



# IMIDO COMPLEXES OF VANADIUM

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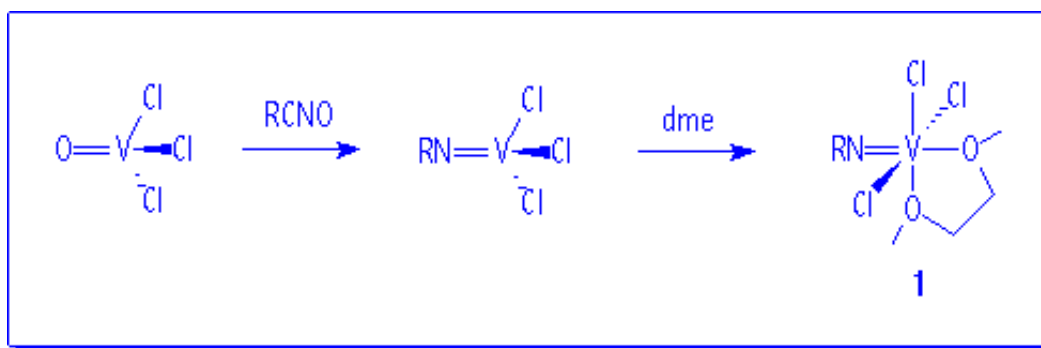
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Imido ligands have been widely used as stabilizing ligands in high-oxidation-state transition metal complexes.<sup>1</sup> Their chemistry has experienced a remarkable growth due to the role they play in many important reactions.

Following our interest in this area, we have extended our recent results<sup>2</sup> in the synthesis of bis(imido) complexes of molybdenum,  $d^0$ -Mo(NR)<sub>2</sub>, to the related  $d^0$  organoimido complexes of vanadium. In this contribution, we describe the synthesis and characterization of several complexes of vanadium containing the imido ligand.

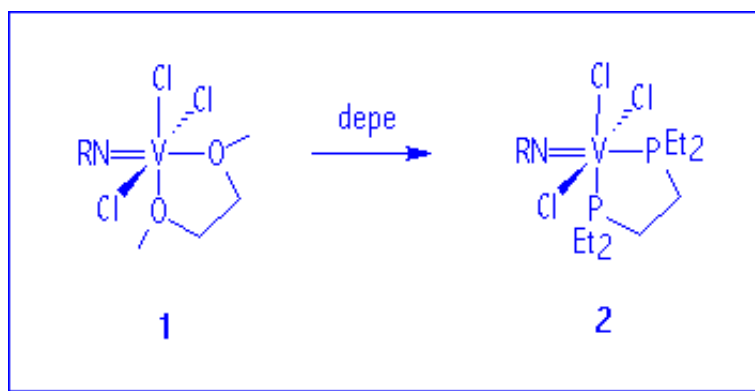
Treatment of VOCl<sub>3</sub> with one equivalent of RCNO in refluxing octane led to V(NR)Cl<sub>3</sub> compounds.<sup>3</sup> The addition of 1,2-dimethoxyethane (dme) to solutions of V(NR)Cl<sub>3</sub> produces the precipitation in a nearly quantitative yield of V(NR)Cl<sub>3</sub>(dme) (R = 2,6-<sup>t</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **1a**; 1-adamantyl, **1b**) as solid materials.



<sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **1** are in agreement with this formulation and the proposed structure is similar to that recently reported for the analogous

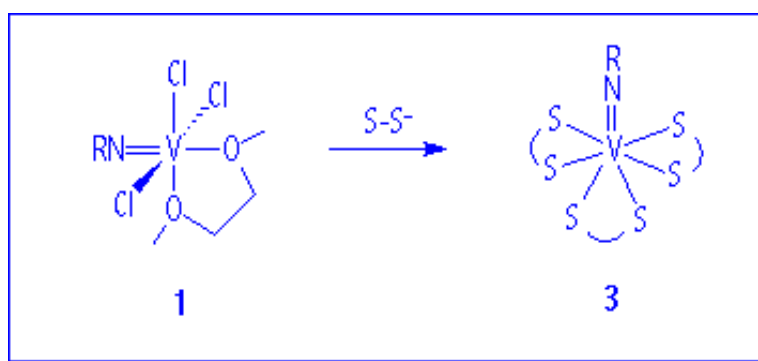
$V(N^tBu)Cl_3(dme)$ .<sup>4</sup> Compounds **1** are employed as suitable starting materials for the synthesis of other imido complexes of vanadium.

Substitution reaction of **1a** with  $Et_2PCH_2CH_2PEt_2$  (depe) affords the expected complex  $V(N-2,6-^iPr_2C_6H_3)Cl_3(depe)$ , **2**.



$^1H$  NMR and  $^{13}C\{^1H\}$  NMR spectra of **2** show, besides the characteristic signals of the 2,6- $^iPr_2C_6H_3$  group, two set of resonances for the unequivalent P-Et and  $CH_2$ -P groups.  $^{31}P\{^1H\}$  NMR spectrum displays two broad resonances at 14.4 and 48.3 ppm. NMR data of **2** suggest a *mer*- distribution of the chloro atoms, similar to that found in the related<sup>2a</sup> organoimido molybdenum complex  $Mo(NR)Cl_3(depe)$ .

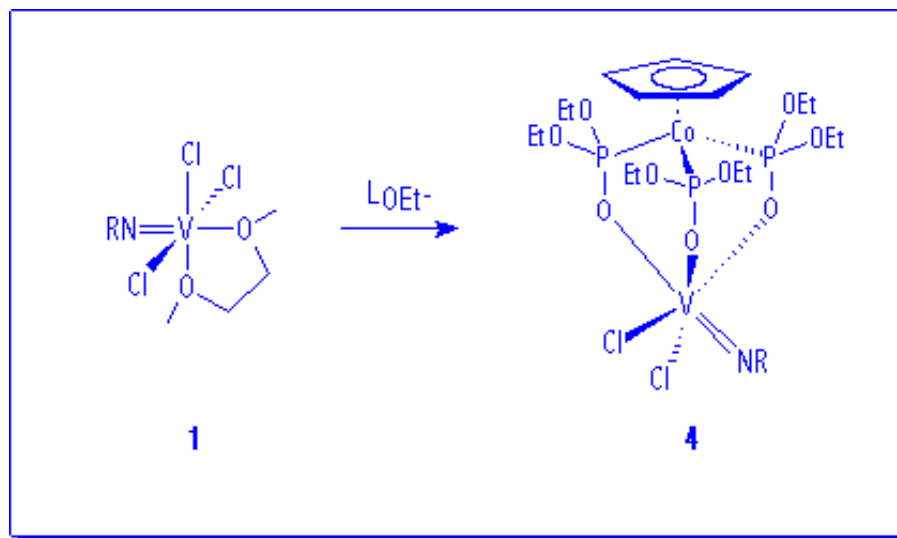
The reaction of **1a** with monoanionic bidentate dithioligands ( $^iPrOCS_2^-$  and  $^iPr_2NCS_2^-$ ) gives  $V(N-2,6-^iPr_2C_6H_3)(S-S)_3$ , ( $S-S = ^iPrOCS_2$ , **3a**;  $^iPr_2NCS_2$ , **3b**).



$^1H$  NMR spectra indicate that the complexes are fluxional at room temperature (*ca.* 298 K). For **3b**, all three dithiocarbamate ligands produce a single pattern ( $CH_3$  broad signal at 1.25 ppm and CH very broad hump at 4.48 ppm), meanwhile **3a** exhibits two separate absorptions (pseudotriplet + doublet, 2:1 ratio) for the methyl substituents of the xanthate ligands. For the latter derivative the  $^1H$  NMR spectrum was recorded at [343 K](#), where the fast limit exchange was reached, and only one collection of signals (doublet + heptet) was observed. At [303 K](#) the methyl groups become different and assuming the structure reported for complex<sup>5a</sup>  $Nb(N-p-C_6H_4CH_3)(S_2CNEt_2)_3$ , the two resonances can be ascribed to the different xanthate ligands occupying the axial and equatorial positions. The

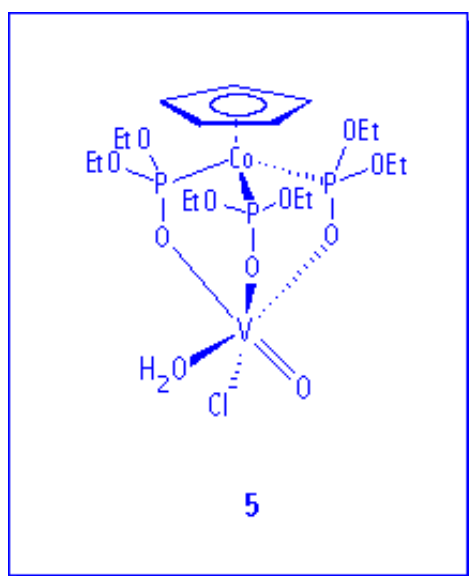
fluxional NMR behavior of these compounds is similar to that reported for the heavier group 5 metals,  $M(NR)(S_2CNR'_2)_3$ .<sup>5</sup>

Interaction of **1** with one equivalent of the monoanionic tripod ligand<sup>6</sup>  $L_{OEt}$  ( $L_{OEt} = (\eta-C_5H_5)Co\{P(O)(OEt)_2\}_3$ ) affords the compounds  $(L_{OEt})V(NR)Cl_2$  ( $R = 2,6\text{-}^iPr_2C_6H_3$ , **4a**; 1-adamantyl, **4b**) as red crystalline materials in good yields.

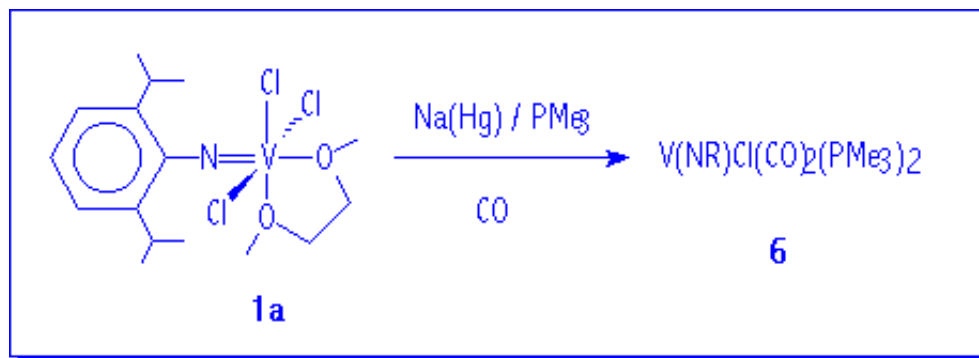


NMR spectra are in conformity with the proposed formulation. So, for example, three signals appear in the  $^1H$  NMR for the methyl groups, three resonances in the  $^{13}C\{^1H\}$  NMR for the methylene groups of the  $L_{OEt}$  ligand and an  $AX_2$  spin system arises in the  $^{31}P\{^1H\}$  NMR spectrum. Related imido compounds of formulation  $(Cp)V(NR)Cl_2$  and  $(Tp)V(NR)Cl_2$  are known.<sup>7</sup>

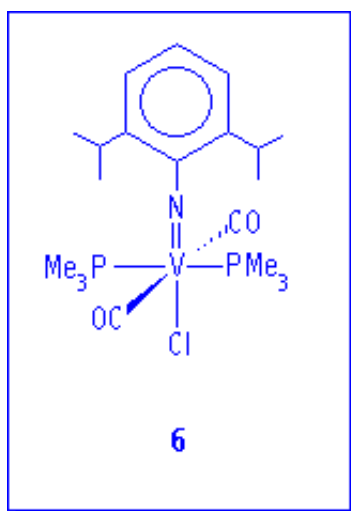
During the synthesis of **3a**, a second product, **5**, can be isolated from this reaction in the form of paramagnetic green crystals. A single crystal of **5** was analyzed by X-ray diffraction methods but unfortunately the refinement process was not possible to be completed. Nevertheless, the results confirm the formulation of **5** as compound  $(L_{OEt})V(=O)Cl(H_2O)$ . A similar vanadium complex,  $(L_{OEt})V(=O)(acac)$ , was previously characterized by X-ray.<sup>8</sup>



Finally, we like to present some preliminary results concerning the reduction of complex  $V(N-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)Cl_3(\text{dme})$  to  $d^2$  organoimido vanadium derivatives. The sodium-amalgam reduction of **1a** in the presence of two equivalents of  $\text{PMe}_3$  under atmosphere of CO produces a red solution from which is possible to isolate red crystals of compound **6**.



**6** is unstable in solution and even in the solid state under nitrogen, decomposing to an unidentified paramagnetic product through CO dissociation. The IR spectrum indicate the coordination of CO displaying a strong band at  $1938\text{ cm}^{-1}$  (Nujol). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a broad plateau-form resonance for the phosphorous atoms at 0.8 ppm, caused by the unresolved coupling to the vanadium nucleus ( $I = 7/2$ ) and quadrupolar relaxation effects.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **6** are in agreement with two *trans*  $\text{PMe}_3$  ligands. The spectroscopic and analytical data agrees with the formulation  $V(N-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)Cl(\text{CO})_2(\text{PMe}_3)_2$  and a possible proposed structure for **6** is shown below. **6** represents, to our knowledge, the first free Cp vanadium(III) imido complex.



## Acknowledgements

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