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# SYNTHESIS AND PROPERTIES OF ALKYLVANADIUM(III) ALKOXIDES

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## Summary

The reactions of $R_3V \cdot THF$ ($R = C_6F_5, CH_2SiMe_3$) with one t-BuOH equivalent result in formation of unstable $R_2V(Ot\text{-}Bu)\cdot THF$, which disproportionates readily to $V^{IV}$ and $V^{II}$ compounds. The interaction of $V(Ot\text{-}Bu)_3$ with $Me_3SiCH_2Li$ in diethyl ether is accompanied by formation of the at-complex $[Me_3SiCH_2V(Ot\text{-}Bu)_3]^-Li^+$ which decomposes with formation of $(Me_3SiCH_2)_2V(Ot\text{-}Bu)_2$ and $[V(Ot\text{-}Bu)_3]^-Li^+$. As a result of exchange reaction of $V(Ot\text{-}Bu)_3$ with one mole of RMgX, the complexes $RV(Ot\text{-}Bu)_2\cdot XMgOt\text{-}Bu$ (R = Me, X = Br, $R = CH_2Ph$, $CH_2SiMe_3$, $C_6F_5$, X = Cl) have been obtained. The insertion of carbon dioxide in vanadium—carbon and vanadium—oxygen bonds has also been investigated.

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## Introduction

In our previous communications it was shown that vanadium(III) derivatives such as $R_2VX$ (X = Hal, OCOR, acac) and $RVHal_2$ ($R = Ph, Me, CH_2Ph, CH_2SiMe_3, C_6F_5$) are unstable. In solution they readily undergo redox disproportionation [1,2]. The similar alkyl vanadium(III) alkoxides $R_nV(OR')_{3-n}$ have not been described in literature. It was the purpose of the present work to investigate the possibility of the preparation of $R_nV(OR')_{3-n}$ and to compare the properties of these compounds with those of previously investigated $R_nVX_{3-n}$ (X = Hal, acac).

## Results and discussion

The synthesis and properties of alkylvanadium(III) alkoxides have been investigated as example $R_nV(Ot\text{-}Bu)_{3-n}$ ($n = 1, 2$). To obtain $R_nV(Ot\text{-}Bu)_{3-n}$ the following reactions can be used:

1. Disproportionation between $R_3V\cdot THF$ ($R = CH_2SiMe_3, C_6F_5$) and $V(Ot\text{-}Bu)_3$.
2. Alcoholysis of the same $R_3V\cdot THF$ with tert-butyl alcohol.

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3. Substitution of t-BuO-group in $V(Ot\text{-}Bu)_3$ by a $\sigma$-ligand by means of $R_2Zn$, RLi or RMgX (R = Me, $CH_2Ph$, $CH_2SiMe_3$, $C_6F_5$).

We have established that $R_3V\cdot THF$ does not react with $V(Ot\text{-}Bu)_3$ in diethyl ether using different molar ratios and over the temperature range from —20°C to 50°C.

Alcoholysis of the V—C $\sigma$-bond in $R_3V\cdot THF$ under the action of t-BuOH is observed even at —78°C. In the presence of excess alcohol, $V(Ot\text{-}Bu)_3$ is isolated in THF medium. At a 1 : 1 ratio of the starting materials the exchange of one $\sigma$-ligand for t-BuO group occurs with formation of RH.

$$R_3V\cdot THF + t\text{-}BuOH \xrightarrow[-78^\circ C]{Et_2O,\ THF} \underset{(I)}{R_2V(Ot\text{-}Bu)\cdot THF} + RH \qquad (1)$$

To isolate complex 1, the temperature of the reaction mixture was increased slowly. The ESR signal characteristic of $V^{IV}$ appears in the ESR spectrum at —20°C, the intensity reaching a maximum in two hours. $R_4V$ was isolated from the reaction solution and $V^{II}$ was found in the precipitate (Table 1). Therefore, even at —20°C, complex 1 undergoes redox disproportionation.

$$R_2V(Ot\text{-}Bu)\cdot THF \xrightarrow[-20^\circ C]{} 0.5R_4V\cdot 2THF + 0.5\ V(Ot\text{-}Bu)_2 \qquad (2)$$

The reaction of $R_3V\cdot THF$ with two equivalents t-BuOH at —78°C should give complex II; $RV(Ot\text{-}Bu)_2$. However, at —78°C $R_3V\cdot THF$ does not react with the second mole of t-BuOH. This is due to the low reactivity of the alcohol as a weak acid. The reaction proceeds at temperatures above —20°C. Under these conditions the complex $(Me_3SiCH_2)_2V(Ot\text{-}Bu)\cdot THF$ disproportionates more rapidly and exchanges the second $Me_3SiCH_2$ ligand for t-BuO-group. This is why in the $(Me_3SiCH_2)_3V\cdot THF$ + 2t-BuOH system the second mole of t-BuOH remains unreacted. $(C_6F_5)_3V\cdot THF$ reacts with the second mole of t-BuOH, but the resultant complex II, $(C_6F_5)V(Ot\text{-}Bu)_2\cdot THF$ disproportionates according to eq. 3:

$$(C_6F_5)V(Ot\text{-}Bu)_2\cdot THF \xrightarrow[-20^\circ C]{THF} 0.5(C_6F_5)_2V(Ot\text{-}Bu)_2 + 0.5V(Ot\text{-}Bu)_2 \qquad (3)$$

It should be mentioned that we failed to isolate $V(Ot\text{-}Bu)_2$ in crystalline form. We have established that $V(Ot\text{-}Bu)_2$ transforms quantitatively into the

TABLE 1

REACTION PRODUCTS FROM THE REACTION OF $R_3V\cdot THF$ (VOC) WITH t-BuOH IN $Et_2O$ or THF at —20°C

| VOC | VOC/t-BuOH | Reaction products (mol/mol VOC) | | | |
|---|---|---|---|---|---|
| | | RH | $R_4V$ | $R_2V(Ot\text{-}Bu)_2$ | $V(Ot\text{-}Bu)_2$ |
| $(Me_3SiCH_2)_3V$ | 1/1 | 0.96 | 0.45 | no | 0.49 |
| $(C_6H_5)_3V$ | 1/1 | 0.95 | 0.42 | no | 0.48 |
| $(Me_3SiCH_2)_3V$ | 1/2 | 0.96 | 0.48 | no | 0.48 |
| $(C_6F_5)_3V$ | 1/2 | 1.90 | no | 0.43 | 0.42 |

crystalline at-complex $[V(Ot\text{-}Bu)_3]^-Li^+$ under the action of t-BuOLi on the reaction mixture. For identification, this complex was prepared specially from $VCl_2\cdot THF$ and excess t-BuOLi [3]. Its ionic structure is confirmed by the preparation of the sodium salt as a result of a one-electron transfer reaction:

$$V(Ot\text{-}Bu)_3 + Ph_2\dot{C}O^-Na^+ \xrightarrow[0^\circ C]{Et_2O,\ THF} [V(Ot\text{-}Bu)_3]^-Na^+ + Ph_2C{=}O \qquad (4)$$

The exchange reaction of metal alcoholates with Grignard reagents or organolithium compounds at the present time to obtain $\sigma$-derivatives of transition metals is used widely [4—6]. Thus, $V(Ot\text{-}Bu)_3$ was used as a starting compound to obtain alkylvanadium(III) butoxides.

The interaction of $V(Ot\text{-}Bu)_3$ with $Me_3SiCH_2Li$ proceeds in toluene at —20°C. After mixing the starting materials (1:1), the reaction mixture gives an ESR signal, the parameters of which corresponds to $(Me_3SiCH_2)_2V(Ot\text{-}Bu)_2$ ($g_i = 1.9666, A_i^{5IV} = -53\ e$ [4]). $[V(Ot\text{-}Bu)_3]^-Li^+$ precipitates from the solution, suggesting the following reaction. Initially the exchange of one t-BuO-group for a $Me_3SiCH_2$ ligand occurs. The t-BuOLi reacts with $V^{III}$ compound to form the ionic complex, which undergoes redox disproportionation.

$$\begin{aligned} V(Ot\text{-}Bu)_3 + Me_3SiCH_2Li \xrightarrow[-20^\circ C]{toluene} &[(Me_3SiCH_2)V(Ot\text{-}Bu)_3]Li \rightarrow \\ &(Me_3SiCH_2)_2V(Ot\text{-}Bu)_2 + [V(Ot\text{-}Bu)_3]Li \qquad (5) \end{aligned}$$

The mild alkylating agent dimethylzinc does not react with $V(Ot\text{-}Bu)_3$ in diethyl ether at temperature between 0° and 20°C.

$V(Ot\text{-}Bu)_3$ interacts with Grignard reagents in diethyl ether at 0°C. When adding one equivalent of RMgX to a $V(Ot\text{-}Bu)_3$ solution the reaction mixture colour becomes blue-green; however, magnesium salts do not participate even on adding dioxane. The finely crystalline compounds of general formula $RV(Ot\text{-}Bu)_2\cdot XMg(Ot\text{-}Bu)$ (III) (R = Me, $CH_2Ph$, $CH_2SiMe_3$, $C_6F_5$) have been isolated with the help of low temperature crystallization:

$$V(Ot\text{-}Bu)_3 + RMgX \xrightarrow[0^\circ C]{Et_2O} RV(Ot\text{-}Bu)_2\cdot XMg(Ot\text{-}Bu) \qquad (6)$$

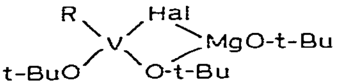
The second mole of RMgX reacts at 20°C. Complex III, being formed in the first stage, seems to react with the second mole. Yet, instead of $R_2V(Ot\text{-}Bu)$, the products of its disproportionation have been found (eq. 2).

Thus, the experimental data from attempts to obtain $R_2V(Ot\text{-}Bu)$ and to isolate $R_2VX$ (X = Hal, acac, $O_2CR$) suggest that $R_2VX$ could not be isolated. Independent of the character of both substituents, $R_2VX$ disproportionates to form $V^{IV}$ and $V^{II}$ compounds.

Different relationships are observed for the monosubstituted $V^{III}$ $RVX_2$ derivatives. $RVHal_2$, which exist as dimers in the solutions undergo redox disproportionation as well as $R_2VHal$.

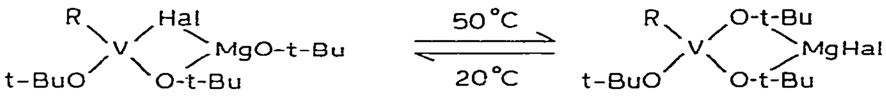
$RV(acac)_2\cdot THF$ and $RV(O_2CR_2)\cdot THF$ were isolated as monomeric hexacoordinated complexes, in which acetylacetonate and carboxylate are $\eta^2$-ligands. Monoalkylvanadium(III)dibutoxides were isolated as monomeric complexes with magnesium. The assignment of the IR spectrum of $MeV(Ot\text{-}Bu)_2 \cdot BrMg(Ot\text{-}Bu)$ complex in toluene or octane solution was carried out by comparison with spectra of the initial compounds $V(Ot\text{-}Bu)_3$ and MeMgBr and, on the other hand, with spectra of $V(Ot\text{-}Bu)_4$ and LiOt-Bu. All the absorption bands characteristic for MeMgBr in the range of 400—4000 $cm^{-1}$ are absent from the spectrum of the complex. This indicates that MeMgBr has reacted completely. Comparing spectra of the complex and $V(Ot\text{-}Bu)_3$, only slight changes typical of the area from 500 to 1000 $cm^{-1}$ were observed. There are intense absorption bands with maxima at 490, 610, 760, 910, 930 and 1000 $cm^{-1}$ in the spectrum of complex. The absorption bands at 490, 640, 780, 930, 960 $cm^{-1}$ were present in the $V(Ot\text{-}Bu)_3$ spectrum. The intense bands at 1175 and 1355 $cm^{-1}$ are the same in both spectra. The IR spectrum of $V(Ot\text{-}Bu)_4$, which is a monomer, has a distinct set of symmetrical and intense absorption bands at 600, 780, 930, 1175 and 1355 $cm^{-1}$.

The comparison of IR spectra of $V(Ot\text{-}Bu)_3$ and $V(Ot\text{-}Bu)_4$ suggests that in $V(Ot\text{-}Bu)_3$ there are non-equivalent t-BuO-groups, some of which are bridging. The conclusion is confirmed by comparison of the spectrum of $V(Ot\text{-}Bu)_3$ with that of LiOt-Bu, for which the intermolecular association is through an oxygen bridge. There is a band at 960 $cm^{-1}$ in the spectra of $V(Ot\text{-}Bu)_3$ and LiOt-Bu, which may be assigned to a bridging t-BuO-group. In contrast, the band at 930 $cm^{-1}$ characterizes an $\eta^1$-bonded t-BuO group. Based upon the above observations the absorption band at 1000 $cm^{-1}$ in the spectrum of the complex may be assigned to a t-BuO-group in a non-symmetrical bridge fragment, V—Ot-Bu- - Mg. Thus, the following tetrahedral structure may be suggested for complex III:



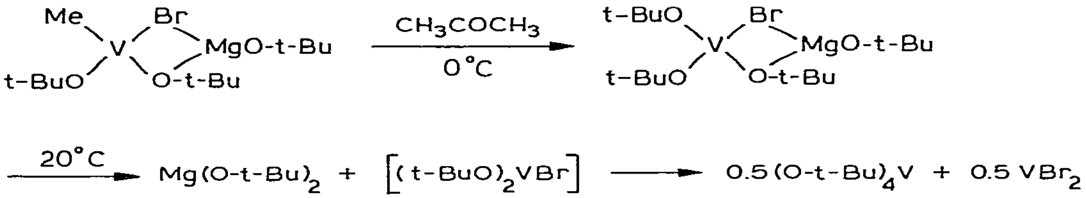
(III)

Investigation of the temperature dependence from 20° to 50° of the IR spectra of complexes III indicates that the bands at 490, 760, 930, 1355 $cm^{-1}$ do not change peak intensity with rising temperature. The peak intensity of bands at 610, 910, 1175 $cm^{-1}$ decreases. In contrast, the peak intensity of the band at 1000 $cm^{-1}$ increases. As this band characterizes a bridging group V—O—Mg, the increase of its intensity may be explained by the increase in number of such groups in complexes III with elevation of temperature. Thus, the complex in solution may be present in two forms, the equilibrium between which shifts considerably with temperature variation within 30°C.

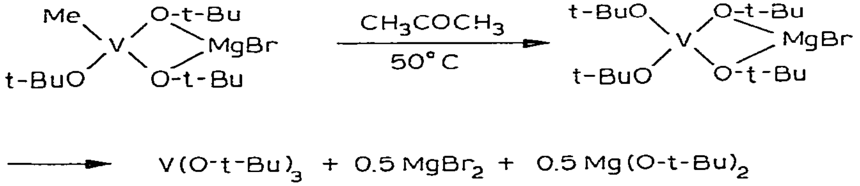


(III) (IIIa)

The chemical existence of two forms is confirmed by reaction with acetone. The interaction of acetone (1 mole) with $MeV(Ot\text{-}Bu)_2 \cdot BrMg(Ot\text{-}Bu)$ at 0°C results in a considerable yield of $V(Ot\text{-}Bu)_4$ and a V(II) derivative precipitates.



If interaction with acetone occurs at 50°C, the main reaction product proves to be $V(Ot\text{-}Bu)_3$.



Complexes III are readily oxidized and hydrolyzed, but they are thermally stable up to 150°C. Thermal decomposition above 150°C is accompanied by isolation of RH (1.0 mol), isobutylene (2.0 mol), isobutane and tert-butyl alcohol (in small quantities) and vanadium oxides and magnesium oxohalides.

We have previously investigated the insertion of carbon dioxide in the vanadium—carbon bond [2]. Complexes III contain V—O, V—C, Mg—O bonds simultaneously, in which $CO_2$ may be inserted. Using an example of these complexes we tried to eluadate the reactivity of these bonds towards $CO_2$ under the same conditions. Complexes III react with $CO_2$ in diethyl ether at —78°C. Initially one mol of $CO_2$ is introduced into the reaction solution. After absorption of $CO_2$ the temperature of the reaction mixture was increased to —20°C; a signal appeared in the ESR spectrum, the parameters of which agree with the parameters for $R_2V(Ot\text{-}Bu)_2$. In addition a residue containing magnesium salts precipitates from the solution: $MgX_2$ (X = Cl, Br) and $Mg(O_2COt\text{-}Bu)_2$. The data obtained indicate that the first mole of $CO_2$ is inserted into Mg—O bonds.

$$RV(Ot\text{-}Bu)_2XMgOt\text{-}Bu + CO_2 \xrightarrow[-78^\circ C]{Et_2O} RV(Ot\text{-}Bu)_2\cdot XMg(O_2COt\text{-}Bu) \qquad (7)$$

The experimental data show complex III to be unstable and to decompose to magnesium salts and with disproportionation of the $RV(Ot\text{-}Bu)_2$ derivative to $V^{IV}$ and $V^{II}$.

The second mole of $CO_2$ is also absorbed at —78°C. When the tempeature of the reaction mixture reaches 20°C, a signal appears in the ESR spectra whose parameters agree with that of $V(Ot\text{-}Bu)_4$. Magnesium salts and $V^{II}$ derivative precipitate from the reaction mixture. A scheme of insertion of two moles of $CO_2$ may be proposed from the results obtained.

$$\begin{gathered} 2MeV(Ot\text{-}Bu)_2\cdot BrMg(Ot\text{-}Bu) + 4CO_2 \xrightarrow[-78^\circ C]{Et_2O} \\ 2(MeCO_2)V(Ot\text{-}Bu)_2\cdot BrMg(O_2COt\text{-}Bu) \xrightarrow[20^\circ C]{} \\ V(Ot\text{-}Bu)_4 + V(O_2CMe)_2 + MgBr_2 + Mg(O_2COt\text{-}Bu)_2 \qquad (8) \end{gathered}$$

Carboxylation of complexes III at —78°C in THF with excess $CO_2$ is accompanied by insertion of $CO_2$ in all three bonds; $V(O_2COt\text{-}Bu)_3$, $MgX_2$ and $Mg(O_2CR)_2$ are isolated from the reaction mixture.

$$\text{III} + 3CO_2 \xrightarrow[-78^\circ C]{THF} RCO_2V(O_2COt\text{-}Bu)_2\cdot XMg(O_2COt\text{-}Bu) \xrightarrow[20^\circ C]{} V(O_2COt\text{-}Bu)_3 + 0.5\ MgX_2 + 0.5\ Mg(O_2CR)_2 \qquad (9)$$

$R = Me, CH_2Ph, CH_2SiMe_3$; $X = Cl, Br$

The pentafluorophenyl complex $C_6F_5V(Ot\text{-}Bu)_2\cdot ClMg(Ot\text{-}Bu)$ is an exception as it absorbs only one mole of $CO_2$. Further insertion of $CO_2$ is not observed, as the $V—C_6F_5$ bond is inert to $CO_2$ at —78°C; even at 20°C and under a $CO_2$ pressure of 2 atm the derivatives $(C_6F_5)_4V\cdot 2THF$ and $(C_6F_5)_3V\cdot THF$ react only slowly with $CO_2$ [2].

The formation of the unsymmetrical derivative VI is observed on carboxylation of $V(Ot\text{-}Bu)_3$ with one mole of $CO_2$:

$$V(Ot\text{-}Bu)_3 + CO_2 \xrightarrow[-78^\circ C]{THF} \underset{(VI)}{(t\text{-}BuOCO_2)V(Ot\text{-}Bu)_2} \qquad (10)$$

The band at 960 $cm^{-1}$, assigned to the bridging group, is conserved in the IR spectrum of this red-violet complex VI in THF solution; the bands at 900 and 930 $cm^{-1}$ dissappear. New bands at 540, 720, 1370 and 1600 $cm^{-1}$ appear. The band at 1600 $cm^{-1}$ may be assigned to C=O fragment in the carbonyl group. Based upon the assignment of the IR spectrum it is believed that the insertion of the first mole of $CO_2$ does not affect the bridging group.

The carboxylation of $V(Ot\text{-}Bu)_3$ with excess $CO_2$ in THF at —78°C results in $V(O_2COt\text{-}Bu)_3$, which readily loses three moles of $CO_2$ in vacuum at 80°C. In turn the resulting $V(Ot\text{-}Bu)_3$ absorbs three moles of $CO_2$ on addition of $CO_2$ in the presence of THF.

$$V(O_2COt\text{-}Bu)_3 \underset{20^\circ C}{\overset{80^\circ C}{\rightleftharpoons}} V(Ot\text{-}Bu)_3 + 3\ CO_2 \qquad (11)$$

## Experimental

All reactions were carried out in an argon atmosphere or in vacuum using deoxygenated and dehydrated solvents. ESR spectra were determined with a EPA-2M radio spectrometer. $Mn^{2+}$ ions in a MgO crystal lattice were used for the calibration of the magnetic field. 2,2,6,6-Tetramethylpiperidoxyl was used as a standard for defining the *g*-factor. IR-spectra were measured with a Specord-75IR. Reaction products were analyzed by GLC.

### *Reaction of tris(trimethylsilylmethyl)vanadium tetrahydrofuranate with tert-butyl alcohol (1:1)*

t-BuOH (10.00 mmol) in 20 ml of $Et_2O$ was added slowly to a $(Me_3SiCH_2)_3V\cdot THF$ solution (10.00 mmol) in 50 ml of $Et_2O$ at —78°C. The temperature of the reaction mixture was raised to 20°C, and the colour changed from blue to green. $Me_4Si$ was found in the solution by GLC, $V^{II}$

(0.0049 g/atm) was determined [7]. The solvent was removed, and $(Me_3SiCH_2)_4V$ (1.50 g, 38%) was extracted from the residue with pentane. M.p. 42°C. (Found: V, 12.67. $C_{16}H_{44}Si_4V$; calcd.: V, 12.78%).

### *Reaction of tris(pentafluorophenyl)vanadium tetrahydrofuranate with tert-butyl alcohol (1:2)*

t-BuOH (10.00 mmol) in 20 ml of $Et_2O$ was added slowly to a $(C_6F_5)_3V \cdot THF$ solution (5.00 mmol) in 50 ml of $Et_2O$ at —78°C. The temperature of the reaction mixture was raised to 20°C, and the colour changed from brown-violet to green. In the solution $(C_6F_5)_2V(Ot\text{-}Bu)_2$ was identified by GLC with isotropic parameters equal to $g_i = 1.972$ and $A_i^{51V} = -52\ e$ [4]. By GLC, $C_6F_5H$ (9.49 mmol) was found and $V^{II}$ (0.0043 g/atm) was determined.

### *Reaction of tris(tert-butoxide)vanadium with sodium ketyl*

$Ph_2\dot{C}\text{-}O^-Na^+$ (8.63 mmol) in 20 ml of $Et_2O$ was added to a $V(Ot\text{-}Bu)_3$ solution (8.63 mmol) in 40 ml of $Et_2O$ at —10°C. The temperature of the reaction mixture was raised to 20°C. The colour changed from blue-violet to crimson, and the crimson residue precipitated. The residue was filtered off and washed with $Et_2O$. The crimson finely crystalline $[(t\text{-}BuO)_3V]Na$ (3.50 g, 94%) was obtained. (Found: V, 11.47. $C_{12}H_{27}NaO_3V$; calcd.: V, 11.67%).

### *Reaction of tris(tert-butoxide)vanadium with trimethylsilylmethyllithium (1:1)*

$Me_3SiCH_2Li$ (3.20 mmol) in 20 ml of toluene was added to a $V(Ot\text{-}Bu)_3$ solution (3.20 mmol) in 20 ml of toluene at —78°C. The temperature of the reaction mixture was raised to 20°C, the colour changed from blue-violet to green, and the crimson residue precipitated. The residue was centrifuged and washed with pentane; $[(t\text{-}BuO)_3V]Li$ (0.42 g,47%) was obtained. (Found: V, 18.25. $C_{12}H_{27}LiO_3V$; calcd.: V, 18.41%). The solvent was removed, $(Me_3SiCH_2)_2V(Ot\text{-}Bu)_2$ (0.36 g, 30%) was isolated from the residue by distillation at 100°C/0.1 mmHg. (Found: V, 13.60. $C_{16}H_{40}Si_2O_2V$; calcd.: 13.75%).

### *Preparation of MeV(Ot-Bu)₂·BrMgOt-Bu*

MeMgBr in 20 ml of $Et_2O$ was added to a $V(Ot\text{-}Bu)_3$ solution (7.41 mmol) in 30 ml of $Et_2O$ at —78°C. The temperature of reaction mixture was raised to 20°C; the colour changed from blue-violet to blue. After an hour the solvent was removed under vacuum and blue $MeV(Ot\text{-}Bu)_2 \cdot BrMgOt\text{-}Bu$ (2.73 g, 96%) was extracted from the residue, decomposition temperature 200°C (DTA) (Found: V, 13.40; Mg, 6.00; Br, 20.45. $C_{13}H_{27}MgBrO_3V$; calcd.: V, 13.10; Mg, 6.24; Br, 20.55%).

### *Acidolysis of MeV(Ot-Bu)₂·BrMgOt-Bu with sulphuric acid*

5 ml of 10% $H_2SO_4$ was added to a solution of complex (0.72 mmol) in 10 ml of toluene at —20°C. Gaseous $CH_4$ (0.64 mmol) was evolved and, in the solution t-BuOH (2.12 mmol) was obtained.

### *Reaction of Me₃SiCH₂V(Ot-Bu)₂·ClMgOt-Bu with trimethylsilylmethylmagnesium chloride (1:1)*

$Me_3SiCH_2MgCl$ (5.00 mmol) in 10 ml of $Et_2O$ was added to a solution of the complex (5.00 mmol) in 30 ml of $Et_2O$ at —20° C. The temperature of the reaction mixture was raised to 20° C and kept so for 24 hours. The colour changed from blue to green and a residue precipitated. $V^{II}$ (0.0022 g/atm) was found in the reaction mixture. The solution was filtered from the residue, the solvent was removed under vacuum, and $(Me_3SiCH_2)_4V$ (0.79 g, 40%) was extracted with pentane; m.p. 42° C.

### *Definition of magnesium in the presence of vanadium*

A 150—200 mg sample of the compound (9—12 mg recalculated for Mg) was mineralized with the mixture of sulphuric and nitric acids to convert vanadium into oxidation state five. The solution obtained was diluted with water to 250 ml. $FeCl_3$ (2 mg) was added to an aliquot of the solution investigated, and the pH adjusted to 6-7 with ammonia solution. The solution was heated to 60—70° C and then cooled to 20° C. The residue was filtered off and washed. In the filtrate magnesium was found by titration with trilone "B" (0.05 *N*).

### *Thermal decomposition of $Me_3SiCH_2V(Ot\text{-}Bu)_2 \cdot ClMgOt\text{-}Bu$*

The complex (4.44 mmol) was heated in a double-bended ampoule to 200° C. Then the ampoule was cooled to 20° C. The gaseous and liquid products were recondensed into the second bend. $Me_4Si$ (3.90 mmol), iso-butylene (8.66 mmol), iso-butane (1.98 mmol) and t-BuOH (1.70 mmol) were found in the condensate. $V^{IV}$ (0.0044 g/atm), Mg (0.0040 g/atm), Cl (0.0043 g/atm) were found in the black residue.

### *Reaction of $MeV(Ot\text{-}Bu)_2 \cdot BrMgOt\text{-}Bu$ with carbon dioxide*

#### *a) In $Et_2O$ at —78° C (1:1)*

112 ml of $CO_2$ (5.00 mmol) was frozen onto a solution of the complex (5 mmol) in 30 ml of $Et_2O$. The temperature of the reaction mixture was raised slowly to 20° C, the colour changed from blue to blue-violet and a residue precipitated. The solvent was removed under vacuum at 10° C, $Me_2V(Ot\text{-}Bu)_2$ (0.45 g, 40%; $g_i = 1.9687$, $A_i^{51V} = -52$ *e* [4]) was isolated from the solution by distillation. 0.0024 g/atm $V^{II}$ was found in the residue.

#### *b) In $Et_2O$ at 20° C (1:2)*

A complex (5.00 mmol) in 30 ml of $Et_2O$ and 224 ml of $CO_2$ (10.00 mmol) was placed in an evacuated ampoule. In an hour the colour changed from blue to green and a residue precipitated. The solvent was removed under vacuum, and $(t\text{-}BuO)_4V$ (0.68 g, 40%) was isolated from the solution by distillation at 90° C/0.1 mmHg. (Found: V, 14.70. $C_{16}H_{36}O_4V$; calcd.: V, 14.87%). 0.0024 g/atm $V^{II}$ was found in the residue.

#### *c) In THF at —78° C ($CO_2$)*

300 ml of $CO_2$ (13.40 mmol) were frozen onto a complex solution (3.55 mmol) in 20 ml of THF. The temperature of the reaction mixture was raised slowly to 20° C; the colour changed from blue to brown-green. The solvent was removed under vacuum, and on heating to 80° C the solution changed colour

from green to blue, $V(Ot\text{-}Bu)_3$ (0.76 g, 80%) was extracted with pentane. (Found: V, 18.70, $C_{12}H_{27}O_3V$ calcd.: V, 18.88%).

*Reaction of tris(tert-butoxide)vanadium with excess $CO_2$*

500 ml of $CO_2$ (22.32 mmol) was frozen onto a $V(Ot\text{-}Bu)_3$ solution (7.00 mmol) in 30 ml of THF. The temperature of the reaction mixture was raised slowly to 20°C; the colour changed from blue-violet to green. The solvent was removed under vacuum at 10°C. Darkgreen $V(O_2COt\text{-}Bu)_3$ (2.50 g, 89%) was obtained. (Found: V, 12.50; $C_{15}H_{27}O_9V$ calcd.: V, 12.71%).

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