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Reaction of [VO(OPr)$_3$] with Hexamethyldisylthiane in the Presence of β-Diketones

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Abstract—The reaction of [VO(OPr)$_3$] (Pr is *n*-propyl) with hexamethyldisylthiane Me$_3$SiSSiMe$_3$ in the presence of β-diketones (acetylacetone (HAcac), hexafluoroacetylacetone (Hfac), and dipivaloylmethane (Dpm)), is studied. In all cases, vanadium(IV) and vanadium(III) β-diketonate complexes of different types are formed. New crystalline modification [V(Acac)$_3$] is obtained in the reaction with HAcac. The mixed-ligand vanadium(III) complex of the composition [V$_2$(Hfac)$_2$(μ-OPr)]$_2$ is formed with Hfac. In the presence of Dpm, the known vanadium(IV) complex [V$_2$O$_2$(Dpm)$_2$(μ-OPr)$_2$] is obtained in which two vanadyl groups VO^{2+} are linked by two bridging propoxy groups. The structures of all products are determined by X-ray diffraction analysis.

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Compared to the well developed chemistry of chalcogenide molybdenum clusters, the chemistry of chalcogenide clusters of the diagonal analog (vanadium) is studied to a lesser extent [1, 2]. Only the clusters with the {V$_2$(μ-S$_2$)$_2$}$^{4+}$ core were rather well studied and are easily available. There are different approaches to the synthesis of these complexes. The trithiocarbonate complex [V$_2$(μ-S$_2$)$_2$(CS$_3$)$_4$]$^{4-}$ was synthesized from [VS$_2$(S$_2$)(SPh)]$^{2-}$ and CS$_2$ [3]. The reaction of dibenzolvanadium [V(η^6-C$_6$H$_6$)$_2$] with dithioacetic acid in toluene afforded [V$_2$(μ-S$_2$)$_2$(CH$_3$CS$_2$)$_4$] [4]. Complexes [V$_2$(μ-S$_2$)$_2$(Et$_2$NCS$_2$)$_4$] and [V$_2$(μ-S$_2$)$_2$(*iso*-Bu$_2$NCS$_2$)$_4$] were synthesized by the reactions of [VS$_4$]$^{3-}$ with thiuram disulfides (R$_2$NCS$_2$)$_2$ [5–8]. The reactions of dithiocarbamates [VO(S$_2$CNEt$_2$)$_3$] and xanthates VO(S$_2$COR)$_3$ with hydrogen sulfide gave [V$_2$S$_4$(S$_2$CNEt$_2$)$_4$] and [V$_2$S$_4$(S$_2$COEt)$_4$] [9]. As can be seen from the data presented, in all known cases, the cluster core {V$_2$(μ-S$_2$)$_2$}$^{4+}$ is coordinated by the bidentate sulfur-containing ligands only. In this work we studied the possibility of obtaining the [V$_2$S$_4$(β-Dike)$_4$] complexes from [VO(OPr)$_3$], free β-diketone, and a sulfidizing agent (hexamethyldisilthiane or hydrogen sulfide). It turned out that no sulfide clusters were formed in any case and the vanadium(IV) and vanadium(III) β-diketonate complexes were the products, whose structures are determined by the nature of β-diketone used.

EXPERIMENTAL

All experiments were carried out under argon using a standard Schlenk technique. Solvents were purified by standard procedures. The starting reagents from commercial sources (Sigma-Aldrich) were used as received. IR spectra were recorded on a Scimitar FSC-2000 spectrophotometer (KBr pellets). Elemental analysis was carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Brabch, Russian Academy of Sciences).

Synthesis of [VO(Dpm)(μ-OPr)]$_2$. Dipivaloylmethane (1.5 mmol, 350 μL) was added to a solution of [VO(OPr)$_3$] (200 μL, 800 μmol) in toluene (5 mL), and the resulting solution was treated with hexamethyldisilthiane (200 μL, 900 μmol). A dark brown solution was stirred for 3 days at ambient temperature and turned green. Green crystals of the product were obtained by the slow evaporation of the solvent in vacuo. The yield was 70%. The structure of the complex was determined by X-ray diffraction analysis. IR, ν, cm^{-1}): 3005 m, 2923 m, 1556 s, 1527 s, 1419 s, 1374 s, 1358 s, 1287 s, 1021 s, 998 s, 936 m, 797 m, 686 m, 609 m, 484 s, 424 m.

Synthesis of [V(Acac)$_3$] (I). Acetylacetone (500 μL, 5 mmol) was added to a solution of [VO(OPr)$_3$] (610 μL, 2.5 mmol) in toluene (5 mL). The solution gradually turned bright red. After the color stabilized, hexamethyldisilthiane (2.1 mL, 9 mmol) was added and the solution turned brown. The solvent was evaporated to a minimum volume, and hexane was added to turbidity. Brown crystals of [V(Acac)$_3$] grew upon keeping the mixture in a refrigerator at –18°C for 2 days. The yield was 80%. IR, ν, cm^{-1}: 2963 m, 2922 m, 2049 w, 1959 w, 1564 s, 1526 s, 1420 s, 1380 s,

Table 1. Crystallographic data and details of diffraction experiments for structures **I** and **II**

Parameter	Value		
	I	**I**	**II**
Molecular formula	$C_{15}H_{21}O_6V$	$C_{15}H_{21}O_6V$	$C_{26}H_{18}F_{24}O_{10}V_2$
FW	348.26	348.26	1048.28
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group; Z	$P2_1/c$; 4	$P2_1/c$; 4	$P\bar{1}$; 2
T, K	100	150	150
a, Å	13.8782(3)	13.9154(6)	9.1764(4)
b, Å	7.4462(2)	7.4779(4)	12.9073(4)
c, Å	16.1939(4)	16.2411(9)	17.4229(6)
α, deg	90	90	68.886(1)
β, deg	99.7420(10)	99.530(2)	85.762(1)
γ, deg	90	90	83.060(1)
V, Å^3	1649.34(7)	1666.69(15)	1909.94(12)
F(000)	728	728	1032
ρ_{calcd}, g/cm^3	1.402	1.388	1.823
μ(MoK_α), mm^{-1}	0.626	0.619	0.657
Crystal size, mm	0.21 × 0.12 × 0.10	0.30 × 0.15 × 0.10	0.50 × 0.35 × 0.08
T_{min}; T_{max}	0.828; 1	0.741; 1	0.735; 0.949
Measured reflections (R_{int})	14003/4517 (0.0237)	11532/4411 (0.0370)	1510/9182 (0.0259)
Observed ($I > 2\sigma(I)$)	3602	2952	6487
$2\theta_{max}$, deg	62.62	62.92	56.60
R_1 (with $I > 2\sigma(I)$)	0.0392	0.0485	0.0493
$wR(F^2)$ (for all reflections)	0.1088	0.1298	0.1491
Goodness-of-fit	1.057	1.048	1.082
$\Delta\rho_{max}/\Delta\rho_{min}$, eÅ^{-3}	0.55/–0.44	0.68/–0.43	1.55/–0.86

1359 s, 1274 s, 1021 s, 997 m, 932 m, 798 m, 667 m, 587 m, 484 m, 445 s, 413 m.

Synthesis of [V(Hfac)$_2$(μ-OPr)]$_2$ (II). Hexafluoroacetylacetone (170 μL) was added to a solution of [VO(OPr)$_3$] (100 μL) in dichloromethane (5 mL), and the solution immediately turned intensively dark brown. Then hexamethyldisilthiane (200 μL) was added. The dark violet solution that formed was stirred for 24 h, and the solvent was distilled off in vacuo at ambient temperature. The product was sublimed when temperature was increased to 100°C and deposited as large black-violet crystals on the walls of a Schlenk vessel. The yield was 60%. The structure of the complex was determined by X-ray diffraction analysis.

X-ray diffraction analysis. All measurements were performed by a standard procedure on a Bruker-Nonius X8Apex automated four-circle diffractometer equipped with a CCD two-coordinate detector (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Reflection intensities were measured in φ and ω scan modes for narrow (0.5°) frames. An absorption correction was empirically applied using the SADABS program [10]. Structures **I** and **II** were solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms using the SHELXTL program package [11]. Hydrogen atoms were refined in the rigid body approximation.

Disorder of the acetylacetonate ligand over two equally probable positions with an "inflection" along the O···O line was observed in structure **I** at T = 150 K. In order to obtain more exact data, the X-ray diffraction analysis was carried out from another single crystal at T = 100 K; however, the disoder remained.

The fluorine atoms of all CF$_3$ groups in structure **II** are disordered over two positions with different contributions, which is a result of rotation.

The crystallographic characteristics of complexes **I** and **II** and details of diffraction experiments are given in Table 1. The CIF files containing the full information on the studied structures were deposited with the Cambridge Crystallographic Data Centre (nos. 864189 (**I**) and 864191 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The possibility for the synthesis of unknown complexes [V_2S_4(β-Dike)$_4$ from [VO(OPr)$_3$], free β-diketone, and a sulfidizing agent was studied. It was assumed that [VO(OPr)$_3$] would react with free β-diketone to generate complexes [VO(β-Dike)$_3$], which could be transformed upon sulfidation into [V_2S_4(β-Dike)$_4$] due to the redox condensation by analogy to xanthates and dithiocarbamates, [VO(ROCS$_2$)$_3$] and [VO(R$_2$NCS$_2$)$_3$] [9]. However, it turned out that hydrogen sulfide treatment of a mixture of [VO(OPr)$_3$] and HAcac resulted only in the quantitative reduction of vanadium(V) to vanadium(IV) to form known [VO(Acac)$_2$] and sulfur. The replacement of the sulfiding agent by hexamethyldisilthiane gave the known complex [V(Acac)$_3$] (**I**) (with a small admixture of [VO(Acac)$_2$]) crystallized in a new modification. The replacement of HAcac by more bulky HDpm changes the "route" of the reaction with hexamethyldisylthiane: the product (after recrystallization from ethanol) was the known binuclear complex [V_2O_2(Dpm)$_2$(μ-OEt)$_2$] [12] in which two vanadyl groups are bound by two bridging ethoxy groups. The new vanadium(III) complex [V_2(Hfac)$_2$(μ-OPr)] (**II**) was obtained when HHfac was used. The complex turned out to be rather volatile, and single crystals suitable for X-ray diffraction analysis were obtained by vacuum sublimation. It should be mentioned that this is the second known complex of the [V(β-Dike)$_2$(μ-OR)]$_2$ type. The first representative of this family of ligands containing acetylacetonate as a chelate and pyrogallol as a bridge was synthesized by the reaction of [VO(Acac)$_2$] with a pyrogallol excess [13]. Thus, attempts to obtain vanadium sulfide clusters with β-diketonate ligands lead to the reduction of vanadium only and the formation of the vanadium(III) and vanadium(IV) β-diketonate complexes, depending on the nature of β-diketone and the sulfiding agent.

The monoclinic (space group $P2_1/c$) modification of [V(Acac)$_3$] obtained in this work (Fig. 1) differs from the known monoclinic ($P2_1/n$) [14] and orthorhombic (*Pbca*) [15] modifications by molecular packing. The geometric characteristics in the molecules in the polymorphous modifications of compound **I** (Table 2) are consistent with each other.

Polymorphism in metal tris(acetylacetonates) has been studied from the mid-1920s [17]. The most modern and complete review [18] systematized the known structural types of these compounds based on the chirality of the [M(Acac)$_3$] molecule, which can take one of two enantiomeric forms (*C* or *C**). The packing in all structures of this type can be considered as distorted monolayer hexagonal (*AAA*). To assign the packing (and, correspondingly, the crystalline phase) to this or another type, a closely packed hexagonal molecular layer is chosen, and the distance between the centers of the molecules in the layer is 7.4–8.1 Å.

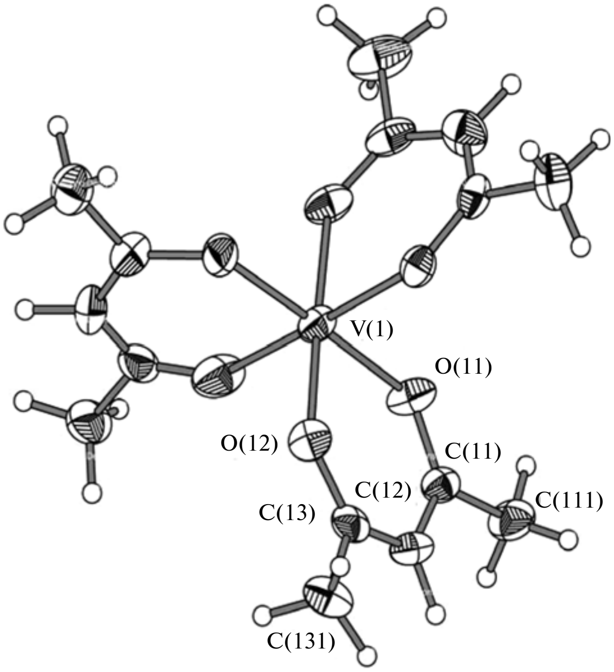

Fig. 1. Structures of molecules [V(Acac)$_3$] in compound **I**.

The specific of the enantiomer (*C* or *C**) is determined for all molecules. According to the mutual arrangement of molecules of this or another type in the layer, the structural type is designated by Greek letters: α, β, γ, δ, and η. Four subtypes α_n (n = 1–4) are distinguished in the α type. In addition, few homochiral structures are ascribed to type *C*. According to this classification, new polymorphous modification **I** is attributed to type α_1, and those described in the literature belong to the β and δ types.

All crystal structures considered [18] and structure **I** belong to the so-called homomolecular type where the crystal includes molecules of only one sort. V.A. Blatov and E.V. Peresypkina developed a conceptual apparatus for the description of packings in homomolecular structures including the concepts of molecular lattice and molecular network [19, 20]. A molecular lattice implies a system of centers of gravity in molecules regardless their shape and a totality of intermolecular contacts in the structure. When a molecular network is formed, the molecules are also "drawn together" into their center of gravity; however, a bond (an edge of the network) is retained between the centers in the obtained three-dimensional network, if at least one intermolecular contact is found between atoms of the corresponding molecules in the structure. Then the molecular lattice and network are examined by topological methods incorporated in the TOPOS program package [21]. For this purpose, the molecular lattice and network are presented by three-dimensional periodical graphs, whose nodes correspond to the centers of gravity of the molecules and the edges correspond to intermolecular contacts or closest

Table 2. Structural parameters of the polymorphous modifications of $[V(Acac)_3]$

Polymorph	β ([15])	δ ([14])	α_1 (this work)	α_2 (this work)
a, Å	15.1901(10)	16.34	13.8782(3)	13.9154(6)
b, Å	13.3920(7)	13.06	7.4462(2)	7.4779(4)
c, Å	16.4043(6)	8.108	16.1939(4)	16.2411(9)
β, deg	90.00(1)	90.00	99.74(1)	99.53(1)
Space group	*Pbca*	$P2_1/n$	$P2_1/c$	$P2_1/c$
Z	8	4	4	4
T, K	120	Room temperature	150	100
α(OVO), deg	86.30(10)–88.74(9)	87.0–87.8	86.81(5)–89.25(5)	87.20(6)–89.09(7)
Capture*	1.38	1.38	1.38	1.38
Angle θ, deg*	27.8	26.5	29.2	29.1

* The parameters were calculated according to [16].

contacts between the centers of gravity (molecular lattice). The topological characteristics, such as coordination sequences, Schläfli symbols, etc. [21], are calculated for the graphs. The basic difference between molecular lattices and molecular networks is that the molecular network "inherits" the properties of the system of intermolecular contacts in the structure, while all information about them is lost in the molecular lattice: the molecules, whose centers of gravity are neighboring, are considered "bound in network" in this case. In other words, the molecular network represents the system of intermolecular contacts, whereas the molecular lattice indicates the mutual arrangement of molecules in crystal. In the general case, their topological characteristics do not coincide.

The principal distinction of the topological approach from that proposed in [18] is that the three-dimensional structure is not divided into closely packed planes but is considered as a single whole. In addition, the algorithm of analysis is entirely automated, which minimizes the factor of subjectivity of a researcher. It seemed interesting to apply this approach to the structures of $[M(Acac)_3]$ and to compare the results with those obtained in [18].

The crystal packings were analyzed by the TOPOS program package for the structures considered in [18] (except for those without coordinates of atoms) using the data on structure **I**. As a significant topological characteristic of the molecular lattice and molecular network we chose a set of the first five members of the coordination sequence indicating the number of nodes in the first, second, etc. coordination sphere about each topologically unique node in the corresponding network. For example, such a traditional characteristic of the packing as a molecular coordination number is turned out to be equal to the first number in the coordination sequence for the molecular network.

The characteristics of the molecular lattice were calculated for all structures, whereas those for the molecular network were characterized only for the structure in which hydrogen atoms are localized (since they are important for the correct determination of all molecular contacts).

It was revealed that a unique set of the first five members of the coordination sequence of the molecular network (Table 3) corresponds to particular "racemic" type (α_n, β, γ, δ, and η), although the characteristics of the molecular lattice for all types, except α_n, coincide. In the α_n phase, the center of gravity of each molecule is surrounded by ten centers of gravity of the neighbors, and the molecular coordination number for α_{1-4} differs, varying from 14 to 19. In the β, γ, δ, and η phases, the center of gravity of each molecule is surrounded by eight rather than ten centers of gravity of the neighbors, and the molecular coordination number varies from 16 to 18. As for the chiral type (C), the number of nodes in the first coordination sphere of the molecular lattice and molecular network coincides with that for α_4; however, differences are observed already in the second sphere.

Thus, to distinguish the α and C packings from others, it is enough to know the topological characteristics of the molecular lattice. An additional calculation of the molecular network makes it possible to unambiguously determine the packing (phase) type.

Finally, one interesting fact should be mentioned: the values of molecular coordination numbers in the $[M(Acac)_3]$ structure significantly exceed the most randomly probable value 14 found [19] by an analysis of 27886 homomolecular structures of organic compounds.

Table 3. Values of the first five members of the coordination sequences of the molecular lattices and networks in compounds [M(Acac)$_3$]*

Type of packing	Coordination sequence 1...5 in molecular lattice	Coordination sequence 1...5 in molecular network
α_1	10 34 74 130 202	16 58 128 226 352
α_2	10 34 74 130 202	18 66 146 258 402
	10 34 74 130 202	17 65 143 257 399
	10 34 74 130 202[1]	17 64 145 255 401
α_3	10 34 74 130 202	17 65 141 253 399
	10 34 74 130 202	17 64 144 252 393
	10 34 74 130 202	14 57 141 253 388
	10 34 74 130 202	16 62 142 250 396
α_4	10 34 74 130 202	19 69 156 279 430
	10 34 74 130 202	17 71 156 273 436
β	8 26 56 98 152	18 72 162 288 450
γ	8 26 56 98 152	18 68 160 286 450
	8 26 56 98 152	17 72 158 288 446
	8 26 56 98 152	17 71 161 285 449
	8 26 56 98 152	18 69 161 287 449
δ	8 26 56 98 152	16 62 138 246 384
η	8 26 56 98 152	17 72 163 294 461
C	10 36 78 138 214	19 69 156 279 430
	10 36 78 138 214	17 71 156 273 436

* The values are given for topologically nonequivalent nodes (corresponding to symmetrically independent molecules).

Table 4. Intermolecular distances in [V(Hfac)$_2$(μ-OPr)]$_2$ (the environment of vanadium(1) is assigned to the first crystallographically independent complex, and vanadium(2) is attributed to the second complex)

Type of bond	Bond length
V(1)–O(1)	1.9349(17)
V(1)–O(1)	1.9884(17)
V(1)–O(11)	1.9929(18)
V–O(12)	2.0115(18)
V(1)–O(21)	2.0067(18)
V(1)–O(22)	2.0068(17)
V(2)–O(2)	1.9681(17)
V(2)–O(2)	1.9549(17)
V(2)–O(31)	1.9990(17)
V(2)–O(32)	2.0053(18)
V(2)–O(41)	2.0056(18)
V(2)–O(42)	1.9995(17)
V(1)–V(1)	3.0126(8)
V(2)–V(2)	3.0183(8)

The unit cell of structure **II** (Fig. 2, Table 4) contains two crystallographically independent complexes [V(Hfac)$_2$(μ-OC$_3$H$_7$)]$_2$. Each of them consists of fragments {V(Hfac)$_2$} (V–O 1.99–2.01 Å) bound by the bridging propoxide ligands (V–O 1.93–1.99 Å) and forming the centrosymmetric Δ the isomer (isomerism is related to the mutual arrangement of the chelating ligands at two {V(Hfac)$_2$} linked by the bridges. The V···V distance (3.0 Å) rather indicates the absence of the direct metal–metal bonding. The geometric parameters of the {V(Hfac)$_2$} fragment are similar to those of [V(Hfac)$_3$] [22]. The molecules of complexes in structure **II** form a bilayer packing. The layers are oriented along the vector $r = b - c$ and differ by the shift of half a period (Fig. 3).

Thus, different β-diketonate vanadium(IV) and vanadium(III) complexes are formed in the vanadium(V) alkoxide–β-diketone–hexamethyldisylthiane system. Sulfur is not transferred from silicon to vanadium, and the role of hexamethyldisylthiane is

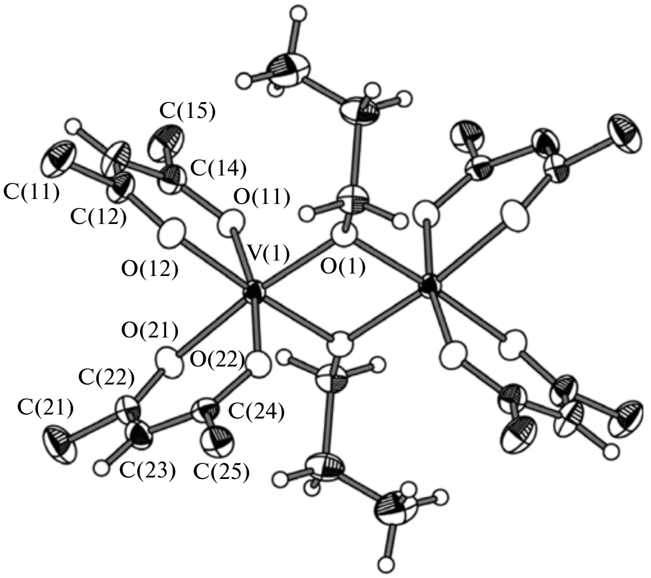

Fig. 2. Structure of one of crystallographically independent [V(Hfac)$_2$(μ-OC$_3$H$_7$)]$_2$. Disordering of all CF$_3$ groups is omitted for clarity.

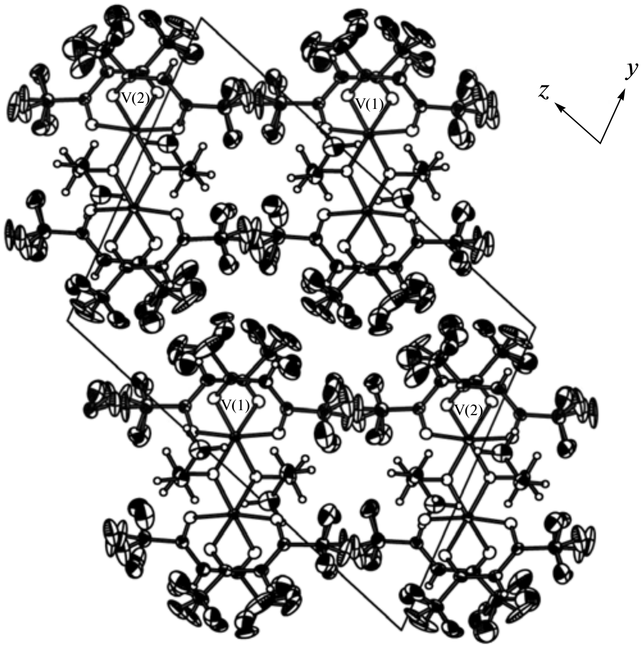

Fig. 3. Crystal packing for complex **II**.

only the reduction of vanadium(V) to vanadium(IV) or vanadium(III) due, most likely, to the oxidation of sulfide sulfur. It can be expected that the reduction of vanadium(V) alcoholates by other silyl reagents, such as R_3SiH or Si_2R_6, in the presence of appropriate ligands can serve as a convenient method for the synthesis of vanadium complexes in low oxidation states.

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