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Synthesis and X-ray characterization of a monomeric Cp-free d^1-imido–vanadium(IV) complex

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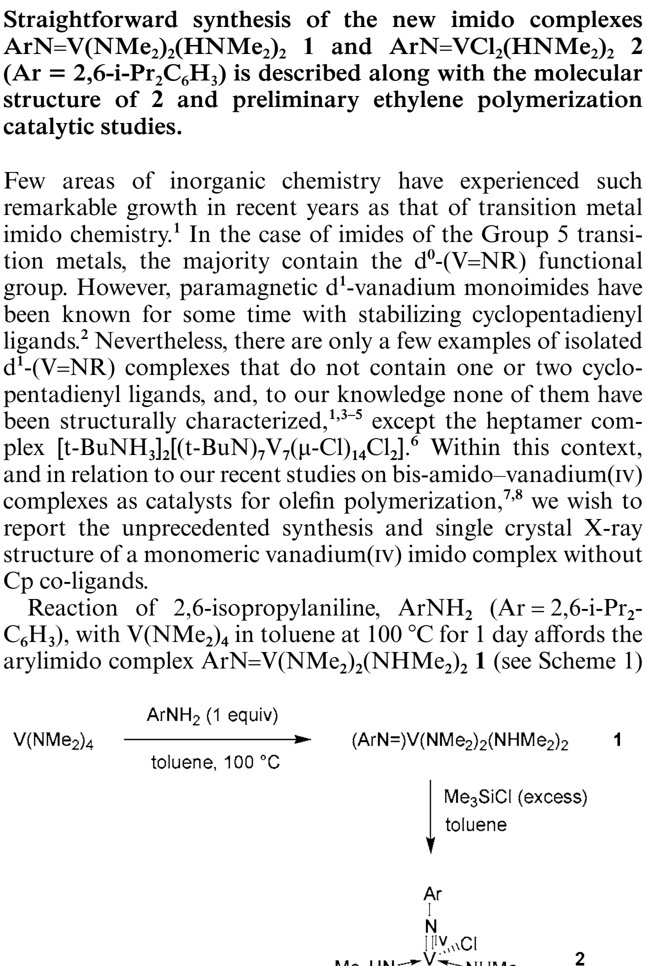
Straightforward synthesis of the new imido complexes $ArN{=}V(NMe_2)_2(HNMe_2)_2$ 1 and $ArN{=}VCl_2(HNMe_2)_2$ 2 ($Ar = 2,6\text{-i-}Pr_2C_6H_3$) is described along with the molecular structure of 2 and preliminary ethylene polymerization catalytic studies.

Few areas of inorganic chemistry have experienced such remarkable growth in recent years as that of transition metal imido chemistry.[1] In the case of imides of the Group 5 transition metals, the majority contain the d^0-(V=NR) functional group. However, paramagnetic d^1-vanadium monoimides have been known for some time with stabilizing cyclopentadienyl ligands.[2] Nevertheless, there are only a few examples of isolated d^1-(V=NR) complexes that do not contain one or two cyclopentadienyl ligands, and, to our knowledge none of them have been structurally characterized,[1,3–5] except the heptamer complex $[t\text{-}BuNH_3]_2[(t\text{-}BuN)_7V_7(\mu\text{-}Cl)_{14}Cl_2]$.[6] Within this context, and in relation to our recent studies on bis-amido–vanadium(IV) complexes as catalysts for olefin polymerization,[7,8] we wish to report the unprecedented synthesis and single crystal X-ray structure of a monomeric vanadium(IV) imido complex without Cp co-ligands.

Reaction of 2,6-isopropylaniline, $ArNH_2$ ($Ar = 2,6\text{-i-}Pr_2\text{-}C_6H_3$), with $V(NMe_2)_4$ in toluene at 100 °C for 1 day affords the arylimido complex $ArN{=}V(NMe_2)_2(NHMe_2)_2$ **1** (see Scheme 1) as a dark red solid, after recrystallization from cold pentane. The bis-chloro analogue, namely $ArN{=}VCl_2(HNMe_2)_2$ **2**, is obtained by treatment of **1** with an excess of chlorotrimethylsilane at room temperature in toluene (Scheme 1, yield = 82% with respect to $V(NMe_2)_4$).† ‡



Scheme 1 Synthesis of complexes **1** and **2**.

The crystal structure of **2** is presented in Fig. 1 and confirms the presence of a bis-dimethylamine adduct.§ The molecular structure is best described as distorted square-pyramid with an axial arylimido that exhibits a V–N distance of 1.654(3) Å, the imido linkage being almost linear (V1–N1–C1 angle = 178.4(3)°). The two chlorine atoms are mutually *trans* with a Cl1–V1–Cl2 angle of 136.48(5)° and V1–Cl bonds of 2.3202(14) and 2.3257(12) Å. The two *trans* dimethylamino ligands form the base of the square-pyramid with the chlorine atoms, and have $V\text{–}N_{amine}$ bonds of 2.018(5) and 2.171(4) Å and a $N_{amine}\text{–}V\text{–}N_{amine}$ angle of 165.23(16)°.

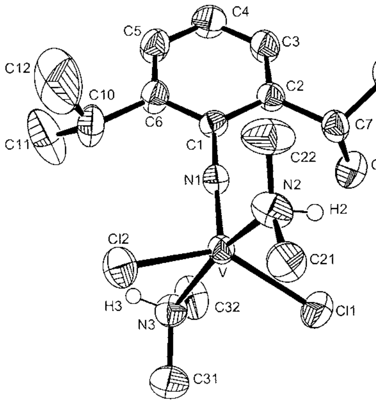


Fig. 1 Molecular structure of **2** with selected bond distances (Å) and angles (°); V1–N1 1.654(3), V1–N2 2.018(5), V1–N3 2.171(4), V1–Cl1 2.3202(14), V1–Cl2 2.3257(12), N1–C1 1.388(5), C1–N1–V1 178.4(3), Cl1–V1–Cl2 136.48(5), N2–V1–N3 165.23(16).

Both **1** and **2** are paramagnetic; EPR spectra of toluene solutions at room temperature show typical eight band patterns for d^1-vanadium(IV) species, with $g = 1.985$, $a(^{51}V) = 65.3$ G and $g = 1.989$, $a(^{51}V) = 92.5$ G, respectively. Additionally, magnetic susceptibility measurements have been carried out on **2**. The effective moment μ_{eff} is $1.744\mu_B$ at 300 K, which is consistent with a V^{IV} unit.

Compound **2** may be the key starting material in a whole new coordination chemistry of vanadium. Preliminary studies show that $HNMe_2$ ligands in **2** can be displaced by amines, phosphines, and 2,2′-bipyridine. For example, after dissolution of **2** in pyridine, the complex $ArN{=}VCl_2(Py)_3$ has been quantitatively synthesized and characterized by single crystal X-ray crystallography.[8]

The complexes **1** and **2** will provide interesting comparisons with their titanium/zirconium analogues[9] and with very recent amido-,[10] bis-amido-[7,8] or linked Cp–amido-[11] vanadium(IV) complexes that are active olefin polymerization catalysts. Indeed, preliminary studies demonstrate that **1** is an active catalyst for ethylene polymerization when 10 equivalents of $EtAlCl_2$ are used as co-catalyst (activity = 2.2×10^4 (g of PE) (mol catalyst)$^{-1}$ h^{-1} atm^{-1}. Similarly, a combination of **2**/MAO (ratio 1/500, MAO = methylaluminoxane) or **2**/$EtAlCl_2$ (ratio 1/10) catalyzes ethylene polymerization at room temperature and under 1 atm of ethylene (with activities of 5.9×10^4 and 1.2×10^5 (g of PE) (mol catalyst)$^{-1}$ h^{-1} atm^{-1}, respectively). Solid polyethylene is obtained in all cases, and in the tests run with $EtAlCl_2$ as activator high molecular weight polyethylene was formed (see Table 1).

In summary, we have described a convenient synthesis of imido–vanadium(IV) complexes **1** and **2**, and, to our knowledge,

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Table 1 Results of ethylene polymerisation runs using pre-catalysts **1** and **2**[a]

Run	Precatalyst	Activator	Time/min	Polymer yield/mg	Productivity/(g of PE) (mol catalyst)$^{-1}$ h^{-1} atm^{-1}	M_n[d]	M_w[d]	M_w/M_n
1	**1**[b]	$EtAlCl_2$	3	35	2.2×10^4	6.285×10^5	1.795×10^6	2.875
2	**2**[c]	MAO	10	254	5.9×10^4	6.490×10^3	2.146×10^4	3.306
3	**2**[b]	$EtAlCl_2$	2	98	1.2×10^5	6.505×10^5	1.933×10^6	2.972

[a] General conditions: 0.025 mmol of pre-catalyst dissolved in 5 g of toluene, 20 °C, 1 atm of ethylene. [b] $EtAlCl_2$ 10 equiv. [c] MAO 500 equiv. [d] Determined by SEC analysis.

the first structurally characterized monomeric d^1-(V=NR) complex that does not possess Cp ligands. We have also demonstrated the activity of such imido complexes as catalysts for ethylene polymerization. Full details of the coordination chemistry, reactivity, and olefin polymerization activity of **1** and **2** and other analogues will be published shortly.

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Notes and references

† Direct synthesis of **2**: A toluene solution (4 g) of 1.00 g of $V(NMe_2)_4$ (4.40 mmol) and 780 mg of 2,6-i-$Pr_2C_6H_3NH_2$ (4.40 mmol) was heated at 100 °C for 1 day giving a dark red solution. After removal of the volatiles, toluene (4 g) and Me_3SiCl (4.00 g) were added and the solution was stirred for 2 days. Removal of the volatiles and recrystallization in cold pentane afforded 1.40 g of dark red-purple crystals of **2** (82%). These compounds release $NHMe_2$ during standard combustion analysis and therefore satisfactory (C,H,N) elemental analyses have not been obtained (and correspond to partial (for **2**) or total (for **1**) loss of the $NHMe_2$ ligands). When **2** is reacted with pyridine however, an exchange reaction occurs leading to red microcrystals of ArN=$VCl_2(Py)_3$. The pyridine ligands of this material are more strongly bound to the metal, permitting a satisfactory elemental analysis to be obtained.

‡ Selected data for **1** and **2**: **1** EPR ($PhCH_3$, 20 °C) $g = 1.985$, $a(^{51}V) = 65.3$ G, IR (KBr) $\nu_{V=N} = 952$ cm^{-1}. **2** EPR ($PhCH_3$, 20 °C) $g = 1.989$, $a(^{51}V) = 92.5$ G. $\mu_{eff} = 1.744\mu_B$ (300 K), IR (KBr) $\nu_{V=N} = 934$ cm^{-1}.

§ Crystallographic data for **2**: $C_{16}H_{31}Cl_2N_3V$, $M = 387.28$, monoclinic, space group $P2_1/n$, $a = 10.6595(13)$, $b = 9.7366(10)$, $c = 20.783(2)$ Å, $\beta = 103.099(14)°$, $U = 2100.9(4)$ Å^3, $Z = 4$, $D_c = 1.224$ Mg m^{-3}, R (R_w) = 0.0905 (0.1374) for 2726 unique data and 213 parameters, GOF = 1.067. Data collection were performed at *ca.* 160 K on a STOE Imaging Plate Diffraction System (I.P.D.S) diffractometer using graphite monochromatized Mo-Kα radiation. The structure was solved by direct methods and subsequent difference Fourier maps. CCDC reference number 186/2265. See http://www.rsc.org/suppdata/dt/b0/b008761k/ for crystallographic files in .cif format.

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