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Surface organometallic chemistry of vanadium(V): reactivity of $(Bu^tN{=})VNp_3$ towards silica

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Abstract

The reaction of $(Bu^tN{=})VNp_3$ towards silica dehydroxylated at 773 K was studied by in situ FT-IR, ^{13}C CP-MAS NMR, ^{51}V MAS NMR, ESR, chemical analysis of the evolved gases and chemical reactivity. Upon heating at 323 K under static vacuum at least four surface organometallic vanadium species are formed. However, after treatment at 373 K under vacuum $(\equiv SiO)_2V({=}NBu^t)Np$ (**B**) appears to be the major surface species. This species reacts with neopentane, at 423 K, via a C–H addition to the V=N bond. Heating of **B** under hydrogen does not lead to surface vanadium hydride species but, presumably, to hydrogenolysis of ≡SiO–V bonds, elimination of NH_2Bu^t and formation of ionic surface species, $[\equiv SiO]^-[Bu^tNH_3]^+$.

Keywords: Surface organometallic chemistry; Vanadium(V); Silica

1. Introduction

The reactivity of organometallic complexes with the surface of partially dehydroxylated amorphous inorganic oxides has been extensively studied for more than 20 years [1]. Among the objectives of such studies is the synthesis of surface-anchored complexes with a defined coordination sphere. In such heterogeneous molecular complexes the metal center bears two types of ligands: (a) the 'solid' ligand, through which the metal is bonded to the surface, usually an oxy-type ligand, and (b) the 'classical' ligands, responsible for the chemical reactivity of the metal complex via their steric and electronic properties. Therefore, in certain cases a new catalytic material, which exhibits much higher activity and/or selectivity for a given reaction, can be obtained. In the last decade, much work has been devoted to the study of the reactivity of alkyl and/or alkylidene complexes of the early transition metals towards the surface of inorganic oxides [2]. The resulting well defined surface organometallic species can be transformed in hydride species, which are able to catalyze, under mild conditions, the hydrogenolysis of alkanes [3], the depolymerization of polyolefins [4], and even the unprecedented metathesis of alkanes [5]. Although a paper related to the thermally induced alkane elimination from silica-supported bis(alkyl)vanadium(IV), leading to surface alkylidene species, has appeared recently [6], there are still no reports concerning the surface organometallic chemistry of vanadium(V). Here we describe our results concerning the reactivity of $(Bu^tN{=})VNp_3$, I, (Np = neopentyl) towards the surface of silica. This kind of complex was expected to be a promising starting material for alkane activation, since C–H bond addition to V=NR bonds had already been reported [7]. Moreover, hydrogenolysis of the resulting surface organometallic species could lead to surface vanadium hydrides. For comparison, in order to reach a better understanding of the surface reaction, some experiments were also carried out with $(Bu^tN{=})V(OBu^t)Np_2$ (**II**).

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2. Experimental

All manipulations were carried out in the absence of solvent, under argon or vacuum. In situ infrared spectra were recorded on an FT Nicolet 520 spectrometer (16 scans, 4.0 cm^{-1} resolution), using special cells described in the literature [8]. Gas phase analyses were performed on an HP 5890 series II gas chromatograph equipped with a flame ionization detector and an Al_2O_3/KCl on fused silica capillary column (50 m × 0.32 mm).

The silica support (Aerosil from Degussa, 200 m^2 g^{-1}) was dehydrated under vacuum (ca. 13.3 mPa) at 773 K overnight, $silica_{(773)}$. Deuterated silica was prepared by heating normal $silica_{(773)}$ under D_2O (> 90%D, 2.9 kPa) at 773 K for 3 h followed by evacuation at that temperature for 3 h. This procedure was repeated three times before a final evacuation at 773 K overnight. For IR experiments a disk of silica (ca. 15 mg) was employed; in all other experiments, when a greater amount was needed, silica was used as a powder. In all studies the samples were prepared by sublimation of the vanadium complex, using standard break-and-seal techniques. Unless stated otherwise, all thermal treatments were carried out under static vacuum. At the end of each experiment, 250 mg of the solid were treated with 10 ml HF (Merck, 48%). After complete evaporation of HF, the residue was dissolved in 50 ml 1 M H_2SO_4 and filtered into a 100 ml volumetric flask. The solution was then treated with 10 ml of 30% aqueous H_2O_2 to form the strongly absorbing red–brown peroxovanadium complex [9]. Its absorbance was measured at 450 nm and the vanadium concentration determined through a calibration curve prepared under the same conditions using ammonium vanadate. $(Bu^tN{=})VNp_3$ and $(Bu^tN{=})V(OBu^t)Np_2$ were prepared according to the literature [10]. *cis*-pent-2-ene and hex-1-ene (Fluka) were purified by passing through a column of activated alumina. Norbornene (Aldrich) was used as received. Acetone was dried with $MgSO_4$ and distilled under argon.

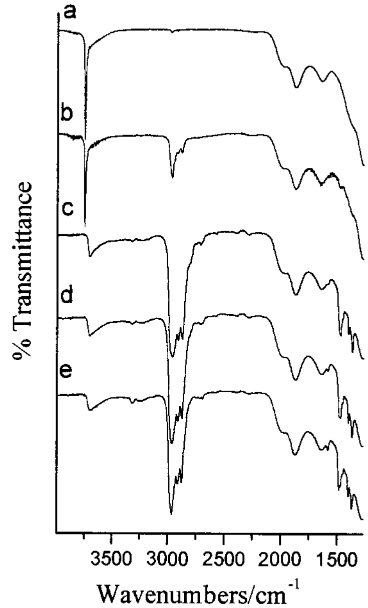

Fig. 1. FT-IR spectra of: (a) $silica_{(773)}$; (b) $silica_{(773)}$ after sublimation of $(Bu^tN{=})VNp_3$ followed by evacuation at room temperature; (c) $silica_{(773)}$ after sublimation of $(Bu^tN{=})VNp_3$, heating at 323 K for 2 h, followed by evacuation at the same temperature; (d) c after heating at 373 K for 2 h and vacuum; (e) d after heating at 423 K for 2 h and vacuum.

2.1. MAS NMR studies

Solid state MAS NMR spectra were recorded on a Bruker AC 300P spectrometer, operating at 75.45 and 78.94 MHz for ^{13}C and ^{51}V, respectively. The probehead was a commercial double-tuned 7 mm double-bearing system from Bruker, allowing spinning frequencies up to 4 kHz. The samples were introduced into the zirconia rotors under a dry argon atmosphere in a glove box and tightly closed. ^{13}C spectra were recorded using the cross-polarization (CP) technique with the following parameters: acquisition time: 0.16 s; pulse length: 9.5 μs; contact time = 5 ms; delay between each scan = 5 s. Typically, 11 000 scans were accumulated. Chemical shifts are given with respect to $SiMe_4$. For ^{51}V MAS NMR, the delay between each scan was 0.2 s, with typically 50 000 accumulations. Chemical shifts are given with respect to $VOCl_3$. All spectra were recorded under high power decoupling.

2.2. ESR experiments

Electron spin resonance measurements were carried out on a Bruker ESP 300 E spectrometer at liquid nitrogen temperature with an X-band frequency, 9.47 GHz. The modulation field frequency and amplitude were 100 KHz and 9.89 G, respectively. The g-values were calibrated by using an external standard, DPPH. The cavity spectrum was subtracted from samples spectra using a Bruker's software, Win EPR.

3. Results

3.1. Infrared studies

When **I** was sublimed onto a disk of SiO_2 pretreated at 773 K overnight, $SiO_{2(773)}$, the white disk turned yellow. At the same time two groups of bands appeared in the ranges 3000–2800 and 1500–1300 cm^{-1}, which can be ascribed to $\nu_{(CH)}$ and $\delta_{(CH)}$, respectively, of the organic ligands of **I**. After evacuation, the intensity of the band at 3747 cm^{-1}, assigned to isolated $\equiv$SiOH

Table 1
NMR data for $(Bu^tN{=})VNp_3/SiO_2$, $(Bu^tN{=})V(OBu^t)Np_2/SiO_2$ and molecular analogues

Complex		$^{51}V/\delta$	$^{13}C/\delta$	Reference
$(Bu^tN{=})VNp_3$		+879		[10]
			31.9{$(CH_3)_3CN$} [a] 33.6 {$(CH_3)_3CCH_2$}; 35.0 {$(CH_3)_3CN$}	This work
$(Bu^tN{=})V(OBu^t)Np_2$		+293		[10]
$(Bu^tN{=})V(OBu^t)_2Np$		−324		[10]
$(Bu^tN{=})V(OBu^t)_3$		−751		[10]
$(Bu^tN{=})V(OSiMe_3)_3$		−698		[10]
$(Bu^tN{=})VCp(OBu^t)Cl$		−763		[11]
$(Bu^tN{=})VCp(NHBu^t)Cl$		−785		[11]
$(Bu^tN{=})VNp_3/SiO_2$	323 K	0 to −600	25; 32	This work
	373 K	−600 to −900	22–33	This work
$(Bu^tN{=})V(OBu^t)Np_2/SiO_2$	323 K	−700 to −900	24.6; 30	This work

[a] In C_6D_6. V–CH_2 was not observed probably due to a coupling with vanadium.

groups, was hardly affected (Fig. 1a,b) showing that the complex was mainly physisorbed on the silica surface. When another amount of I was sublimed and the system was heated at 323 K for 2 h, the band at 3747 cm^{-1} disappeared (Fig. 1c) and neopentane was observed in the gas phase (spectrum not shown)[1]. After heating from 373 up to 473 K (Fig. 1d,e) a decrease in the intensity of the bands assigned to the organic ligands was observed while the intensity of a group of bands at 3400–3200 cm^{-1} was significantly increased. These bands can be ascribed to $\nu_{(NH)}$ of an amine ligand; the corresponding $\delta_{(NH)}$ vibration appeared at 1577 cm^{-1}. These assignments were confirmed using a deuterated silica. The bands at 3400–3200 cm^{-1} were replaced by new ones at 2475 and 2399 cm^{-1}, corresponding to $\nu_{(ND)}$ vibrations, in agreement with an isotopic exchange, while a band expected at 1163 cm^{-1} ($\delta_{(ND)}$) could not be detected due to the restrictions imposed by the presence of silica. The band at 1577 cm^{-1} was no longer present.

In the case of **II**/silica, the reaction seemed to proceed in the same way as **I**/silica: heating at 323 K led both to the detection of neopentane in the gas phase and to the consumption of the isolated OH groups of silica.

3.2. MAS NMR and ESR studies

The ^{13}C CP MAS NMR spectrum of I/silica after thermal treatment at 323 K showed two broad resonances at δ 25 and 32, in contrast with the three resonances observed for **I** in solution (Table 1). After heating at 373 K those resonances were replaced by a broader one in the 22–33 region. The slight shift to higher frequencies observed in the spectrum of **II**/silica must be due to the presence of the *t*-butoxide ligand.

Fig. 2 shows the ^{51}V MAS NMR spectra of **I** and **II**/silica after treatment at 323K. While **II**/silica presents a fine structure spectrum, the spectrum of **I**/silica shows only a very broadened signal spread from δ 0 to − 600, suggesting the formation of reduced vanadium sites. Although rotation in other frequencies should allow for the identification of the true resonance value for the **II**/silica vanadium species, no unambiguous conclusion could be reached. This may be due to the presence of two or more surface species, in agreement with the appearance of at least nine signals, instead of the eight ones expected from a nucleus with $I = 7/2$, leading to a

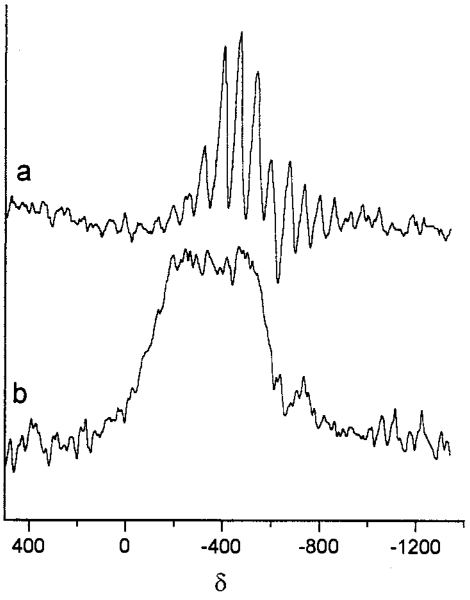

Fig. 2. ^{51}V MAS NMR spectra of $(Bu^tN{=})V(OBu^t)Np_2/silica_{(773)}$ (a) and $(Bu^tN{=})VNp_3/silica_{(773)}$ (b) after heating at 323 K for h. 78.94 MHz, 50.000 accumulations.

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[1] Disappearance of the band at 3747 cm^{-1} was also observed in another experiment when the system was allowed to stand at room temperature (ca. 300 K) for at least 2 h. A common experiment at room temperature usually takes 30 min; within this time there was almost no reaction (Fig. 1a,b). Therefore, in order to ensure a complete reaction, in further experiments the system was heated at 323 K immediately after sublimation.

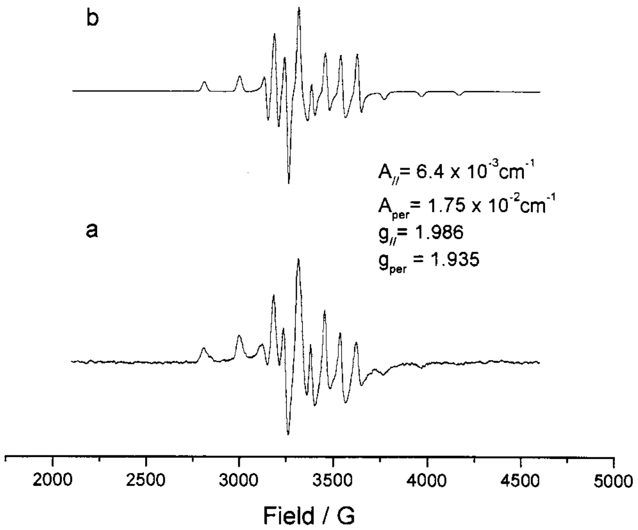


Fig. 3. ESR spectra of (Bu^{t}N=)VNp$_3$/silica$_{(773)}$ after heating at 373 K for 2 h: (a) experimental; (b) simulated.

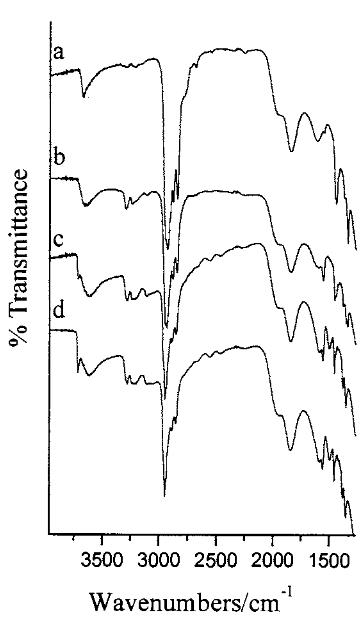


Fig. 4. FT-IR spectra of: (a) (Bu^{t}N=)VNp$_3$/silica$_{(773)}$ after heating at 323 K; (b) a after reaction with hydrogen (ca. 88 kPa), at room temperature, for 7 h; (c) b after heating at 373 K for 15 h under hydrogen (ca. 88 kPa); (d) c after heating at 423 K for 16 h under hydrogen (ca. 88 kPa).

more complicated spectrum. The formation of reduced vanadium sites upon reaction between **I** and silica was confirmed by ESR experiments, which revealed the presence of vanadium(IV) species (Fig. 3a). The spectrum was simulated assuming an axial symmetry of the vanadium species (Fig. 3b), giving a reasonable agreement with the experimental spectrum when the number and position of lines are considered. However, the experimental relative intensities of the lines are quite different, suggesting the presence of several vanadium(IV) species in slightly different adsorption sites on the surface.

3.3. Monitoring of the surface reaction

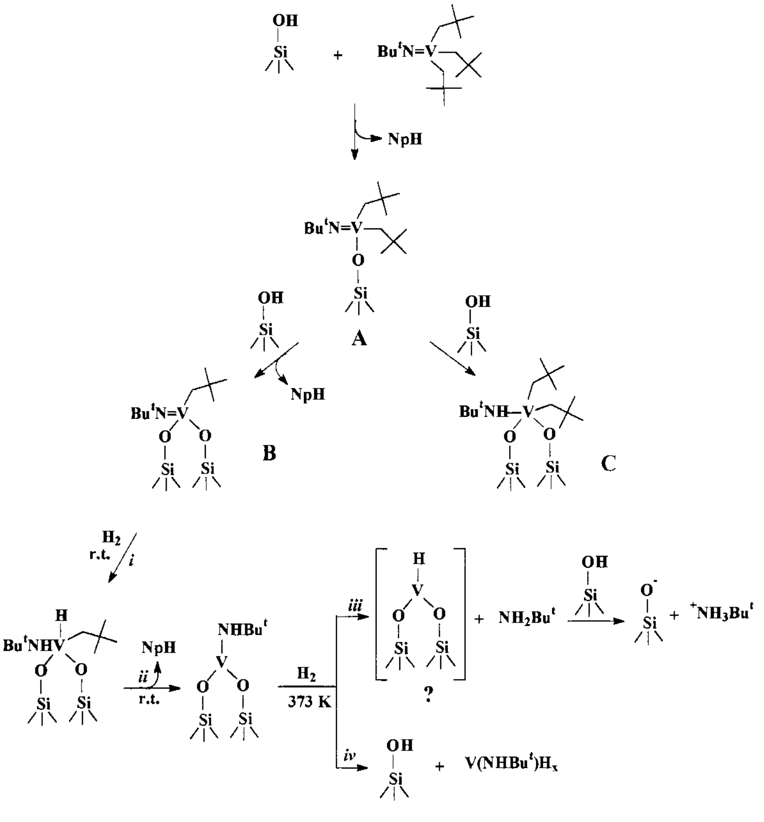
Using larger amounts of I and silica, the neopentane released during the surface reaction upon heating at different temperatures was quantified through GC analyses. When the system was heated at 323, 373 and 423 K [Np]/[V] molar ratios were determined to be 1.6, 2.0 and 1.9, respectively (average of two to four measurements, with an error of ca. 3%). At 423 K isobutylene was also observed ([isobutylene]/[V] ca. 0.1). Although the neopentane given off during the reaction of **II** with silica was not quantified, the release of ^{t}butyl alcohol was never observed.

3.4. Chemical reactivity

The neopentane released during the thermal treatment could originate either from an attack of ≡SiOH groups to the V–C bond or from an α-H abstraction involving two neopentyl ligands, in which case a neopentylidene ligand would be formed. In order to verify whether such a ligand was present, **I**/silica pre-treated at 323 and 373 K was allowed to react with simple alkenes, viz. hex-1-ene and *cis*-pent-2-ene at room temperature. For both thermal treatments no metathesis exchange product was observed in the gas phase. A strained cyclic alkene (norbornene), which easily undergoes ring opening metathesis polymerization, was also allowed to react with the solid, but no consumption of the monomer could be detected. A pseudo-Wittig reaction with acetone also failed to give the expected product, ruling out the formation of an alkylidene ligand.

3.5. Reactivity of *I*/*SiO$_2$* towards hydrogen

When a disk of **I**/SiO$_2$, pretreated at 323 or 373 K, was allowed to react with hydrogen (ca. 88 kPa, 7 h) at room temperature, the resulting infrared spectrum showed an increase in the intensity of the bands assigned to $\nu_{(NH)}$ and $\delta_{(NH)}$ bands (Fig. 4b). At the same time, the intensity of the bands in the 3000–2800 and 1480–1300 cm^{-1} regions was decreased, while neopentane was observed in the gas phase (spectrum not shown). After heating at 373 K for 15 h (ca. 88 kPa), two new bands appeared, at 1611 and 1522 cm^{-1} (Fig. 4c), region where $\nu_{(VH)}$ vibrations are expected [12,13]. Simultaneously, a weak band at 3747 cm^{-1}, assigned to isolated silanol groups, reappeared. The intensity of this band increased with further heating under hydrogen (Fig. 4d). In parallel experiments, using greater amounts of **I**/SiO$_2$, we could verify that the restoration of the isolated ≡SiOH groups was related to a decrease of the vanadium concentration (ca. 25 wt.%).



Scheme 1.

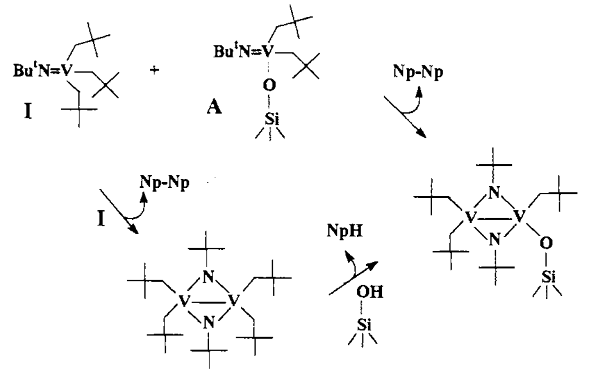
In another series of experiments, after heating at 373 K under hydrogen for 15 h the system was evacuated at the same temperature for 2 h. The band at 1522 cm^{-1} disappeared while the band at 3747 cm^{-1} reappeared. When this system was allowed to react with methyl iodide (ca. 540 kPa) no modification in the intensity of the band at 1611 cm^{-1} could be observed. This band was also not affected by the addition of water (ca. 29 kPa) or ethylene (16 kPa).

4. Discussion

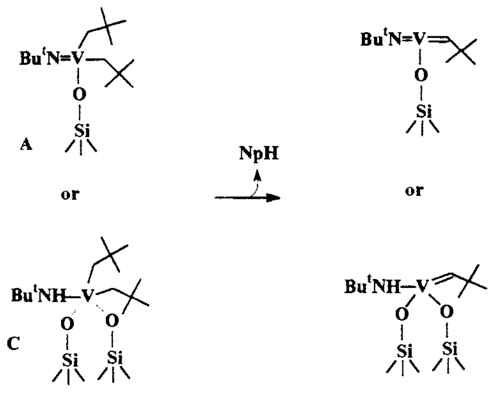
Several kinds of silanol groups have been distinguished on the surface of silica, their concentration being a function of the thermal treatment. Thus, it has been reported that silica Aerosil 200, after evacuation at 773 K has only free silanol groups (1.91 OH nm^{2-}), mainly isolated on the outer surface (1.55 OH nm^{2-}) and characterized by a sharp $\nu_{(OH)}$ band at 3747 cm^{-1}. Minor amounts of free silanols are located in the inner surface (0.34 OH nm^{2-}), some of them being exchangeable by D_2O (0.25 OH nm^{2-}). They appear as a broad $\nu_{(OH)}$ band around 3670 cm^{-1} [14]. Therefore, in this work silica was treated at 773 K overnight in order to ensure a low density of isolated silanol groups allowing for the possibility that each molecule of the vanadium complexes react with only one ≡SiOH group.

In situ FT-IR experiments showed that $(Bu^tN{=})VNp_3$ and $(Bu^tN{=})V(OBu^t)Np_2$ do not react promptly with the surface of $silica_{(773)}$ at room temperature. However, upon heating at 323 K for 2 h both complexes seem to react with silica via an electrophilic attack of the ≡SiOH groups to their neopentyl ligands. In the case of $(Bu^tN{=})VNp_3/SiO_2$, the release of 1.6 mol of neopentane per mol of vanadium suggests the occurrence of the reactions depicted in Scheme 1, where the surface reaction would proceed mostly through the electrophilic attack of one (species **A**, ca. 40%) or two (species **B**, ca. 60%) ≡SiOH groups to the neopentyl ligands of $(Bu^tN{=})VNp_3$. Minor amounts of **C** could also be formed via a 1,2 addition of an ≡SiOH group to the [V]=N bond, in agreement with the presence of weak $\nu_{(NH)}$ and $\delta_{(NH)}$ bands in the corresponding infrared spectrum. The presence of two major species with one or two [V]–O–Si≡ bonds is in agreement with the ^{51}V MAS NMR spectrum of $(Bu^tN{=})V(OBu^t)Np_2/SiO_2$: also in this case the reaction proceeds via the release of neopentane, and the vanadium resonances are shifted to lower frequencies, which is expected when a neopentyl ligand is replaced by an alkoxide or another electron withdrawing ligand (Table 1). Another minor species susceptible to be formed, which would account for the ESR results indicating the presence of vanadium(IV) atoms, is depicted in Scheme 2. Dimerization through reductive elimination of 2,2,5,5-tetramethylhexane has been reported for both **I** and **II** in solution [10] and could take place during the sublimation process. Alternatively, the reduced species could originate from a reaction between **I** and **A**. The proposed species has two vanadium atoms in different coordination spheres, which should lead to different features in their respective ESR spectra. Since the reduced species are always formed in very minor amounts, a better characterization is rather complicated.

When the system is heated at 373 K for 2 h (**I**/SiO_2[373]) the concentration of released neopentane reaches 2.0 mol of neopentane per mol of grafted vanadium. Our first idea was that an α-H abstraction from a neopentyl ligand leading to a neopentylidene ligand might have taken place (Scheme 3). However, the surface species did not present the chemical reactivity characteristic of such a ligand: thus, neither metathetical exchange reactions with alkenes nor a pseudo-Wittig reaction with acetone could be observed for the system, ruling out such a hypothesis. Therefore, the most plausible reaction which could account for the total amount of neopentane given off would be a further eletrophilic attack of ≡SiOH groups from the surface to a neopentyl ligand from species **A**. In this case, at 373 K there would be almost 100% of species **B** on the surface of silica (the reduced vanadium(IV) species seemed not to have been affected by the thermal treatment). Since silica$_{(773)}$ is expected to have a surface hydroxyl concentration around 1.9 OH per nm^2 [14][2], for the amounts of vanadium grafted in all our experiments (1.4–1.7 wt.%) there would be enough OH groups to allow for the formation of only species like **B**.



Scheme 2.



Scheme 3.

When the **I**/SiO_2[373] system (now containing essentially species **B**) was heated at 423 K for 2 h, isobutylene appeared in the gas phase while the concentration of neopentane slightly decreased. Simultaneously, an increase in the intensity of the bands assigned to $\nu_{(NH)}$ and $\delta_{(NH)}$ vibrations was also observed (vide supra and Fig. 1e). These results can be explained by a C–H addition of neopentane to the [V]=N double bond of **B** followed by β-methyl migration and release of isobutylene. The addition of alkanes to [M]=C or [M]=N double bonds is characteristic of d^0 early transition metals, having already been described for Ti, Zr, V, and Ta compounds [7,15–17]. On the other hand, when the **I**/SiO_2[373] system was treated under hydrogen, at room temperature, the changes observed in the infrared spectrum (increase in the intensity of the bands assigned to $\nu_{(NH)}$ and $\delta_{(NH)}$ vibrations; decrease in the intensity of the bands assigned to organic groups), as well as the release of neopentane could be accounted for by the reactions depicted in Scheme 1(i,ii): hydrogen addition to the V=N bond followed by reductive elimination of neopentane. The same sequence of reactions has been proposed in the case of $(\equiv SiO)_2Ta(=CHCMe_3)Np$ [18]. A further heating of the system at 373 K led to the appearance of two bands assignable to $\nu_{(VH)}$ vibrations, suggesting the formation of [V]–H surface species. The disappearance of one of these bands (at 1522 cm^{-1}) upon heating under vacuum at 373 K along with the appearance of the band assigned to isolated ≡SiOH groups and the loss of vanadium from the surface, strongly suggest the hydrogenolysis of [V]–O bonds (Scheme 1, pathway iv). Although hydrogenolysis of [M]–OSi bonds has not been reported for other surface organometallic precursors, in particular the Ta species mentioned above, the presence of the amino ligand (a better π-donor than O-containing ligands) in the coordination sphere of vanadium might favor such a reaction. The band at 1522 cm^{-1} could be due to a $\nu_{(VH)}$ vibration from a physically adsorbed vanadium hydride species, removed under vacuum. On the other hand, if a vanadium hydride surface species were indeed formed, it would be expected to react with methyl iodide with the release of methane. Metal hydrides are highly reactive towards halogenated hydrocarbons, their reaction with methyl iodide being largely used to quantify the amounts of

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[2] According to DEGUSSA's technical note: 2 OH nm^{-2}, as determined by titration with $LiAlH_4$.

surface hydride species [2b,c,18–21]. However, our system not only failed to react with methyl iodide but was also inert towards water and ethylene. Therefore, if a surface vanadium hydride species were indeed formed, its lack of reactivity would be rather surprising. Another explanation for the features in the FT-IR spectra of B upon heating under hydrogen would be the formation of ionic species (Scheme 1, pathway iii): the band at 1611 cm^{-1} could also be ascribed to the asymmetric angular deformation of N–H in $-NH_3^+$ species [22]. The fate of the hydride intermediate, however, is not clear.

5. Conclusions

When $(Bu^tN{=})VNp_3$ is allowed to react, at 373 K under vacuum, with a silica previously dehydroxylated at 773 K, $(\equiv SiO)_2V({=}NBu^t)Np$ (B) appears to be the major surface species. In very minor amounts, $(\equiv SiO)_2(Bu^tNH)VNp_2$ and a reduced vanadium(IV) species seem also to be formed. Species B reacts with neopentane, at 423 K, via a C–H addition to the V=N bond. Heating of B under hydrogen does not lead to surface vanadium hydride species but, presumably, both to hydrogenolysis of ≡SiO–V bonds and elimination of NH_2Bu^t, followed by formation of ionic surface species, $[\equiv SiO]^-[Bu^tNH_3]^+$. It can also be concluded that an imido ligand should be avoided when the goal is the preparation of an alkylidene and/or a hydride surface species.

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