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Synthesis and Structural Characterization of Non-Homoleptic Carbamato Complexes of V(V) and W(VI), and Their Facile Implantation on Silica Surfaces

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Abstract:	The vanadium(V) amido-carbamato derivatives VO(NR ₂)(O ₂ CNR ₂) ₂ (R = Me, 1; Et, 2) were obtained by reaction of VOCl ₃ with preformed carbamato species (ammonium or sodium carbamates). Mixed W(VI) chlorido-carbamato compounds, 4-5, were obtained by reaction of WOCl ₄ with stoichiometric amounts of sodium diethylcarbamate. All the products were characterized by analytical and spectroscopic (IR, multinuclear NMR) methods, and by X-ray diffraction in the case of 4. DFT calculations were useful to elucidate the structures of the compounds and to give insight into the various reaction pathways. The combination of 2 or 5 with amorphous silica gave solid materials which were characterized by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Energy Dispersive X-ray Spectroscopy (EDS) coupled to Scanning Electron Microscopy (SEM).
Author Comments:	To the Editor

	<p>Eur. J. Inorg. Chem.</p> <p>Pisa, 2017 October 25th Dear Editor, please find uploaded the manuscript:</p> <p>"Synthesis and Structural Characterization of Non-Homoleptic Carbamato Complexes of V(V) and W(VI), and Their Facile Implantation on Silica Surfaces"</p> <p>by G. Bresciani, M. Bortoluzzi, S. Zacchini, A. Gabbani, F. Pineider, F. Marchetti and G. Pampaloni</p> <p>that we would like to be considered for publication in European Journal of Inorganic Chemistry as a Paper.</p> <p>Metal-carbamato complexes constitute an interesting class of compounds exhibiting interesting features. Although synthetic pathways to homoleptic carbamates are well established, the synthesis of mixed systems containing additional ligands is not trivial. This is especially true for what concerns high valent transition metals, usually manifesting high reactivity and moisture sensitivity. Herein, we report on the preparation of novel and stable vanadium and tungsten carbamato compounds, containing additional oxido, halido and/or amido ligands. All the products, being highly moisture sensitive, have been fully characterized by elemental analysis, IR and multinuclear NMR spectroscopy, and single crystal X-ray diffraction. Furthermore, DFT calculations have been carried out to give insight into structural and mechanistic aspects. Finally, we demonstrate that a selection of new compounds can be easily implanted on amorphous silica: the ICP-OES/EDS/TEM characterization of the resulting materials is discussed.</p> <p>With my best regards,</p> <p>Guido Pampaloni</p>
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Synthesis and Structural Characterization of Non-Homoleptic Carbamate Complexes of V(V) and W(VI), and Their Facile Implantation on Silica Surfaces

Giulio Bresciani,^[a,b] Marco Bortoluzzi,^[b,c] Stefano Zacchini,^[b,d] Alessio Gabbani,^[a] Francesco Pineider,^[a,b] Fabio Marchetti ^{§,[a,b]} and Guido Pampaloni ^{*,[a,b]}

Keywords: Vanadium, tungsten, amido derivatives, carbamate derivatives, X-ray structures, DFT calculations

The vanadium(V) amido-carbamato derivatives VO(NR₂)(O₂CNR₂)₂ (R = Me, **1**; Et, **2**) were obtained by reaction of VOCl₃ with preformed carbamate species (ammonium or sodium carbamates). Mixed W(VI) chlorido-carbamato compounds, **4-5**, were obtained by reaction of WOCl₄ with stoichiometric amounts of sodium diethylcarbamate. All the products were characterized by analytical and spectroscopic (IR, multinuclear NMR) methods, and by X-ray diffraction in the case of **4**. DFT calculations were useful to elucidate the structures of the compounds and to give insight into

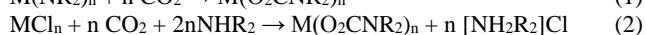
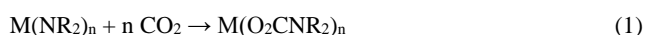
the various reaction pathways. The combination of **2** or **5** with amorphous silica gave solid materials which were characterized by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Energy Dispersive X-ray Spectroscopy (EDS) coupled to Scanning Electron Microscopy (SEM).

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Introduction

The possibility to use carbon dioxide as a cheap, abundant and non-toxic C1 synthon is one of the most appealing goals of modern synthetic chemistry.¹

Dialkylamides of general formula M(NR₂)_n, containing the central metal atom in its maximum oxidation state (d⁰ electronic configuration), are known to react in solution with CO₂ yielding homoleptic carbamate complexes (Eq. 1).² A more convenient synthetic route starting from easily available metal chlorides was proposed in 1978 (Eq. 2).³



Metal-carbamato species are interesting materials that have investigated as suitable precursors for chemical vapour deposition processes,⁴ and in homogeneous catalysis.⁵ More in detail, *N,N*-diisopropylcarbamato complexes of Ru(II) have been found to promote the H₂-hydrogenation of alkenes,⁶ while homoleptic carbamates of group 4 and group 5 transition metals have been proposed as catalytic precursors for the polymerization reactions of

cyclic esters, other than alkenes.⁷

There is a current interest in expanding the family of metal-carbamato complexes to mixed systems, i.e. metal compounds containing additional ligands of different type. For instance, it has been demonstrated that mixed metal halide-carbamates may exhibit better activities in catalytic processes, compared to the corresponding homoleptic carbamates.⁸

A number of non-homoleptic carbamates of middle to late transition metals, containing additional alkyl, phosphine and carbonyl ligands, have been synthesized by different synthetic approaches.⁹ On the other hand, well defined synthetic protocols giving access to mixed halide-carbamates or amide/carbamates are significantly more rare.¹⁰ This is true in particular for high valent, early transition compounds, due to their high reactivity associated to the high oxidation state of the metal centre and the generally observed moisture sensitivity. In the framework of our research on the coordination chemistry of early transition metal compounds,¹¹ we recently reported the straightforward preparation and some preliminary reactivity of mixed halide-carbamates of group 4 metals.¹²

With the aim of individuating possible synthetic pathways to new metal carbamate complexes, we moved to carry out a synthetic study on high valent vanadium and tungsten complexes. Herein, we describe the results of this work, leading to the preparation of mixed amido-carbamato and chlorido-carbamato complexes. X-ray diffraction methods and DFT calculations have been used in several cases to elucidate structural and mechanistic aspects. The implantation of two of the new compounds on silica, facilitated by the disruption of the carbamate frame,¹³ will be described, including the solid state characterization of the obtained materials.

Results and Discussion

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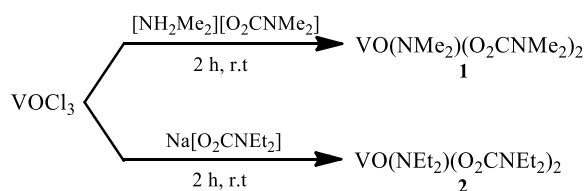
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In order to follow a feasible route recently adopted for the synthesis of mixed fluoro-alkoxido¹⁴ and mixed fluoro-azido¹⁵ complexes, the reactions of VOF₃ with Me₃SiNR₂ (R = Me, Et) were performed. We could not identify any product from these reactions, and intractable oils were obtained when we treated the reaction mixtures with CO₂ (the ¹³C NMR spectra displayed in every case several resonances in the carbonyl region).

Otherwise, the thermally unstable vanadium(V) mixed amido/carbamato **1** was isolated in satisfactory yield from the reaction of [NH₂Me₂][O₂CNMe₂] with VOCl₃ in 3:1 molar ratio (Scheme 1).

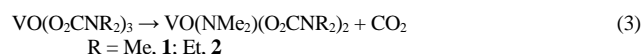
The ethyl substituted derivative **2** was obtained by using the sodium salt Na(O₂CNEt₂), produced from the reaction of NaH with NHEt₂ in the presence of CO₂ at atmospheric pressure.¹⁶ Such sodium salt is a room temperature stable solid, easy to handle, and therefore preferable to the ammonium analogue which, in turn, must be prepared in situ.¹⁷



Scheme 1. Reactions of VOCl₃ with *N,N*-dialkylcarbamato salts.

Compounds **1** and **2** were characterized by analytical and spectroscopic methods. They are very sensitive to moisture and not stable in chlorinated hydrocarbon solutions over prolonged times (the NMR spectra were recorded quickly after the dissolution in CDCl₃). It is evident from the ¹H and ¹³C NMR spectra of **1-2** that the alkyl groups of the amido ligand are not equivalent due to hindered rotation around the metal centre.

It is interesting to note that the reaction analogous to that described in Scheme 1 but performed on NbOCl₃ has a different outcome, NbO(O₂CNR₂)₃ being obtained as a dinuclear compound containing an heptacoordinated niobium centre.¹⁸ The smaller vanadium (V) ion, compared to niobium(V), presumably makes the heptacoordinated species prone to the decomposition of one carbamato unit, leading to a hexacoordinated vanadium product, Eq. 3.



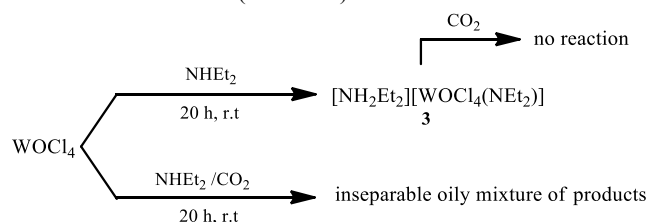
The reaction affording **1-2** has been modelled by DFT calculations. The DFT-optimized structure for R = Me, depicted in Figure 1, shows a distorted tetrahedral arrangement of the ligands. An additional long V...O interaction (V–O5 2.409 Å) *trans* to V=O is hypothesized. The subsequent reaction leading to the amido/carbamato (Eq. 3) is thermodynamically viable ($\Delta H = -4.8$ kcal mol⁻¹).

Figure 1 about here, double column

It is likely that the elimination of CO₂ is preceded by the coordination of one [O₂CNMe₂]⁻ ligand through the nitrogen atom. Such an intermediate has been computationally optimized and it is depicted in Figure 1. As observable, one ligand has κ²-*N,O* coordination mode. The relative energy of this species is only 4.4 kcal mol⁻¹ higher than that of the starting species. The DFT-optimized geometry of the product **1** is a distorted square pyramidal (Figure 1), with the amido and the [O₂CNMe₂]⁻ ligands (one κ¹, the other one κ²*O,O*-coordinated) occupying basal sites. As in VO(O₂CNR₂)₃, a weak V...O interaction (V–O5 2.375 Å) *trans* to V=O is present.

To obtain W(VI) carbamates, we planned to follow the general route starting from the chlorido precursor WOCl₄, allowing this to react with NHEt₂ and then with CO₂. A prompt reaction occurred upon NHEt₂ addition but, surprisingly, the resulting mixture did not absorb CO₂. After work up, the crystalline compound

[NH₂Et₂][WOCl₄(NEt₂)], **3**, could be isolated in good yield. It was characterized by analytical and spectroscopic methods, and by X-ray diffraction. As expected, **3**, once isolated, was unreactive towards carbon dioxide (Scheme 2).



Scheme 2. Reaction of WOCl₄ with NHEt₂/CO₂.

The alternative approach to prepare the carbamate complex, *i.e.* from NHEt₂/CO₂ followed by the addition of WOCl₄, afforded an oily mixture which was not investigated further. The ¹H and ¹³C spectra of the mixture showed many signals, some of them very broad. All the attempts to separate any product by fractional crystallization invariably led to the isolation of **3** (probably the most stable species in the mixture).

The crystal structure of [NH₂Et₂][WOCl₄(NEt₂)], **3**, is composed of discrete [NH₂Et₂]⁺ cations and [WOCl₄(NEt₂)]⁻ anions (Figure 2 and Table 1). The latter anion is a distorted octahedral W(VI) complex, containing one oxido and one amido NEt₂ ligand in *cis* position, as well as four chloride ligands. The W(1)–O(1) [1.703(2) Å] interaction is typical for a W=O double bond¹⁹ and shows a strong *trans* effect. Thus, the *trans* W(1)–Cl(3) bond [2.5766(7) Å] is considerably elongated compared to W(1)–Cl(1) [2.3709(7) Å] and W(1)–Cl(2) [2.3603(7) Å], which are in mutual *trans* position. W(1)–Cl(4) [2.4302(7) Å] displays an intermediate value, suggesting that the NEt₂ amido group exerts a *trans* effect smaller than the oxido-ligand, but greater than a chlorido one. Some intermolecular H-bonds are present involving the chlorido ligands of the anion and the NH₂ group of the cation.

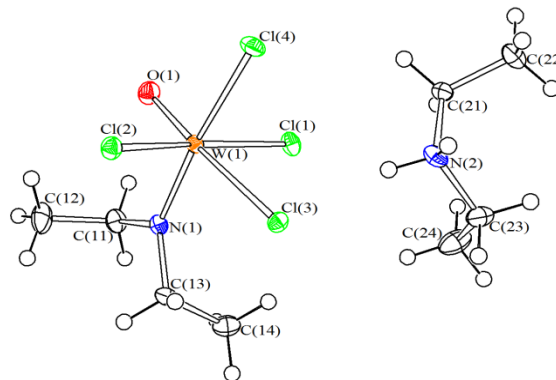
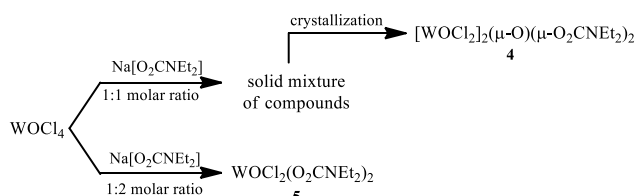


Figure 2. View of [NH₂Et₂][WOCl₄(NEt₂)], **3** with key atoms labelled. Displacement ellipsoids are at the 50% probability level.

Table 1. Selected bond distances (Å) and angles (°) for **3**.

W(1)–O(1)	1.703(2)	W(1)–N(1)	1.920(2)
W(1)–Cl(1)	2.3709(7)	W(1)–Cl(2)	2.3603(7)
W(1)–Cl(3)	2.5766(7)	W(1)–Cl(4)	2.4302(7)
N(1)–C(11)	1.495(4)	N(1)–C(13)	1.485(4)
N(2)–C(21)	1.492(3)	N(2)–C(23)	1.492(4)
O(1)–W(1)–Cl(3)	176.16(7)	Cl(1)–W(1)–Cl(2)	165.01(2)
Cl(4)–W(1)–N(1)	171.54(7)	O(1)–W(1)–N(1)	94.22(10)
W(1)–N(1)–C(11)	121.94(19)	W(1)–N(1)–C(13)	128.01(19)
C(11)–N(1)–C(13)	110.0(2)	C(21)–N(2)–C(23)	116.7(2)

The reaction between preformed NaO₂CNEt₂ and WOCl₄ in 1:1 molar ratio was not selective; a solid mixture of products being obtained. Crystallization of the raw material from CH₂Cl₂/pentane afforded crystals of [WOCl₂]₂(μ-O)(μ-O₂CNEt₂)₂, **4** (Scheme 3), which were characterized analytically, spectroscopically and by X-ray diffraction.

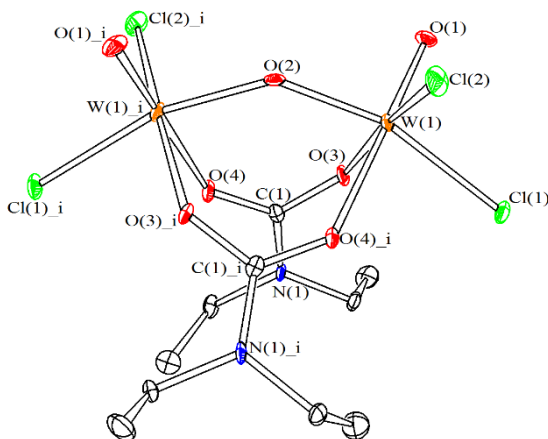


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Scheme 3. Reactions of WOCl_4 with $\text{NaO}_2\text{CNEt}_2$.

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The molecular structure of **4** is represented in Figure 3, whereas the most relevant bond distances and angles are reported in Table 2. The molecule is located on a crystallographic 2-fold axis, resulting in a symmetric dimer. This is composed of two identical W(VI) octahedral moieties containing three terminal (one oxido and two chlorido) and three bridging (one oxido and two O_2CNEt_2 groups) ligands. The terminal W(1)–O(1) interaction [1.691(5) Å] possesses a very strong π -character, which makes the *trans* W(1)–O(4)_i bond [2.171(5) Å] shorter than W(1)–O(3) [1.971(5) Å]. As a result, the bridging carbamate ligands are not symmetrically bonded, as also evidenced by C(1)–O(3) [1.306(9) Å] being longer than C(1)–O(4) [1.266(9) Å]. Conversely, the W–O(2)–W bridge is perfectly symmetric [W(1)–O(2) 1.891(2) Å].



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Figure 3. View of $[\text{WOCl}_2]_2(\mu\text{-O})(\mu\text{-O}_2\text{CNEt}_2)_2$, **4** with key atoms labelled. Displacement ellipsoids are at the 50% probability level. H-atoms have been omitted for clarity.

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Table 2. Selected bond distances (Å) and angles (°) for **4**.

W(1)–O(1)	1.691(5)	W(1)–O(2)	1.891(2)
W(1)–O(3)	1.971(5)	W(1)–O(4) _i	2.171(5)
W(1)–Cl(1)	2.3199(18)	W(1)–Cl(2)	2.2920(19)
C(1)–O(3)	1.306(9)	C(1)–O(4)	1.266(9)
C(1)–N(1)	1.309(10)		
Cl(1)–W(1)–O(2)	162.9(2)	Cl(2)–W(1)–O(3)	167.29(16)
O(1)–W(1)–O(4) _i	177.7(2)	W(1)–O(2)–W(1) _i	143.4(4)
W(1)–O(3)–C(1)	131.2(5)	O(3)–C(1)–O(4)	122.0(7)
C(1)–O(4)–W(1) _i	137.3(5)	O(3)–C(1)–N(1)	117.6(7)
O(4)–C(1)–N(1)	120.4(7)		

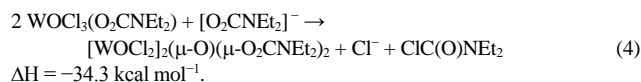
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By comparison of NMR spectra, we observed that **4** was contained in the mixture obtained from $\text{NaO}_2\text{CNEt}_2$ and WOCl_4 (1:1 molar ratio). On the other hand, the mononuclear compound $\text{WOCl}_2(\text{O}_2\text{CNEt}_2)_2$, **5**, was isolated in high yields when WOCl_4 and $\text{NaO}_2\text{CNEt}_2$ were mixed in a 1:2 molar ratio in dichloromethane at room temperature (Scheme 3).

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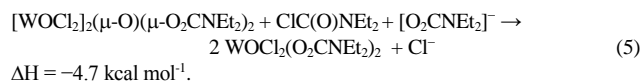
DFT calculations were used to find out a plausible mechanism leading to **4**. The reaction probably starts with the formation of $\text{WOCl}_3(\text{O}_2\text{CNEt})$, whose DFT-optimized structure is depicted in Figure 4. The geometry of this species is distorted square pyramidal, with the oxido ligand in apical position. The $[\text{O}_2\text{CNEt}]^-$ ligand exhibits $\kappa^1\text{O}$ coordination mode, although a long $\text{W}\cdots\text{O}$ interaction ($\text{W}\cdots\text{O}3$ 2.291 Å) *trans* to $\text{W}=\text{O}$ is present. The formation of the dinuclear compound **4**, *i.e.*, the source of the μ -

oxido ligand, could be ascribed either to water traces or to the possible combination of $\text{WOCl}_3(\text{O}_2\text{CNEt})$ with uncoordinated $[\text{O}_2\text{CNEt}]^-$, see Eq. 4. We performed NMR experiments to clarify this point, but they revealed not conclusive.



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Although the chlorido/carbamato exchange reaction of WOCl_4 with an excess of ligand appears the simplest way to **5**, its formation by reaction of **4** with ClC(O)NEt_2 cannot be ruled out, on considering the enthalpy variation for the reaction reported in Eq. 5.



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The most stable DFT-optimized structure of **5** (Figure 4) shows a distorted pentagonal bipyramidal geometry, with one chlorido ligand and two $[\kappa^2\text{O},\text{O}-\text{O}_2\text{CNEt}_2]^-$ anions in equatorial position and the other chlorido and the oxido-ligand in apical position.

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Figure 4 about here, double column

Reactions of $\text{VO}(\text{NEt}_2)(\text{O}_2\text{CNEt}_2)_2$, **2**, and $\text{WOCl}_2(\text{O}_2\text{CNEt}_2)_2$, **5**, with amorphous silica.

It has been shown that cationic implantation on silica can be effectively carried out with Group 4 metals,²⁰ niobium and tantalum,²¹ tin(IV),²² palladium(II),²³ platinum(II),²⁴ gold(I),²⁵ copper(II)²⁶ and lanthanides,²⁷ by using *N,N*-dialkylcarbamato complexes of general formula $\text{M}(\text{O}_2\text{CNR}_2)_n$ as precursors.

This method is based on the reaction of *N,N*-dialkylcarbamato complexes, generally soluble in organic solvents, with proton-active substances of even moderate acidity, such as the silanol groups on a silica surface. The grafting reaction is completely shifted to the products due to the release of carbon dioxide. Equation (6) represents such a grafting reaction of a homoleptic transition metal *N,N*-dialkylcarbamate $\text{M}(\text{O}_2\text{CNR}_2)_n$, whereby a $\equiv\text{SiO-M}$ bond is formed on the silica surface.



Mixtures of grafted species can be obtained by using non-homoleptic metal carbamates such as $\text{TiCp}^\#_2(\text{O}_2\text{CNR}_2)$, $\text{Cp}^\# = \text{C}_5\text{H}_5$, C_5Me_5 .²⁰

Due to the availability of the first examples of vanadium(V) amidocarbamate and tungsten(VI) chlorocarbamate derivatives, we decided to examine the reactivity of **2** and **5** with amorphous silica.

Fast reactions were observed with change of colour of the toluene suspensions from colourless to pale red-brown or pale green, according to the nature of the metal reactant. The moisture sensitive solids (named **Si-2** and **Si-5**) were characterized using two different techniques: ICP-OES and Energy Dispersive X-ray Spectroscopy (EDS) coupled to Scanning Electron Microscopy (SEM). The former technique gives information on the average metal and silicon content of the bulk sample, while SEM/EDS allows to perform microanalysis on selected areas of the sample and thus to check its homogeneity.

The metal-to-silicon atomic ratio determined by EDS on a relatively large area of the sample of **Si-5** (magnification of 400x) was consistent with the ICP-OES value; instead slightly different values were detected for **Si-2** by the two techniques (see Table 3). The metal-to-silicon atomic ratio was comparable for the samples of the two products, suggesting that the distinct reactions of **2** and **5** with silica resulted in the loading of comparable amounts of metal. A representative SEM image of **Si-2** is reported in Figure 5. The corresponding image of **Si-5** is provided as Supporting Information (Figure S1).

SEM images of the functionalized silica powders show that both the samples contain a small amount of aggregates that are brighter in contrast. These brighter regions are richer in metal content, as confirmed by EDS analysis in the selected areas. The metal-rich aggregates can arise from a small amount of unreacted metal complex which has not been removed during the work up procedure. Since the metal-to-silicon ratios obtained with EDS analysis on a large area of the samples substantially match the respective ICP-OES values, we can reasonably assume that these brighter regions are statistically negligible over the whole sample. Regarding **Si-5**, EDS analysis revealed the presence of a measurable amount of chlorine atoms, suggesting that metal grafting to the silica surface may take place with loss of both carbamate and chloride ligands. Blank experiments confirmed the absence of chlorine in the pure silica powders.

Table 3. Metal/silicon and metal/chloride atomic ratios related to **Si-2** and **Si-5**, determined by ICP-OES and EDS.

	M/Si (ICP)	M/Si (EDS) (Atomic ratio)	M/Cl(EDS)
Si-4	0.030	0.022	---
Si-7	0.027	0.027	0.69

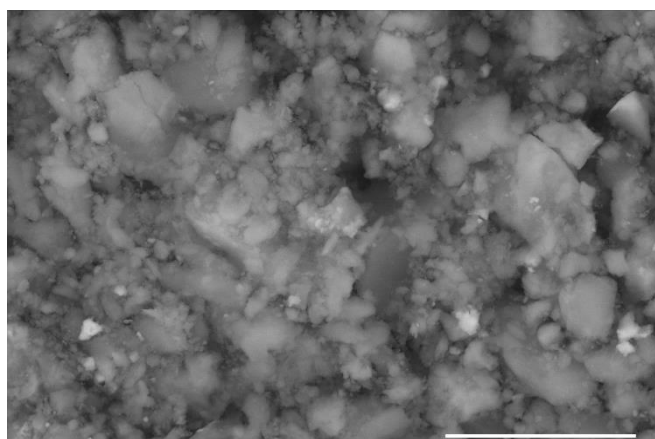


Figure 5. A representative SEM image of **Si-2**. The scale bar is 20 μm .

Conclusions

An explorative study has led us to find new synthetic routes to access stable (under strictly inert atmosphere) non homoleptic carbamates of high valent vanadium and tungsten, containing additional oxido, chloride and/or amido ligands, according to the cases.

The synthesis of group 5 metal carbamates can be better achieved in one pot, using the appropriate amine and CO_2 as reactants. Indeed both $\text{VO}(\text{NMe}_2)(\text{O}_2\text{CNMe}_2)_2$ (from VOCl_3) and $\text{NbO}(\text{O}_2\text{CNR}_2)_3$ (from NbOCl_3 ¹⁸) have been obtained with this strategy, the vanadium compound being presumably formed through the intermediacy of the heptacoordinated $\text{VO}(\text{O}_2\text{CNMe}_2)_3$.

On the other hand, $\text{VO}(\text{NEt}_2)(\text{O}_2\text{CNEt}_2)_2$ and mixed W(VI) halido-carbamato have been more conveniently obtained from VOCl_3 or WOCl_4 , respectively, and preformed sodium diethylcarbamate as carbamate transferor. IR and multinuclear NMR spectroscopy, X-ray diffraction and DFT calculations have allowed the proposal of structures and reaction pathways. In principle, the interaction of selected compounds with silica take advantage of the oxophilicity of the high valent metal centre, and the presence of carbamate units as favourable sites for fast linkage, via CO_2 elimination. EDS/SEM analyses of the resulting materials indicate that the grafting reaction could involve also the dissociation of chloride ligands, in accordance with previous findings on analogous systems.^{20,28}

Experimental Section

General Considerations

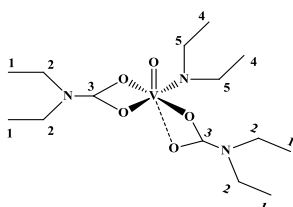
Warning. The metal products reported in this paper are highly moisture-sensitive, thus they were stored in sealed glass tubes under nitrogen or argon once obtained, and rigorously anhydrous conditions were required for the reaction and crystallization procedures. All the operations were carried out under an atmosphere of prepurified argon. The glass reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. Solvents (Sigma Aldrich) and diethylamine (Sigma Aldrich, 99.5%) were distilled from appropriate drying agents before use. NaH (Strem, 60% suspension in mineral oil) was stirred with hexane to remove the oil, recovered by filtration, dried in vacuo at room temperature and stored in sealed glass tubes under nitrogen atmosphere. WOCl_4 was prepared according to literature procedure.²⁹ VOCl_3 (Strem, 99%) were stored under argon atmosphere as received. Commercial silica (Grace, SD 3217/50; surface area, 318 $\text{m}^2 \text{g}^{-1}$; pore volume, 2.22 $\text{cm}^3 \text{g}^{-1}$) was treated at 160 °C for 12 h *in vacuo* (ca. 0.01 mmHg) to eliminate the physisorbed water and then stored in flame-sealed vials under an atmosphere of argon. The total silanol content (3.4 mmol g^{-1}) was assumed to correspond to the weight loss (as water) by calcination at 850 °C. Infrared spectra were recorded at 298 K on a FTIR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. Infrared spectra of liquid compounds were recorded at 298 K on FT-IR Spectrum 100 Perkin Elmer. ^1H , ^{13}C and ^{51}V NMR spectra were recorded at 298 K with a Bruker Avance II DRX 400 spectrometer. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent.

C, H, N analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Volhard method³⁰ on samples prepared by dissolution of the solid in aqueous Na_2CO_3 at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to acidic pH. Vanadium was analyzed by ICP-OES with a ThermoOptekIRIS Advantage Duo instrument.

Synthesis of $\text{VO}(\text{NMe}_2)(\text{O}_2\text{CNMe}_2)_2$, **1.** Operating under CO_2 atmosphere, $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$ (0.6 mL, 4.65 mmol) was added to a solution of VOCl_3 (0.1 mL, 1.06 mmol) in toluene (10 mL) and the resulting mixture was stirred for 2 hours. The solid was removed by filtration and the volatiles were removed from the filtrate. The pale green solid was washed with pentane (2 x 5 ml) and dried in vacuo at room temperature, affording $\text{VO}(\text{NMe}_2)(\text{O}_2\text{CNMe}_2)_2$, **1** (0.192 g, 63% yield) as a green solid sensitive to moisture. Anal. Calc. for $\text{C}_8\text{H}_{18}\text{N}_3\text{O}_5\text{V}$: C, 33.46; H, 6.32; N, 14.63; V, 17.73. Found: C, 33.23; H, 6.08; N, 14.29; V, 17.24. ^1H NMR (CDCl_3) δ = 5.26 (br, 3H, CH_3 amide), 4.34 (br, 3H, CH_3 amide), 3.00 (s, 12H, CH_3 carbamate) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ = 167.1 (C=O), 43.5 (C amide), 35.2 (C amide), 21.6 (C carbamate) ppm. $^{51}\text{V}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) δ = -186 ($\Delta\nu_{1/2}$ = 88 Hz) ppm.

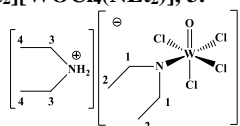
Preparation of sodium carbamate. $\text{Na}(\text{O}_2\text{CNEt}_2)$ was prepared by a slight modification of the procedure reported in literature.¹⁶ A suspension of NaH (2.00 g, 83.3 mmol) in THF (100 mL) was treated with NH_4Et_2 (13 mL, 126 mmol). Hence CO_2 (atmospheric pressure) was introduced into the system. When the absorption had ceased (ca. one hour), a colourless light solid was obtained. The reaction mixture was left stirring for additional 20 h under CO_2 atmosphere. The carbamate was obtained as colourless hygroscopic solid after evaporation of solvent and drying *in vacuo*. Yield: 9.8 g, 84%. IR (solid state): ν = 2967w-m, 2930w, 2901vw, 1574m-s, 1555s, 1483vs, 1421vs, 1375m, 1363w-m, 1306vs, 1226w, 1217w, 1082m, 1070w, 1058w, 966vw, 930w, 823w, 812m-s, 779w.

Synthesis of $\text{VO}(\text{NEt}_2)(\text{O}_2\text{CNEt}_2)_2$, **2.**



VOCl₃ (0.020 mL, 0.21 mmol) was added to a suspension of NaO₂CNEt₂ (0.117 g, 0.84 mmol) in CH₂Cl₂. Immediate gas evolution took place with formation of an orange solution. The reaction mixture was stirred for 18 hours at room temperature. The solid was eliminated by filtration and the filtrate was dried in vacuo at room temperature. A viscous red liquid, identified as VO(NEt₂)(O₂CNEt₂)₂, **2**, was obtained. Yield: 0.067 g, 85%. Anal. Calc. for C₁₄H₃₀N₃O₅V: C, 45.28; H, 8.14; N, 11.31; V, 13.72. Found: C, 45.53; H, 8.48; N, 11.33; V, 13.41. ¹H NMR (CDCl₃) δ = 5.17 (br, 2H, C5H), 4.50 (br, 2H, C5H) 3.30 (q, 8H, C2H), 1.60 (t, 3H, C4H), 1.11 (t, 12H, C1H), 1.05 (t, 3H, C4H) ppm. ¹³C{¹H} NMR (CDCl₃) δ = 166.7 (C3), 66.7 (C5), 56.6 (C5), 40.2 (C2), 17.9 (C4), 15.2 (C4), 13.8 (C1) ppm. ⁵¹V{¹H} NMR (CDCl₃) δ = -184 (Δν_{1/2} = 85 Hz) ppm.

Synthesis of [NH₂Et₂][WOCl₄(NEt₂)], **3**.



Diethylamine (0.14 mL, 1.35 mmol) was added to a suspension of WOCl₄ (0.229 g, 0.67 mmol) in hexane (10 mL). The mixture was stirred for 20 hours and then was added pentane (10 mL). The supernatant liquid was separated from the solid which was dried in vacuo at room temperature affording [NH₂Et₂][WOCl₄(NEt₂)], **3** (0.283 g, 87% yield), as a highly moisture sensitive green solid. Anal. Calc. for C₈H₂₂Cl₄N₂O: C, 19.69; H, 4.54; N, 5.74; Cl, 29.06. Found: C, 19.34; H, 4.61; N, 5.46; Cl, 29.24. ¹H NMR (CDCl₃) δ = 7.08 (br, NH₂), 5.67 (q, 2H, C1H) 5.13 (q, 2H, C1H), 3.31 (br, 4H, C3H), 1.68 (t, 3H, C2H), 1.51 (m, 9H, C2H, C4H) ppm. ¹³C{¹H} NMR (CDCl₃) δ = 62.9 (C1), 50.2 (C1), 43.8 (C3), 16.2 (C2), 11.6 (C2), 10.4 (C4) ppm. Crystals suitable for X-ray analysis were grown from a double layered mixture hexane/THF stored at 243 K for one week.

Reaction of WOCl₄ with NaO₂CNEt₂.

WOCl₄/NaO₂CNEt₂ molar ratio 1:1. A suspension of WOCl₄ (0.110 g, 0.32 mmol) in CH₂Cl₂ was treated with NaO₂CNEt₂ (0.044 g, 0.32 mmol). The reaction mixture was stirred for 18 hours at room temperature, then the solid was recovered by filtration and washed with CH₂Cl₂ (10 mL). The filtrate was evaporated to dryness and the red residue washed with pentane (2 x 10 ml) and dried in vacuo. Yield: 0.070 g. ¹H NMR (CDCl₃) δ = 3.78-3.68 (m, CH₂), 3.53 (m, CH₂), 3.44 (q, CH₂), 3.38-3.29 (m, CH₂), 1.40-1.35 (m, CH₃), 1.32 (t, CH₃), 1.23 (t, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃) δ = 168.1 (C=O), 158.7 (C=O), 47.1 (CH₂), 46.5 (CH₂), 43.7 (CH₂), 43.3 (CH₂), 40.2 (CH₂), 40.0 (CH₂), 13.3 (CH₃), 14.2 (CH₃), 13.5 (CH₂), 13.4 (CH₃), 13.3 (CH₃), 13.2 (CH₃) ppm.

The solid was dissolved in dichloromethane and the solution was layered with pentane. Yellow crystals of W₂O₂Cl₄(μ-O₂CNEt₂)₂(μ-O), **4**, suitable for X-ray analysis formed after one week at 243 K. Anal. Calc. for C₁₀H₂₀Cl₄N₂O₄W₂: C, 16.19; H, 2.72; N, 3.78; Cl, 19.12. Found: C, 16.58; H, 2.51; N, 3.45; Cl, 19.45.

WOCl₄/NaO₂CNEt₂ molar ratio 1:2. Isolation of WOCl₂(O₂CNEt₂)₂, **5.** A suspension of WOCl₄ (0.40 g, 1.17 mmol) in CH₂Cl₂ was treated with solid NaO₂CNEt₂ (0.33 g, 2.37 mmol). The reaction mixture was stirred for 15 hours at room temperature, then the solid was recovered by filtration and washed with CH₂Cl₂ (2 x 5 mL). The filtrate was evaporated to dryness, thus the green residue washed with pentane (2 x 10 ml) and dried in vacuo affording **5** (0.52 g, 88% yield) as a green, highly

moisture sensitive microcrystalline solid. Anal. Calc. for C₁₀H₂₀Cl₂N₂O₅W: C, 23.88; H, 4.01; N, 5.57; Cl, 14.09. Found: C, 23.57; H, 3.87; N, 5.41; Cl, 14.46. IR (solid state): ν = 2965w-m, 1641m (C=O), 1569w-br, 1445vw, 1420w, 1384vw, 1318w, 1258m-s, 1080m-s, 1016s, 967m-s, 849m, 791vs, 762m-s cm⁻¹. ¹H NMR (CDCl₃) δ = 3.53 (m, 2H, CH₂), 1.30 (t, 3H, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃) δ = 168.1 (C=O), 40.0 (CH₂), 39.7 (CH₂), 13.4 (CH₃), 13.3 (CH₃) ppm.

Reaction of VO(NEt₂)(O₂CNEt₂)₂, **2**, and WOCl₂(O₂CNEt₂)₂, **5** with amorphous silica.

a. VO(NEt₂)(O₂CNEt₂)₂: Compound **2** (0.230 mg, 0.62 mmol) was dissolved in 10 mL of toluene and the solution was added to a suspension of silica (0.884 g, OH/M molar ratio = 4,7) in 30 mL of toluene. The mixture was stirred at 25°C for 18 h and then filtered. The pale red brown solid was washed with toluene (3 x 5 mL) and dried in vacuo at room temperature.

b. WOCl₂(O₂CNEt₂)₂. Silica (0.869 mg) was suspended in 40 mL of toluene and added of **5** (0.181 mg, 0.36 mmol, OH/M molar ratio = 8,2). The mixture was stirred at 25°C for 20 h and then filtered. The pale green solid was washed with toluene (2x10 mL) and dried in vacuo for 3h at room temperature.

X-ray crystallography.

Crystal data and collection details for **3** and **4** are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON100 detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).³¹ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F².³² Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Table 4. Crystal data and experimental details for **3** and **4**.

	3	4
Formula	C ₈ H ₂₂ Cl ₄ F ₆ N ₂ O	C ₁₀ H ₂₀ Cl ₄ N ₂ O ₇ W ₂
<i>F</i> _w	487.92	789.78
<i>T</i> , K	100(2)	100(2)
<i>λ</i> , Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> , Å	21.9191(15)	14.6803(11)
<i>b</i> , Å	12.9937(9)	11.8321(9)
<i>c</i> , Å	13.8389(19)	11.9556(9)
<i>α</i> , °	90	90
<i>β</i> , °	126.8420(10)	107.959(2)
<i>γ</i> , °	90	90
Cell Volume, Å ³	3154.3(5)	1975.5(3)
<i>Z</i>	8	4
<i>D</i> _c , g cm ⁻³	2.055	2.655
<i>μ</i> , mm ⁻¹	7.986	12.211
<i>F</i> (000)	1872	1464
Crystal size, mm	0.160×0.130×0.090	0.160×0.140×0.110
<i>θ</i> limits, °	1.950–27.998	2.256–25.999
Reflections collected	23510	12365
Independent reflections	3811 [<i>R</i> _{int} = 0.0340]	1955 [<i>R</i> _{int} = 0.598]
Data / restraints / parameters	3811 / 0 / 145	1955 / 24 / 114
Goodness of fit on <i>F</i> ²	1.089	1.158
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0194	0.0338
<i>wR</i> ₂ (all data)	0.0418	0.0834
Largest diff. peak and hole, e Å ⁻³	1.100 / -1.230	1.243 / -2.297

SEM/EDS

SEM/EDS analysis was performed on a SEM-FEG Quanta 450, with an accelerating voltage of 15 kV. The images were collected using a backscattered electron detector. Si-4 and Si-7 powders were deposited on a conductive tape before the introduction in the high vacuum chamber. EDS analysis was performed with a Quanta XFlash EDS detector to obtain local metal-to-silicon and metal-to-chloride atomic ratios for the two samples.

ICP-OES

ICP-OES analysis of the Silicon, Vanadium and Tungsten content in samples Si-2 and Si-5 was performed with an Ar plasma spectrometer ICP Perkin Elmer Optima 2000 OES DV.

Computational studies

The computational geometry optimizations were carried out without symmetry constrains, using the hybrid-GGA EDF2 functional³³ in combination with the 6-31G** basis set (ECP-based LANL2DZ basis set for elements beyond Kr).³⁴ The “restricted” formalism was always applied. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.³⁵ Further optimization of selected geometries was carried out using the range-separated DFT functional ω B97X,³⁶ in combination with the split-valence polarized basis set of Weigend and Ahlrichs, with ECP for tungsten centres.³⁷ The C-PCM implicit solvation model was added to ω B97X calculations, considering chloroform as continuous medium.³⁸ The software used for C-PCM/ ω B97X calculations was Gaussian 09,³⁹ while EDF2 calculations were performed with Spartan 16.⁴⁰

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Supplementary Material

Cartesian coordinates of all DFT-optimized compounds are collected in a separated .xyz file. CCDC reference numbers 1526866 (3) and 1526867 (4) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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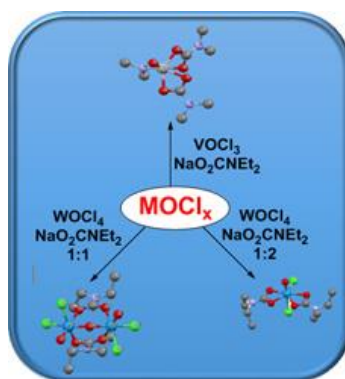
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Carbamato Complexes, Amido complexes, Vanadium, Tungsten

Giulio Bresciani, Marco Bortoluzzi, Stefano Zacchini, Alessio Gabbani, Francesco Pineider, Fabio Marchetti, and Guido Pampaloni

Synthesis and Structural Characterization of Non-Homoleptic Carbamato Complexes of V(V) and W(VI), and Their Facile Implantation on Silica Surfaces

Keywords: Vanadium, Tungsten, Amido derivatives, Carbamato derivatives, DFT calculations



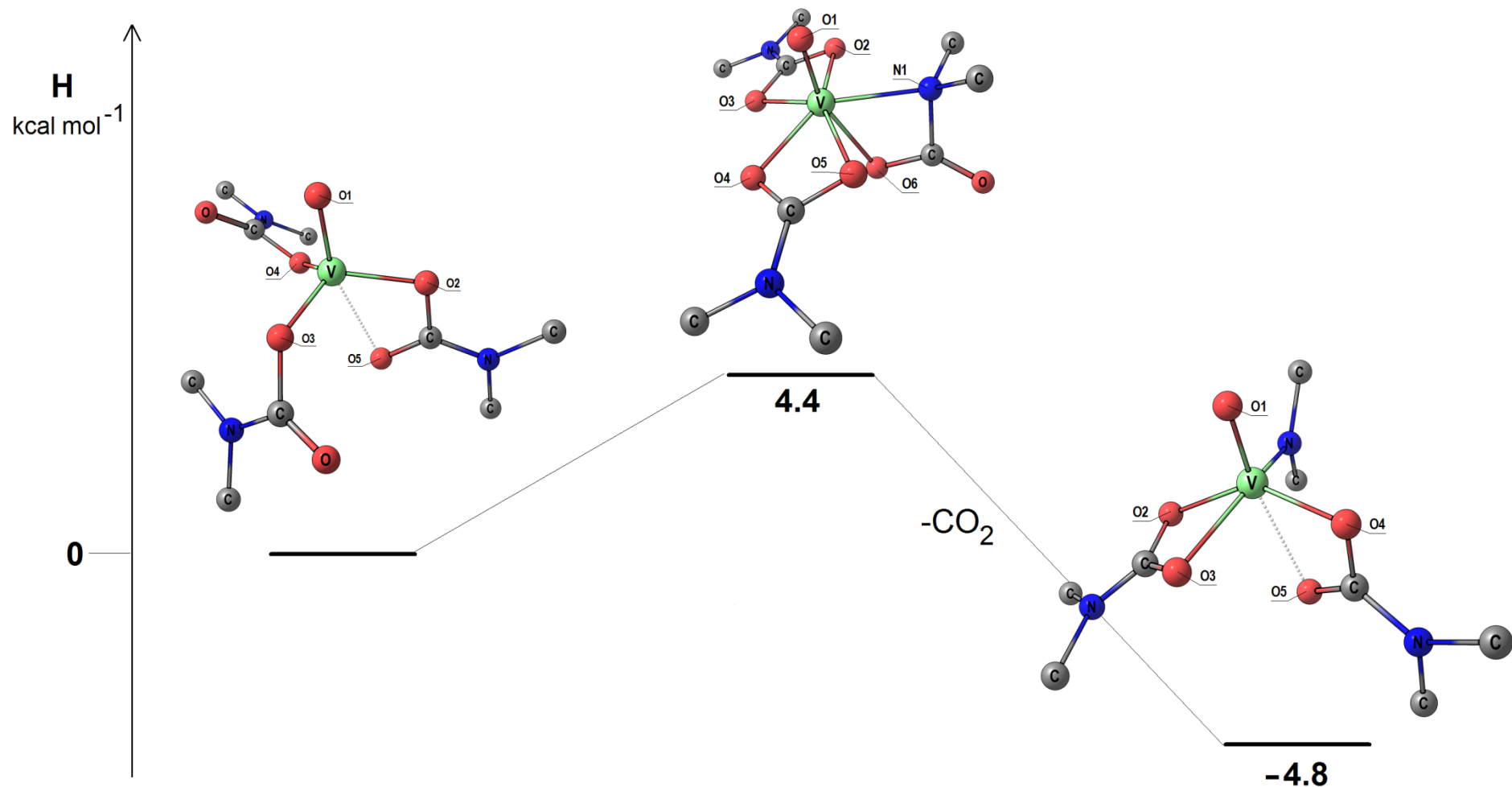


Figure 1. DFT-optimized geometry of $\text{VO}(\kappa^1\text{-O}_2\text{CNMe}_2)_3$, $\text{VO}(\kappa^2\text{-N},\text{O}-\text{O}_2\text{CNMe}_2)(\kappa^2\text{-O},\text{O}-\text{O}_2\text{CNMe}_2)_2$ and $\text{VO}(\text{NMe}_2)(\kappa^1\text{-O}-\text{O}_2\text{CNMe}_2)(\kappa^2\text{-O},\text{O}-\text{O}_2\text{CNMe}_2)_3$ (**1**), together with their relative enthalpy values (C-PCM/ ω B97X calculations). Hydrogen atoms have been omitted for clarity. Selected computed bond lengths (\AA) for $\text{VO}(\kappa^1\text{-O}_2\text{CNMe}_2)_3$: V–O1 1.527, V–O2 1.848, V–O3 1.761, V–O4 1.779, V–O5 2.409. Selected computed angles ($^\circ$) for $\text{VO}(\kappa^1\text{-O}_2\text{CNMe}_2)_3$: O1–V–O2 102.4, O1–V–O3 103.8, O1–V–O4 105.1, O1–V–O5 162.6, O2–V–O3 112.8, O2–V–O4 119.3, O3–V–O4 111.5. Selected computed bond lengths (\AA) for $\text{VO}(\kappa^2\text{-N},\text{O}-\text{O}_2\text{CNMe}_2)(\kappa^2\text{-O},\text{O}-\text{O}_2\text{CNMe}_2)_2$: V–O1 1.532, V–O2 2.054, V–O3 2.001, V–O4 2.001, V–O5 2.087, V–O6 2.130, V–N1 2.180. Selected computed angles ($^\circ$) for $\text{VO}(\kappa^2\text{-N},\text{O}-\text{O}_2\text{CNMe}_2)(\kappa^2\text{-O},\text{O}-\text{O}_2\text{CNMe}_2)_2$: O1–V–O2 94.4, O1–V–O3 103.6, O1–V–O4 102.4, O1–V–O5 92.7, O1–V–O6 159.0, O1–V–N1 96.5, O2–V–O3 63.5, O4–V–O5 63.0, O6–V–N1 62.8. Selected computed bond lengths (\AA) for **1**: V–O1 1.535, V–O2 1.993, V–O3 2.106, V–O4 1.945, V–O5 2.375, V–N1 1.800. Selected computed angles ($^\circ$) for **1**: O1–V–O2 108.4, O1–V–O3 99.5, O1–V–O4 99.9, O1–V–O5 159.4, O1–V–N1 100.5, O2–V–O3 63.6, O2–V–O4 142.7, O2–V–N1 92.6, O3–V–O4 88.4, O3–V–N1 152.8, O4–V–N1 106.0.

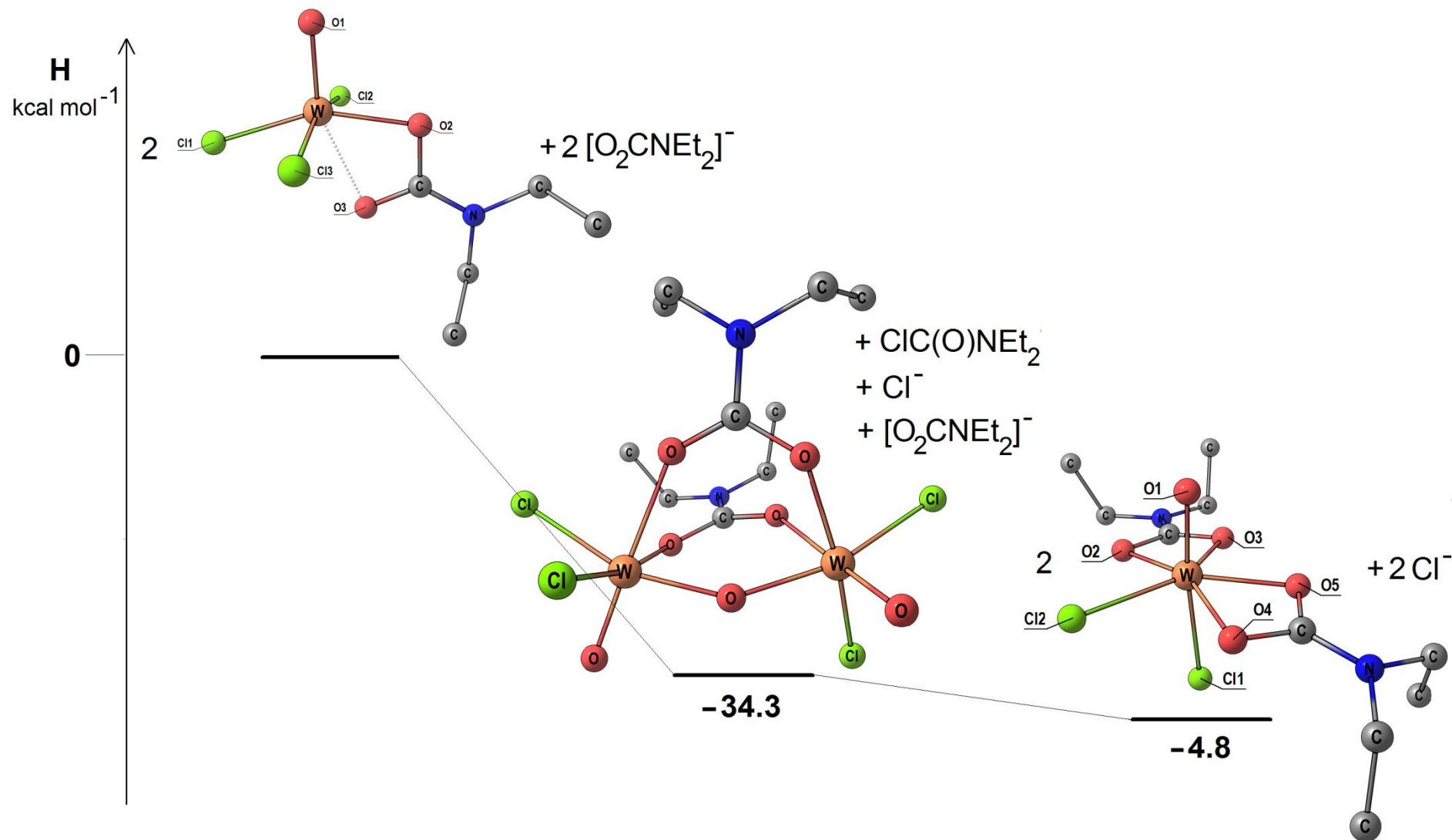


Figure 4. DFT-optimized geometry of $\text{WCl}_3(\text{O}_2\text{CNEt}_2)$, $[\text{WCl}_2]_2(\mu\text{-O})(\mu\text{-O}_2\text{CNEt}_2)_2$ (4) and $\text{WCl}_2(\text{O}_2\text{CNEt}_2)_2$ (5), together with their relative enthalpy values (C-PCM/ ω B97X calculations). Hydrogen atoms have been omitted for clarity. Selected computed bond lengths (\AA) for $\text{WCl}_3(\text{O}_2\text{CNEt}_2)$: W–O1 1.669, W–O2 2.006, W–O3 2.291, W–Cl1 2.298, W–Cl2 2.326, W–Cl3 2.329. Selected computed angles ($^\circ$) for $\text{WCl}_3(\text{O}_2\text{CNEt}_2)$: O1–W–O2 97.3, O1–W–O3 157.5, O1–W–Cl1 107.3, O1–W–Cl2 96.8, O1–W–Cl3 97.3, O2–W–O3 60.2, O2–W–Cl1 155.3, O2–W–Cl2 87.8, O2–W–Cl3 87.4. Selected computed bond lengths (\AA) for 5: W–O1 1.680, W–O2 2.103, W–O3 2.089, W–O4 2.105, W–O5 2.086, W–Cl1 2.500, W–Cl2 2.330. Selected computed angles ($^\circ$) for 5: O1–W–O2 96.2, O1–W–O3 92.3, O1–W–O4 95.9, O1–W–O5 92.5, O1–W–Cl1 173.4, O1–W–Cl2 96.4, Cl2–W–O2 79.8, Cl2–W–O3 141.0, Cl2–W–O4 80.0, Cl2–W–O5 141.1.



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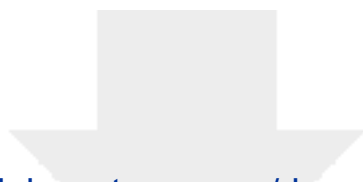
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