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Synthesis and Properties of Some Dialkylamido Vanadium(V) Derivatives

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The preparation and reactivity of some dialkylamido derivatives of vanadium(V), ($VO(NR_2)_3$), ($VO(NR_2)_2(OR')$), ($VO(NR_2)(OR')_2$) and $Li(VO(NR_2)(OR')_3)$ is reported. Expected substitution of NR_2 by OR' and OCH_2CF_3 was observed. Moreover, with RSH substitution is accompanied by redistribution. A similar rearrangement was found to occur during the insertion of CS_2 in $V–NR_2$ leading to ($VO(S_2CNR_2)_3$). The ^1H NMR shifts of the isopropoxy group protons in the complexes ($VOX(Oi\text{-}Pr)_2$) were used to establish the following sequence of donor abilities for the anionic ligand X: $Cl < OCH_2CF_3 < Oi\text{-}Pr < N(Si_2Me_6) < NEt_2$.

Introduction

Although the chemistry of metal alkoxides $M(OR)_n$ [1] and dialkylamides $M(NR_2)_n$ [2] has been extensively developped during the last ten years and their possible use as intermediates in the synthesis of various derivatives emphasized [3], the preparation and properties of dialkylamido compounds of vanadium(V) have not been investigated till now and, as far as we know, only the preparation of the mixed species ($VO(NSi_2Me_6)_x(Oi\text{-}Pr)_{3-x}$) has been previously mentioned (with x = 1,2) [4].

As part of a general study of organic derivatives of titanium(IV) and vanadium(V) devoted to such matters as the nature of the metal–ligand bond and comparative ligand reactivities paralleled with spectroscopic data [5–8], we now describe convenient procedures for the preparation of ($VO(NR_2)_x(OR')_{3-x}$) with x = 1, 2, 3 and $Li(VO(NR_2)(OR')_3)$ (R = Et; R′ = i-Pr), compare the donor ability of the NR_2 group with other anionic ligands and investigate the reactivity of the vanadium(V)–nitrogen bond toward substitution and insertion reagents.

Results and Discussion

Preparation and Characterization

The following equation represents the general method used for the introduction of the dialkylamido group

TABLE I. Analytical data and V=O Stretching Elongation Frequency.

Compound	% C exp. (calc)	% H exp. (calc)	% N exp. (calc)	% V exp. (calc)	$\nu_{V=O}$ cm^{-1}
$VO(NEt_2)_3$	51.5	10.6	13.9	18.3	
	(50.9)	(10.6)	(14.8)	(18.0)	
$VO(NEt_2)_2(Oi\text{-}Pr)$	48.6	9.3		18.7	1003
	(48.8)	(10.0)		(18.9)	
$VO(NEt_2)(Oi\text{-}Pr)_2$	45.8	9.0	4.6	20.0	1002
	(46.7)	(9.3)	(5.4)	(19.8)	
$VO(SEt)_3$	29.3	6.1		22.0	
	(28.8)	(6.0)		(20.3)	
$VO(S_2CNEt_2)_3$	35.2	6.0	8.4	11.0	950
	(35.2)	(5.9)	(8.2)	(10.0)	
$Li[VO(OR)_3(NEt_2)]$[a]	47.6	9.4	4.0	16.0	1002
	(48.3)	(9.6)	(4.3)	(15.8)	

[a] % Li exp. 2.1 (calc. 2.1).

TABLE II. ^1H NMR Data. Chemical Shifts[a] of $VO(NEt_2)_x(Oi\text{-}Pr)_{3-x}$.

Compound	NCH_2CH_3		$OCH(CH_3)_2$	
	CH_2 quartet	CH_3 triplet	CH septuplet	CH_3 doublet
$VO(NEt_2)_3$	3.68	1.15		
$VO(NEt_2)_2(Oi\text{-}Pr)$	3.88–3.73	1.26	4.82	1.31
$VO(NEt_2)(Oi\text{-}Pr)_2$	3.91	1.28	4.83[b]	1.32
$VO(Oi\text{-}Pr)_3$			5.30	1.43

[a] In ppm downfield with respect to TMS as internal standard measured in CCl_4. [b] Broadened septuplet.

TABLE III. NMR Data. ^{13}C Chemical Shifts[a] of $VO(NEt_2)_x$-$(Oi\text{-}Pr)_{3-x}$.

Compound	$N\text{-}CH_2\text{-}CH_3$		$OCH(CH_3)_2$	
	αC	βC	αC	βC
$VO(NEt_2)_3$	53.0 52.5	16.5 16.0		
$VO(NEt_2)_2(Oi\text{-}Pr)$	54.9	15.0	b	26.5
$VO(NEt_2)(Oi\text{-}Pr)_2$	54.9	15.0	82.5 81.5	26.5 25.6
$VO(Oi\text{-}Pr)_3$			82.0 81.4	25.7

[a] In ppm downfield with respect to TMS as internal standard measured in solution in $CDCl_3$. [b] Not clearly apparent.

TABLE IV. ^1H Chemical Shifts of Isopropoxy Groups in $VOX(Oi\text{-}Pr)_2$[a].

Compound	$OCH(CH_3)$	
	CH septuplet	CH_3 doublet
$VO(Oi\text{-}Pr)_2Cl$	5.52	1.50
$VO(Oi\text{-}Pr)_2(OCH_2CF_3)$	5.40	1.46
$VO(Oi\text{-}Pr)_3$	5.30	1.43
$VO(Oi\text{-}Pr)_2(NSi_2Me_6)$	5.04	1.37
$VO(Oi\text{-}Pr)_2(NEt_2)$	4.83[b]	1.32

[a] In ppm downfield with respect to TMS as internal standard measured in solution in CCl_4. [b] Broadened septuplet.

$$(VOCl_x(OR')_{3-x}) + x\ LiNR_2 \xrightarrow{\text{pentane}} (VO(NR_2)_x(OR')_{3-x}) + x\ LiCl$$

$$x = 1, 2, 3; R = C_2H_5; R' = CH(CH_3)_2$$

For the case when x = 0 an addition reaction is observed:

$$(VO(OR')_3) + LiNR_2 \rightarrow Li[VO(NR_2)(OR')_3]$$

(see Table I).

In the infrared spectra, the assignment of the vanadium–nitrogen stretching mode is unambiguously deduced from $(VO(NEt_2)_3)$ as $\nu_{(V-N)} = 612\ cm^{-1}$ (to be compared with $\nu_{(Ti-N)} = 610\ cm^{-1}$ in $((Ti(NEt_2)_4)$ [9]). But the characteristic (V=O) band expected near 1000 cm^{-1} is sometimes concealed by the symmetric NC_2 stretching mode in the same region (Table I).

NMR Spectroscopic Data

The ^1H and ^{13}C NMR spectra indicated the existence of non equivalence due to the crowed conditions about the central vanadium atom. For instance, the methine protons of $OCH(CH_3)_2$ appeared as a broadened septuplet in the mixed derivative $(VO(NEt_2)(Oi\text{-}Pr)_2)$ and the methylene protons of $N(CH_2CH_3)_2$ in $(VO(NEt_2)_2(Oi\text{-}Pr)]$ appeared as two quartets at 3.88 (more intense) and 3.73 ppm (less intense) (Table II). Similarly the ^{13}C resonance signals of the α-carbon of $OCH(CH_3)_2$ is observed as a complex multiplet in any derivative of the series while other signals may be split into two peaks (of equal intensity or not) (Table III). Moreover, an evolution of chemical shifts is observed when x is varied. For instance, the progressive shielding of the nuclei (^1H and ^{13}C) of $OCH(CH_3)_3$ when x is increased may be explained by the more effective donor ability of dialkylamido groups, compared with alkoxo ones. Furthermore, as an extension of a previous work [5–7] the ^1H NMR shifts of the isopropoxy group in the complexes $(VOX(Oi\text{-}Pr)_2)$ were used to establish the following sequence of donor ability for the anionic ligand X: $Cl < OCH_2CF_3 < Oi\text{-}Pr < N(Si_2Me_6)_2 < NEt_2$ according to data collected in Table IV.

Reactivity

Dialkylamido derivatives have been previously used as intermediates in the synthesis of various derivatives, owing to the ability of the metal–nitrogen bond to be involved in either substitution or insertion reactions [2, 3]. In view of these characteristics, we have considered interesting to study the reactivity of the vanadium–nitrogen bond and more precisely we have investigated the possibility of synthesizing new alkoxy derivatives of oxo-vanadium(V), using $(VO(NR_2)(OR')_2)$ as a precursor.

Substitution reactions

The expected reaction $(VO(NR_2)(OR')_2)$ + R''-OH → $(VO(OR'')(OR')_2)$ + HNR_2 proceeded smoothly when R'' = isopropyl and CH_2CF_3, leading in the latter case to the new derivative $(VO(OCH_2CF_3)(OCH(CH_3)_2)_2)$.

Attempts to attach a cyclopentadienyl group by reaction with C_5H_6 according to the equation:

$$(VO(NR_2)(OR')_2) + C_5H_6 \rightarrow (VO(C_5H_5)(OR')_2) + HNR_2$$

were unsuccessful. This contrasts with the ready formation of $((C_5H_5)Ti(OR')_3)$ from $(Ti(NR_2)(OR')_3)$ under similar experimental conditions [10]. The difference may be due to lower stability of the $(C_5H_5)V$ bond compared with $(C_5H_5)Ti$ bond.

When reacting thiol in stoichiometric amount, the expected monothioalkyl compound $VO(SR'')(OR')_2$ is not obtained owing to the quantitative redistribution reaction described by the scheme:

$$(VO(NR_2)(OR')_2) + R''SH \rightarrow 1/3(VO(SR'')_3) + 2/3(VO(OR')_3) + HNR_2$$

The new trisubstituted derivative $VO(SCH_2CH_3)_3$ was obtained as a black insoluble solid. $VO(OR')_3$ and HNR_2 also formed were identified in the filtrate. In the course of complementary investigations about the synthesis of thioalkyl derivatives of vanadium(V), we also found possible to introduce the thioalkyl group by action of thiol on alkoxy derivatives with elimination of alcohol.

Insertion reactions

It is well known that carbon disulfide is readily inserted into metal–nitrogen bonds affording dithiocarbamates [1]. By reaction of CS_2 with $(VO(NR_2)(OR')_2)$ in pentane we obtained the yellow complex $(VO(S_2CNR_2)_3)$ – previously prepared by a different way [11] – which was fully characterized by elemental analysis and IR spectroscopy.

The overall reaction is:

$$(VO(NR_2)(OR')_2) + CS_2 \rightarrow 1/3(VO(S_2CNR_2)_3) + 2/3(VO(OR')_3)$$

$VO(OR')_3$ was identified in the filtrate.

By action of carbon dioxide insertion also occurred. The formation of the carbamate group O_2CNEt_2 is monitored via IR (strong absorptions in the 1450–1550 cm^{-1} region assignable to the O_2CN moiety) and ^1H NMR spectroscopy (quartet at 3.12 and triplet at 0.9 ppm). This is in agreement with the values obtained by Chisholm [12] for Ti(IV) and V(IV) carbamates. Further investigations are in progress.

We also observed that apparent insertion of a nitrile can take place. In the IR spectrum of the brown compound obtained, the C≡N band was completely absent and new bands had appeared in the 1560–1660 region assignable to C═N. This is very similar with the previously reported insertion of a nitrile into the Ti–N bond of $(Ti(NR_2)_4)$ [13]. Full analytical and spectroscopic characterization of the products will be published later on.

Experimental

All reactions were carried out under nitrogen with precautions to avoid hydrolysis. Mixed complexes $(VOCl_{3-x}(Oi\text{-}Pr)_x(x = 0, 1, 2, 3)$ were prepared by the literature method [14, 15]. The lithium reagent $LiNEt_2$ was freshly prepared by reaction of diethylamine with butyllithium (15% solution in hexane, from Merck). Molecular weight determinations were made cryoscopically in benzene.

The ^1H NMR spectra were recorded on a Perkin–Elmer R 12 spectrometer at 33 °C. All the spectra were registered for carbon tetrachloride solutions and are referenced to TMS as the internal standard.

^{13}C NMR spectra were obtained from a Fourier transform spectrometer (Brucker WH 90) operating at room temperature, with complete noise decoupling of the protons. All the spectra were registered for deuterochloroform solutions and are referenced to TMS as the internal standard.

Infrared data were obtained using a Perkin–Elmer spectrophotometer model 577 as capillary films or Nujol mulls.

Conductivity measurements were obtained from benzene solutions, with a Philips PW 950 conductivity bridge and a conductivity cell with platinum electrodes.

Elemental analyses (C, H, N, Li) were performed by the Service Central de Microanalyse du CNRS. Vanadium was determined in our laboratory as V_2O_5.

Preparation of Diethylamido Bis Isopropoxy Oxovanadium(V)

$VOCl(Oi\text{-}Pr)_2)$ (3.70 g, 16.8 mmol) in 5 ml hexane was added to a solution of $LiNEt_2$ (16.8 mmol) in 10 ml hexane, at –20 °C, to give a red solution. After 1 hr stirring, the solution was allowed to warm to room temperature, filtered and the solvent removed. The residue was distilled at 0.01 mm to give $(VO(NEt_2)(Oi\text{-}Pr)_2)$ as a brown red liquid (b.p. 60–61 °C/0.01 mm). Yield 65%. This compound is monomeric in benzene.

Preparation of Bis Diethylamido Isopropoxy Oxovanadium(V) and Tris Diethylamido Oxovanadium (V)

The above procedure was used with $LiNEt_2$ (49.2 mmol in 30 ml hexane) and ($VOCl_2$(Oi-Pr)) (4.85 g, 24.6 m*M*); and $LiNEt_2$ (190.7 mmol in 115 ml hexane) and $VOCl_3$ (11.0 g, 63.5 mmol). Distillation of the residues gave red liquids. (VO(NEt_2)$_2$ (Oi-Pr)), b.p. 74.76 °C/0.01 mm. Yield: 60%; (VO(NEt_2)$_3$) b.p. 121 °C/0.01 mm. Yield: 17%. Both compounds are monomeric in benzene.

Preparation of Lithium Oxovanadium Diethylamido Tris Isopropoxide

(VO(Oi-Pr)$_3$) (5.24 g, 21.4 mmol) in 5 ml hexane was added, at room temperature, to a solution of $LiNEt_2$ (21.5 mmol) in 13 ml hexane. The red solution was stirred for 2 hr and left overnight at 4 °C to give a bright red precipitate. After filtration, the precipitate was washed with pentane and dried *in vacuo*. Yield 50%. The microcrystalline solid Li[VO(Oi-Pr)$_3$(NEt_2)] is insoluble in pentane, hexane, nitrobenzene, acetonitrile and slightly soluble in benzene (0.1 M/l) and non ionic (10^{-2} μmho/cm).

Reaction of (VO(NEt$_2$)(Oi-Pr)$_2$) with Alcohols

Excess of isopropyl alcohol (15 g, 25 mmol) was added to (VO(NEt_2)(Oi-Pr)$_2$) (0.33 g, 1.2 mmol) in 5 ml pentane, at 0 °C. After stirring for 10 min, the solvent was removed under reduced pressure. $HNEt_2$ and (VO(Oi-Pr)$_3$) were characterized by ^{1}H NMR spectroscopy.

Similarly, the reaction of (VO(NEt_2)(Oi-Pr)$_2$) (0.90 g, 3.5 mmol) with an excess of 2,2,2-trifluoroethanol CF_3CH_2OH (1.20 g, 12 mmol) gave, after evaporation, a liquid identified as (VO(OCH_2CF_3)(Oi-Pr)$_2$) [16]. This compound is monomeric in benzene.

Reactions of (VO(NEt$_2$)(Oi-Pr)$_2$) with the Thiol C$_2$H$_5$SH

C_2H_5SH (0.27 g, 5.5 mmol) was added to (VO(NEt_2)(Oi-Pr)$_2$) (1.11 g, 4.5 mmol) in 10 ml pentane at −20 °C. A vigorous reaction took place and a black precipitate appeared immediately. After stirring for 1 hr, the solution was filtered and the black residue washed with pentane, dried under reduced pressure and weighed (0.35 g, 98% Yield).

The filtrate was evaporated at 10^{-2} mm Hg and the residue characterized by its ^{1}H NMR spectra as (VO(Oi-Pr)$_3$) (0.70 g, 98% yield). (VO(SC_2H_5)$_3$) is insoluble in all organic solvents.

Reaction of (VO(NEt$_2$)(Oi-Pr)$_2$) with Carbon Disulfide

An excess of CS_2 (1.5 g, 19.7 mmol) was added to (VO(NEt_2)(Oi-Pr)$_2$) (1.33 g, 5.1 mmol) in 10 ml pentane at room temperature. After stirring for 12 hr, a yellow solid precipitated which was filtered off, dried under reduced pressure, and identified as VO(S_2CNEt_2)$_3$ [11] (0.70 g, yield: 80%).

Evaporation of the filtrate gave a liquid characterized as (VO(Oi-Pr)$_3$) (0.79 g, yield: 95%) by its ^{1}H NMR spectra. (VO(S_2CNEt_2)$_3$) is insoluble in all common organic solvents.

Reaction of (VO(NEt$_2$)(Oi-Pr)$_2$) with Carbon Dioxide

A slow stream of CO_2 was bubbled through a solution of (VO(NEt_2)(Oi-Pr)$_2$) (1.38 g, 5.3 mmol) in 10 ml pentane, for ½ hr, at room temperature and the solvent removed from the mixture under reduced pressure to leave a red liquid.

Reaction of (VO(NEt$_2$)(Oi-Pr)$_2$) with a Nitrile

A large excess of propionitrile (12.0 g, 218 mmol) was added to (VO(NEt_2)(Oi-Pr)$_2$) (0.76 g, 2.9 mmol) and the mixture stirred at room temperature for 4 days. A brown precipitate formed which was filtered from the supernatant liquid and washed with pentane; 0.17 g of this material was obtained.

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