$ with Me_3SiCH_2MgCl in THF solution at −60° C. By this method several new simple vanadium alkyls were prepared: R_3V and R_4V ($R = CH_2Ph, Me_3SiCH_2, C_6F_5$, Mes). The compounds were prepared in order to compare their reactivity and its dependence on the valency of the vanadium and the nature of the σ-substituent.

The compounds $(C_6F_5)_3V \cdot THF$ (II), $(Me_3SiCH_2)_3V \cdot THF$ (IV), $(C_6F_5)_4V \cdot 2\ THF$ (III), $(Me_3SiCH_2)_4V$ (V) and $(PhCH_2)_4V \cdot 2\ Et_2O$ (VI) were chosen for this purpose.

Acid hydrolysis was usually employed for the identification of the compounds. The hydrolyses were carried out in inert atmosphere with the use of 5—10% sulphuric acid or 6 N hydrochloric acid. The hydrolysis of C_6F_5-containing derivatives proceeds less readily than that of complexes IV, V and VI. The complexes studied are eventually hydrolyazed with cleavage of all the V—C σ-bonds. On hydrolysis of complex IV, a rapid change in colour of the organic layer from blue to green takes place. Complex V was identified in the green solution by ESR spectroscopy. The aqueous layer is violet in coloured comprises V^{2+} ions. The formation of redox disproportionation products indicates that the slow stage of the hydrolysis is the substitution of the σ-ligands, as decomposition of the intermediate occurs more readily.

$$\begin{tikzcd} R_3V + HX \arrow[r] & {[R_2VX] + RH} \arrow[d] \\ & \tfrac{1}{2}R_4V + \tfrac{1}{2}VX_2 \end{tikzcd}$$

$R = CH_2SiMe_3, C_6F_5; X = OH, Cl, HSO_4$

The reaction with mercuric chloride is a means of identifying a metal—carbon σ-bond. We found earlier that complex III reacts with mercuric chloride according to eq. 7:

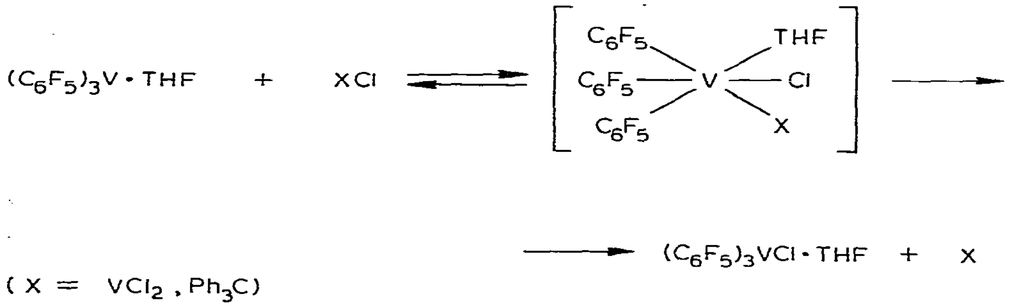
$$(C_6F_5)_4V + 2\ HgCl_2 \xrightarrow[60^\circ C]{THF} 2(C_6F_5)_2Hg + VCl_4 \tag{7}$$

The trivalent vanadium derivative $(C_6F_5)_3V \cdot THF$ in contrast to III, forms $(C_6F_5)HgCl$ and calomel with an excess of mercuric chloride. Exchange interaction in this case is accompanied by a redox reaction, as evidenced by isolation of equivalent quantities of calomel and VCl_4.

$$(C_6F_5)_3V + 4\ HgCl_2 \xrightarrow[60^\circ C]{THF} 3\ C_6F_5HgCl + \tfrac{1}{2}Hg_2Cl_2 + VCl_4 \tag{8}$$

Interesting results were obtained in the exchange reaction of complex II with the halides VCl_3 and Ph_3CCl. As a result, oxidation of V^{III} to V^{IV}, with an increase of coordination number from 4 to 5 occurred. Initial $(C_6F_5)_3V \cdot THF$ was converted into $(C_6F_5)_3VCl \cdot THF$. In addition, from the reaction of complex II with $VCl_3 \cdot 3\ THF$, $VCl_2 \cdot 2\ THF$ was formed and from the reaction with Ph_3CCl, the radical $Ph_3C\cdot$ was found ($g = 2.003$).

On the basis of the experimental data it seems that complex II undergoes oxidative addition in two stages. At first the intermediate octahedral complex forms, which then irreversibly decomposes into the above-mentioned termination products.



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Binary alkyls of vanadium, similar to Grignard reagents, enter into addition reactions with ketones. Tetramethyl- and tetrabenzyl-vanadium readily react at —60 to —10°C with two moles of acetone, forming insertion products such as the already known $Me_2V(Ot\text{-}Bu)_2$ [11], and green $(PhCH_2)_2V(OCMe_2CH_2Ph)_2$ with isotopic ESR parameters ($g_i = 1.9720$; $A_i^{51V} = -48.3 \pm 0.5\ e$) close to the ESR parameters for $(PhCH_2)_2V(Ot\text{-}Bu)_2$ [11]. Subsequent insertion does not

$$R_4V + 2\ Me_2CO \xrightarrow[-60^\circ C]{Et_2O} R_2V(OCMe_2R)_2 \qquad (10)$$

$R = Me, CH_2Ph$

occur; the coordination site is screened by the large alkoxy groups and coordination of further acetone molecules is hindered. Complex III also reacts with acetone. However, the reaction proceeds only at 20°C after several hours, with the formation of unidentified products.

Recently, interest has been attracted by the problem of the insertion reaction of carbon dioxide into transition metal—carbon σ-bonds. However, the number of publications on the subject is extremely limited. The interaction of carbon dioxide with covalent compounds of vanadium has not been investigated.

In this work we studied the carboxylation of binary alkyls of tri- and tetravalent vanadium. Reactions were carried out in THF and toluene. It was ascertained that in the more polar solvent THF the insertion of CO_2 occurred more readily than in toluene. Reactions of complexes II and IV with carbon dioxide were studied in various ratios of reactants (from 1 : 1 to 1 : 10). As a result of the interaction of complex II with one mole of CO_2, the formation of the paramagnetic complex III was detected by ESR ($g_i = 1.978$ and $A_i^{51V} = -85\ e$). The reaction of complex IV with one mole of CO_2 also gave tetravalent vanadium, complex V with $g_i = 1.968$ and $A_i^{51V} = -51\ e$. In parallel with the formation of III and IV the isolation of equivalent quantities of carboxylates of divalent vanadium, $V(OCOC_6F_5)_2$ and $V(OCOCH_2SiMe_3)_2$, takes place. These data make it possible to conclude that the interaction of II and IV with one mole of CO_2 takes place by a common route, independent of the σ-substituent. The reaction of complex IV with CO_2 stops at the stage of insertion of one mole even with an excess of CO_2 in reaction mixture. Only bubbling CO_2 at low temperature (—20° C) through a solution of IV in THF led to complete carboxylation, giving $V(OCOCH_2SiMe_3)_3$ (VII). Complex II absorbs a second mole of carbon dioxide to give $(C_6F_5)V(OCOC_6F_5)_2$ (VIII). The interaction of II with CO_2 in 1 : 3 ratio or with an excess leads to the formation of $(C_6F_5OCO)_3V$ (IX). The carboxylate derivatives of trivalent vanadium, VII and IX, are green microcrystalline powders and do not have the coordinated solvent ligands.

The results obtained suggest the following route for the process. The first stage is the insertion of a mole of carbon dioxide:

$$\underset{}{R_3V + CO_2 \rightarrow \underset{(X)}{[R_2V(OCOR)]}} \qquad (11)$$

The complex formed (X) decomposes under the reaction conditions employed. The reaction products found make it possible to conclude that carboxylate derivatives X decompose by formation of intermediate complex with double carboxylate bridges. It is known that vanadium readily forms such complexes [12]. In these transitional complexes, as well as in intermediate complexes with two halide bridges, the exchange of a bridging carboxyl group for a σ-ligand occurs, followed by disproportionation.

$$\underset{(X)}{[R_2V(OCOR)]} \rightarrow \tfrac{1}{2}R_4V + \tfrac{1}{2}V(OCOR)_2 \qquad R = CH_2SiMe_3,\ C_6F_5 \qquad (12)$$

The fact that complex IV reacts with only one mole of CO_2 demonstrates that complex X decomposes more rapidly than the insertion of the second mole takes place. The reaction is complete at this stage as we found that complex V does not absorb CO_2. Nevertheless, at low temperatures the disproportionation slows down and further insertion of CO_2 with formation of the final product (VII) becomes possible. For pentafluorophenyl compounds with an excess of CO_2 the disproportionation rate of complex X is lower than the rate of insertion of the second mole of CO_2, which is why the reaction proceeds further with formation of compound VIII. Under the action of excess CO_2 it converts to IX.

$$\underset{(X)}{[(C_6F_5)_2V(OCOC_6F_5)]} \xrightarrow{CO_2} \underset{(VIII)}{C_6F_5V(OCOC_6F_5)_2} \xrightarrow{CO_2} \underset{(IX)}{V(OCOC_6F_5)_3} \qquad (13)$$

We found by studying carboxylation of binary alkyls of tetravalent vanadium that compounds III and VI, containing coordinating solvent molecules, react readily with CO_2. Compounds not containing such ligands do not react with CO_2. We also studied the carboxylation of complex V, derivatives $R_2V(Ot\text{-}Bu)_2$ (R = Me, CH_2Ph) under various conditions. No absorption of carbon dioxide was observed. It would be expected that initial coordination of a carbon dioxide molecule onto the transition metal atom would occur, followed by displacement of the coordinated ligand and insertion of CO_2 into the V—R bond to form carboxylates. It is equally likely that migration of the alkyl group to the coordinated carbon dioxide takes place. The interaction of complex III with excess CO_2 gives $(C_6F_5OCO)_3V$ (IX) and C_6F_5H. The carboxylate $(PhCH_2OCO)_3V$ is also a product of the carboxylation of compound VI. When the reaction is carried out in toluene or pentane, a mixture of V^{II} and V^{III} carboxylates (3 : 1) is formed. Independent of the solvent, dibenzyl is separated in both reactions. In the reaction of complex III with CO_2 in toluene, the formation of toluene radical ion was detected by ESR spectroscopy.

The total experimental data indicate the following. It is likely that, similar to R_3V, for R_4V derivatives a stepwise insertion of CO_2 is observed. The first stage of the process is also the insertion of a CO_2 molecule:

$$R_4V + CO_2 \rightarrow \underset{(XI)}{[R_3V(OCOR)]} \rightarrow [R] + \underset{(X)}{[R_2V(OCOR)]} \tag{14}$$

Compound XI, similar to $(C_6F_5)_3V(acac)$ and $Me_3V(Ot\text{-}Bu)$ [11,13], is unstable and decomposes giving the intermediate complex X. Complex X is formed in the first stage of insertion of CO_2 into $R_3V \cdot THF$. Consequently, the further route of the reaction is described by the scheme proposed for $R_3V \cdot THF$. For $R = C_6F_5$, as one would expect, subsequent carboxylation leads to formation of IX. There are two competing reactions with $R = CH_2Ph$: (i) further carboxylation to $(PhCH_2OCO)_3V$; (ii) redox disproportionation. $(PhCH_2)_4V$ formed according to eq. 12, again enters into reaction with CO_2 until complete depletion.

Thus, the studies conducted demonstrate that the following types of reactions are characteristic for binary alkyl vanadium compounds: (i) oxidative addition (only for R_3V), (ii) cleavage of the σ-bond, and (iii) insertion into the σ-bond.

It was found that cleavage and insertion reactions proceed readily, which is why the intermediate compounds R_2VX (X = Cl, OH, HSO_4, OCOR, acac) are formed in the first stage of various reactions. R_2VX decomposes in solution, independently of the nature of X by formation of dinuclear transition complexes with double bridges. Decomposition of these complexes occurs by redox disproportionation.

Experimental

All reactions were carried out in an argon atmosphere or in vacuum using deoxygenated and dehydrated solvents. ESR spectra used were determined with a ERA-2M radio spectrometer. Mn^{2+} in a MnO crystal lattice was as a standard for calibration of the magnetic field. 2,2,6,6-tetramethylpiperidoxyl was used as a standard for defining the *g*-factor. Reaction products were analysed by GLC.

Reaction of trichlorotris(tetrahydrofuran)vanadium with benzylmagnesium chloride (1 : 1)

$PhCH_2MgCl$ (8.60 mmol) was added slowly to a suspension of complex I (8.60 mmol) in 50 ml of diethyl ether at —10° C. The colour of the reaction mixture changed from blue to greenish-brown and a dark residue precipitated.

Dibenzyl was found in the solution (4.29 mmol). A red-brown residue precipitated when 3 g of pyridine in 30 ml of acetone were added. It was filtered out, recrystallized from mixture of acetone with methanol (3 : 1) and dried in vacuo. $VCl_2 \cdot 4\ C_5H_5N$ (8.44 mmol) was obtained. (Found: Cl, 16.28; V, 11.54; $C_{20}H_{20}Cl_2N_4V$ calcd.: Cl, 16.21; V, 11.64%.)

Dioxan (30 ml) was added to the reaction solution in a parallel experiment. The precipitate was filtered off and it was found to contain 0.0085 g atom of magnesium.

Reaction of trichlorotris(tetrahydrofuran)vanadium with pentafluorophenylmagnesium chloride (1 : 1)

A tetrahydrofuran solution of pentafluorophenylmagnesium chloride (0.60 mmol) was slowly added to a suspension of I (8.60 mmol) in 70 ml of diethyl ether at —10° C. The colour of the reaction mixture changed from blue to greenish-brown and a dark residue precipitated. Pentafluorobenzene (7.32 mmol) was found in the solution. After treatment of the reaction mixture with pyridine, $VCl_2 \cdot 4\ C_5H_5N$ (8.44 mmol) was obtained.

Reaction of trichlorotris(tetrahydrofuran)vanadium with benzylmagnesium chloride (1 : 2)

Complex I (4.87 mmol) was slowly added to an ether solution of benzylmagnesium chloride (9.74 mmol) at —15° C. After an hour the temperature of the reaction mixture was raised to 0° C and 2.5 ml of dioxan in 50 ml of hexane was added. The precipitate was filtered off from the greenish-brown solution. Tetrabenzylvanadium was identified from its characteristic ESR anisotropic parameters: $g = 1.965 \pm 0.005$; $H \simeq 80\ e$ at —196° C. The yield of tetrabenzylvanadium was determined by its conversion to tetrakis(t-butoxide)vanadium under treatment of excess t-butyl alcohol. $(t\text{-}C_4H_9O)_4V$ (2.05 mmol) was obtained (b.p. 90° C/13.3 Pa) with isotropic ESR parameters: $g_i = 1.9645$; $A_i^{51V} = -68\ e$). Literature data [14]: $g_i = 1.964$; $A_i^{51V} = -68\ e$.

$VCl_2 \cdot 4\ C_5H_5N$ (2.40 mmol) was separated from the precipitate. Complexometry of the precipitate gave 0.0048 g atom of magnesium.

Reaction of trichlorotris(tetrahydrofuran)vanadium with pentafluorophenylmagnesium chloride (1 : 2)

Complex I (19.73 mmol) was slowly poured into a tetrahydrofuran solution of pentafluorophenylmagnesium chloride (39.46 mmol) at —15° C. After an hour the temperature of the reaction was raised to room temperature and 8 ml of dioxan in 30 ml of diethyl ether were added. Following that the solvents were removed from the reaction solution under vacuum. The precipitate obtained was washed with diethyl ether and $(C_6F_5)_4V \cdot 2\ THF$ (7.30 g, 43%) was separated by low temperature crystallization. It was identified by its ESR parameters: $g_i = 1.978$ and $A_i^{51V} = -85\ e$, which agree with literature data [13]. From the residue $VCl_2 \cdot 4\ C_5H_5N$ (4.00 g, 47%) was isolated.

Reaction of trichlorotris(tetrahydrofuran)vanadium with trimethylsilylmethylmagnesium chloride (1 : 2)

Complex I (8.70 mmol) was slowly poured into an ether solution of trimethylsilylmethylmagnesium chloride (17.40 mmol) at —15° C. After an hour the temperature of the reaction mixture was raised to room temperature and 4.0 ml of dioxan was added. The solvent was then removed under vacuum and the residue was extracted with pentane to yield tetrakis(trimethylsilylmethyl)vanadium (1.56 g, 45%), m.p. 42° C. (Found: C, 49.34; H, 11.10; V, 12.59. $C_{12}H_{44}Si_4V$ calcd.: C, 48.12; H, 11.03; V, 12.78%.) $VCl_2 \cdot 4\ C_5H_5N$ (1.70 g, 43%) was isolated from the residue after washing with pentane. In addition, 0.0171 g atom of magnesium was found in the residue by complexometry.

Reaction of trichlorotris(tetrahydrofuran)vanadium with benzyllithium (1 : 3)

Complex I (10.00 mmol) was added to a solution of benzyllithium (30.00 mmol) in 70 ml of tetrahydrofuran at —78° C. The temperature of the reaction mixture was slowly raised to —10° C with continuous stirring. The colour of the reaction mixture became blue and lithium salts precipitated. The solvent was removed completely at —10° C under vacuum and tribenzylvanadium was extracted from the precipitate with cooled diethyl ether. 70 ml of solution containing 0.0450 g atom of V^{III} were obtained. The colour of an ether solution of $(PhCH_2)_3V$ stored at 0° C changed quickly from blue to brown and a black precipitate appeared.

Preparation of tris(pentafluorophenyl)(tetrahydrofuran)vanadium

Complex I (10.00 mmol) was slowly added to a solution of pentafluorophenyllithium (30.00 mmol) in tetrahydrofuran. The temperature of the reaction mixture was gradually raised to room temperature with constant stirring. A violet solution was obtained and was filtered out from the precipitate of LiCl. Then the solvent was completely removed under vacuum. The residue was dissolved in diethyl ether, filtered out and the solvent was again removed under vacuum. The viscous brown oil obtained was washed three times with pentane. The cooling of the resulting pentane solution gave a brown powder of $(C_6F_5)_3V \cdot THF$ (5.3 g, 85%), m.p. 10° C (Found: V, 8.15; $C_{22}H_8F_{15}OV$ calcd.: V, 8.17%.)

Acidolysis of $(C_6F_5)_3V \cdot THF$ with sulphuric acid. 20 ml of 5% sulphuric acid was added to a suspension of tris(pentafluorophenyl)(tetrahydrofuran)vanadium (1.20 mmol) in 10 ml of toluene. Pentafluorobenzene (3.51 mmol) and THF (1.11 mmol) were found in the organic layer.

Reaction of tetrachlorovanadium with trimethylsilylmethyllithium (1 : 4)

VCl_4 (10.00 mmol) in 50 ml of diethyl ether was added dropwise to a hexane solution of Me_3SiCH_2Li (40.00 mmol) at 20° C for one hour. The resulting green reaction solution was filtered out from LiCl and then the solvents were removed under vacuum. The residue was solved in 30 ml of pentane and the pentane was cooled to —78° C giving dark green crystals of $(Me_3SiCH_2)_4V$ (2.80 g, 70%), m.p. 42° C. (Found: C, 48.63; H, 10.98; V, 12.59. $C_{16}H_{44}Si_4V$ calcd.: C, 48.12; H, 11.02; V, 12.78%.)

Preparation of tris(trimethylsilylmethyl)(tetrahydrofuran)vanadium

Me_3SiCH_2MgCl (40.00 mmol) in 70 ml of diethyl ether was slowly added to the suspension of I (13.40 mmol) in 70 ml THF at —78° C. The temperature of the reaction mixture was raised up to 0° C with continuous stirring, the colour changing from red to blue, and 8.0 ml of dioxan was added. After that the solvents were completely removed under vacuum, without raising temperature higher than +10°C. The residue was dissolved in 100 ml of a mixture Et_2O with hexane (2 : 1), filtered off, concentrated and cooled to —50° C, giving dark violet crystals (3.10 g, 60%), m.p. 75°C (dec). (Found: C, 49.77; H, 10.64; V, 13.36. $C_{16}H_{41}Si_3OV$ calcd.: C, 50.00; H, 10.68; V, 13.28%.)

Acidolysis of $(Me_3SiCH_2)_3V \cdot THF$ with sulphuric acid. 10 ml (10%) of sulphuric acid was added to the solution of $(Me_3SiCH_2)_3V \cdot THF$ (5.40 mmol) in 20 ml of toluene at —10° C. The temperature was then raised up to 0° C. Me_4Si (15.20 mmol) and THF (5.00 mmol) were found in the organic layer.

Reaction of tris(pentafluorophenyl)(tetrahydrofuran)vanadium with mercuric chloride

$HgCl_2$ (3.67 mmol) was added to a solution of II (0.80 mmol) in 20 ml of THF. The colour of the reaction mixture changed from brown-violet to crimson and a white precipitate of calomel was formed. The solution was filtered out from calomel, the solvent was removed under vacuum and the residue was solved in hot water. After cooling of the water solution, C_6F_5HgCl (2.21 mmol), m.p. 165° C, was crystallized. Hg_2Cl_2 (0.38 mmol) was determined iodometrically.

Reaction of tris(pentafluorophenyl)(tetrahydrofuran)vanadium with triphenylchloromethane (1 : 1)

A solution of II (1.19 mmol) in THF was mixed in an evacuated ampoule with triphenylchloromethane (1.19 mmol) in 20 ml of diethyl ether. The colour of the reaction mixture changed from violet to crimson. Tris(pentafluorophenyl)-vanadium chloride ($g = 1.977$) was identified from its isotropic ESR parameters: $A_i^{51V} = -81$ e. Literature data [13]: $g_i = 1.977$, $A_i^{51V} = -81$ e. Triphenylmethyl radical: $g = 2.003$.

Reaction of tris(pentafluorophenyl)(tetrahydrofuran)vanadium with trichlorotris(tetrahydrofuran)vanadium (1 : 1)

A solution of II (1.69 mmol) in 30 ml of diethyl ether was added to a solution of I (1.69 mmol) in 30 ml tetrahydrofuran at —10° C. The temperature of the reaction mixture was then raised to room temperature, the solvents were removed and $(C_6F_5)_3VCl \cdot THF$ (1.64 mmol) was extracted from the residue with diethyl ether. (Found: V, 8.05; Cl, 5.43; $C_{22}H_8F_{15}OClV$ calcd.: V, 7.73; Cl, 5.38%.) Isotropic ESR parameters: $g_i = 1.977$; $A_i^{51V} = -81$ e. The residue left after the extraction of $(C_6F_5)_3VCl \cdot THF$ was treated with pyridine; $VCl_2 \cdot 4\ C_5H_5N$ (1.69 mmol) was separated out.

Reaction of tris(trimethylsilylmethyl)(tetrahydrofuran)vanadium with carbon dioxide

i) In toluene solution. A solution of IV (11.50 mmol) in 70 ml of toluene and 260 ml (11.50 mmol) of CO_2 (1013 GPa 0° C) were placed in an evacuated ampule. After 48 h at 0° C the colour of the reaction mixture changed from blue to green and a dark oil formed. Then the solvent was removed under vacuum and $(Me_3SiCH_2)_4V$ was washed out from the residue with pentane. A solution of V (5.21 mmol) was obtained having the following ESR parameters: $g_i = 1.968$;

$A_i^{51v} = -51$ *e*. Literature data [2]: $g_i = 1.968 \pm 0.001$; $A_i^{51v} = -50 \pm 1$ *e*. After extraction of $(Me_3SiCH_2)_4V$, the residue was dried in vacuo. $(Me_3SiCH_2OCO)_2V$ 2 THF (5.30 mmol) was obtained. (Found: V, 11.26; $C_{18}H_{38}Si_2O_6$ calcd.: V, 11.16%.) Vanadium oxidation state equals +2.

ii) In tetrahydrofuran solution. A strong stream of CO_2 was passed through a solution of IV (8.00 mmol) in 70 ml THF with stirring at —20°C for 3 h. The colour of the reaction mixture changed from blue to green. After acidolysis of the reaction solution (30 ml 10% HCl) Me_3SiCH_2COOH (20 mmol) was found acidometrically.

Reaction of tris(pentafluorophenyl)(tetrahydrofuran)vanadium with carbon dioxide

i) In diethyl ether solution. A solution of II (3.00 mmol) in 50 ml of diethyl ether and 68 ml (3.00 mmol) carbon dioxide (1013 GPa, 0°C) was placed in an evacuated ampoule. After 48 h the formation of $(C_6F_5)_4V \cdot 2\ Et_2O$ was detected at 20°C by ESR spectroscopy; $g_i = 1.978$ and $A_i^{51v} = -85$ *e*. 0.0014 g atom V^{IV} and 0.0014 g atom V^{II} were detected in solution [15].

ii) In tetrahydrofuran solution. A solution of II (3.00 mmol) in 70 ml of THF and 220 ml (9.28 mmol) of CO_2 (1013 GPa, 0°C) were placed in an evacuated ampoule. a) After 2 h at 20°C the colour of the reaction mixture changed from brown to violet. Then the solvent and unreacted CO_2 were removed under vacuum and the residue was dried in vacuo. $(C_6F_5)V(OCOC_6F_5)_2 \cdot THF$ (VIII) (2.00 g, 94%) was obtained. (Found: V, 6.98. $C_{30}H_8F_{15}O_5V$ calcd.: V, 7.16%). Interaction of $(C_6F_5)V(OCOC_6F_5)_2 \cdot THF$ with mercuric chloride: $HgCl_2$ (3.68 mmol) was added to a solution of VIII (1.40 mmol) in 20 ml THF. After alkaline hydrolysis (30 ml 10% KOH), the solution was filtered from the settled mercury oxide, acidified, and C_6F_5COOH were extracted with diethyl ether.

After recrystallization from hot water, C_6F_5HgCl (1.10 mmol), m.p. 165°C, and C_6F_5COOH (2.40 mmol), m.p. 103°C, were found. b) After 6 days at 20°C the colour of the reaction mixture became green. The solvent was removed under vacuum, and the green residue was dried. $(C_6F_5OCO)_3V$ (IX) (1.96 g, 96%) was obtained. (Found: V, 7.40. $C_{21}F_{15}O_6V$ calcd.: V, 7.46%.)
Acidolysis of $(C_6F_5OCO)_3V$ with sulphuric acid. 15 ml (5%) sulphuric acid was added to a suspension of IX (0.73 mmol) in 40 ml Et_2O, then the organic layer was separated after evaporation of the ether. C_6F_5COOH (2.27 mmol), m.p. 103°C, was obtained.

Reaction of tetrakis(pentafluorophenyl)bis(etherate)vanadium with carbon dioxide

A solution of III (1.33 mmol) in 30 ml THF and 200 ml (8.93 mmol) of CO_2 (1013 GPa, 0°C) were placed in an evacuated ampoule. After 10—15 h at room temperature the colour of the reaction mixture became green. C_6F_5H (0.48 mmol) and $(C_6F_5)_2$ (0.24 mmol) were detected in solution. The solvent was removed under vacuum, the green residue was washed out with pentane and dried in vacuo. $(C_6F_5OCO)_3V$ (0.89 g, 95%) was obtained. (Found: V, 7.40. $C_{21}F_{15}O_6V$ calcd.: V, 7.46%.)

Reaction of tetrabenzylbis(etherate)vanadium with carbon dioxide

i) In pentane solution. A solution of VI (0.81 mmol) in 30 ml of pentane and 100 ml (4.46 mmol) CO_2 (1013 GPa, 0°C) were placed in an evacuated ampoule. In 4 days at 0°C the solution grew colourless and a brown solid precipitated. Dibenzene (0.66 mmol) was found in the solution. According to the method given in ref. 15, V^{II} (0.0061 g atom) and V^{III} (0.00022 g atom) were found in the solid.

ii) In diethyl ether solution. A strong stream of CO_2 was passed through a solution of VI (10.00 mmol) in 100 ml of diethyl ether with stirring at —20°C for 2 h. The colour of the reaction mixture became brown-green and a dark solid precipitated. After acidolysis of the reaction mixture (20 ml of 10% sulphuric acid), dibenzene (6.00 mmol) and phenylacetic acid (30.00 mmol) were found in the organic layer.

Reaction of tetramethylvanadium with acetone

3.00 ml (40.00 mmol) of acetone was slowly added to Me_4V (10.00 mmol) in 100 ml of diethyl ether with stirring at —78°C. The temperature of the reaction mixture was then raised to room temperature, and the colour of the solution became violet. The solvent was removed under vacuum and $Me_2V(Ot\text{-}Bu)_2$ was extracted from the residue with pentane. After removing pentane, the residue was distilled at 35—40°C. $Me_2V(Ot\text{-}Bu)_2$ (0.68 g, 30%), with isotropic ESR parameters: $g_i = 1.9687$; $A_i^{51V} = -51.5 \pm 0.4\ e$, was separated. Literature data [12]: $g_i = 1.9687$; $A_i^{51V} = -51.5\ e$.

Reaction of tetrabenzylvanadium with acetone

3.0 ml (40.00 mmol) of acetone was added to a solution of VI (10.00 mmol) in 100 ml of diethyl ether with stirring at —20°C. Then the temperature of the reaction mixture was raised to room temperature, the solvent was removed under vacuum and $(PhCH_2)_2V \cdot (OCMe_2CH_2Ph)_2$ was extracted from the residue with pentane. Pentane was removed under vacuum and a green, undistillable in vacuum, oil (1.91 g, 50%) was obtained.

Isotropic ESR parameters: $g_i = 1.9720$; $A_i^{51V} = 48.5 \pm 0.05\ e$.

Acidolysis of $(PhCH_2)_2V(OCMe_2CH_2Ph)_2$. 20 ml of 10% sulphuric acid was added to a solution of $(PhCH_2)_2V(OCMe_2CH_2Ph)_2$ (4.15 mmol) in 30 ml of hexane at —10°C. Toluene (7.65 mmol) was found in the organic layer.

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