

# Synthesis of $\alpha$ -diimine V(III) complexes and their role as ethylene polymerisation catalysts

Stefano Milione, Gabriella Cavallo, Consiglia Tedesco and Alfonso Grassi\*

Università di Salerno, Dipartimento di Chimica, 84081-Baronissi, Italy.  
E-mail: grassi@chem.unisa.it

Received 4th July 2001, Accepted 28th January 2002

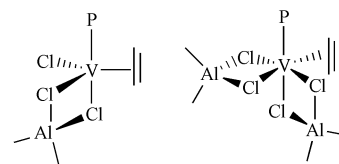
First published as an Advance Article on the web 20th March 2002

Two novel  $\alpha$ -diimine vanadium complexes,  $[\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NPh}]\text{V}(\text{THF})\text{Cl}_3$  (**1**) and  $\{[2,6-(i\text{-Pr})_2\text{Ph}]\text{N}=\text{CH}-\text{CH}=\text{N}[2,6-(i\text{-Pr})_2\text{Ph}]\}\text{VCl}_3$  (**2**) were synthesized by ligand exchange reaction of  $\text{VCl}_3(\text{THF})_3$  with the appropriate  $\alpha$ -diimine ligand. The chemical structure of **1** was determined by X-ray crystallography and found to consist of a vanadium atom in a distorted octahedral geometry with the oxygen atom of the coordinated THF, two nitrogen atoms of the diimine ligand and one chlorine atom in the same plane. Complexes **1** and **2** were characterized by FT-IR,  $^1\text{H}$  NMR, elemental analysis and **2** was identified as the THF free V(III) diimine complex. The behavior of **1** and **2** as ethylene polymerisation catalysts was preliminarily explored after activation with MAO or  $\text{AlEt}_2\text{Cl}$  and compared with that of  $\{2,6\text{-bis}[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{Me})_2(\text{C}_5\text{H}_3\text{N})]\}\text{VCl}_3$  (**3**) under similar conditions. Upon activation of **1–3** with  $\text{AlEt}_2\text{Cl}$ , moderate polymerisation activities were observed at  $-40^\circ\text{C}$  whereas the corresponding MAO activated catalysts exhibit lower activity. The molar concentration of the active sites at  $-40^\circ\text{C}$  is rather low (found in the range 5–12% of total vanadium) and results from slow alkylation of the complexes followed by reduction of V(III) catalysts to inactive V(II) species. At  $50^\circ\text{C}$  an increase of the ethylene polymerisation activities of the **1–3**- $\text{AlEt}_2\text{Cl}$  catalysts was observed and the trend of the productivity values follows the steric hindrance at the metal center. Alkylation of the diimine ligands of the **1–3** catalysts with  $\text{AlEt}_2\text{Cl}$  producing deactivation of the active sites is only partially active under polymerisation conditions whereas the reaction of **1** and **2** with MAO produces fast degradation of the active species.

## Introduction

Vanadium based olefin polymerisation catalysts were among the first homogeneous Ziegler–Natta catalysts discovered in the early 60's.<sup>1</sup> Indeed, a combination of  $\text{VCl}_4$  with  $\text{AlEt}_2\text{Cl}$  in aliphatic solvent at low temperature leads to soluble catalysts which polymerise propene to a syndiotactic polymer<sup>2</sup> and copolymerise ethene with linear 1-olefins.<sup>3</sup> The stereospecific propene polymerisation proceeds through a secondary monomer insertion and the stereoregularity of the polymer product is relatively high whereas the regioregularity is poor.<sup>4</sup> However the thermal stability of the active species is rather low and the 1-olefin polymerisation process fails at room temperature because of fast decomposition of the catalyst through a reduction pathway of the V(III) and V(IV) precursors to inactive V(II) species.<sup>5</sup> V(acac)<sub>3</sub> based catalysts, properly activated with alkylaluminium compounds, were later discovered and found to be more thermally stable than  $\text{VCl}_4$  based catalysts:<sup>6</sup> V( $\beta$ -diketonate)<sub>3</sub> are currently employed in the synthesis of EP (ethylene–propylene) and EPDM (ethylene–propylene–diene monomer) elastomers.<sup>7</sup> Despite the extensive applications of the vanadium catalysts, the structure of the active species is to date largely unknown and several efforts have been devoted recently to synthesize model compounds and/or more thermally robust catalysts. Some preliminary reports in the literature suggested that V(III) alkyl complexes, stabilized in the trigonal bipyramidal geometry by coordination of one of the  $\text{AlEt}_2\text{Cl}$  molecules *via*  $\mu\text{-Cl}$  bridges (see Scheme 1) could be responsible for the catalytic activity of these systems.<sup>8</sup> On the contrary, other authors suggested an octahedral environment of the vanadium atom by analogy with the active sites on  $\text{TiCl}_4/\text{MgCl}_2$  supported catalysts.<sup>9</sup>

Recently alkyl vanadium (III) compounds bearing amidinate<sup>10</sup> and amide<sup>11</sup> ligands have been synthesized with differ-



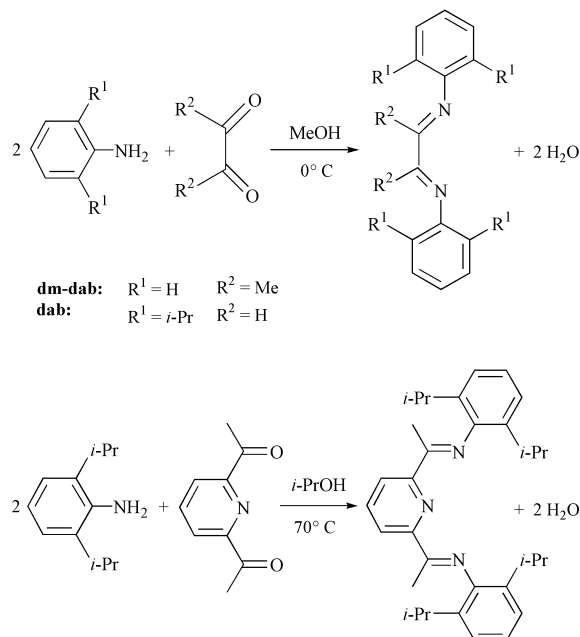
**Scheme 1** Proposed models for the active species in the  $\text{VCl}_4\text{-AlEt}_2\text{Cl}$  catalyst.

ent coordination geometry and their polymerisation activity investigated to shed light on the steric and electronic requirements determining the olefin polyinsertion reaction. These complexes produce short lived ethylene polymerisation catalysts and are inactive in propene polymerisation. Aiming to design new vanadium catalysts we speculated that the  $\text{AlEt}_2\text{Cl}$  ligand of the active species model (see Scheme 1) could be replaced by neutral  $\alpha$ -diimine ligands. During our investigation, Gambarotta *et al.* reported the synthesis of  $\{2,6\text{-bis}[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{Me})_2(\text{C}_5\text{H}_3\text{N})]\}\text{VCl}_3$ , in which the diimine–pyridyl ligand (**bie-py**) acts as *N,N,N*-tridentate.<sup>12</sup> Upon activation with MAO this compound polymerises ethene with good activity (see *infra* for more details) but is inactive in propene polymerisation. To decrease the steric hindrance at the metal center we designed two novel  $\alpha$ -diimine vanadium complexes, bearing the *N,N*-bidentate  $[\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NPh}]$  (**dm-dab**) and  $\{[2,6-(i\text{-Pr})_2\text{Ph}]\text{N}=\text{CH}-\text{CH}=\text{N}[2,6-(i\text{-Pr})_2\text{Ph}]\}$  (**dab**) ligands. In addition we replaced the isopropyl groups in **dab** with hydrogen atoms in **dm-dab** in order to assess the role played by this group in vanadium catalysed olefin polymerisation. Theoretical calculations stressed the relevance of the isopropyl groups of the *N*-aryl moiety to reduce the  $\beta$ -hydrogen migration rate from the growing polyolefin chain to the metal<sup>13</sup> and indeed highly active ethylene polymerisation catalysts were obtained with diimine complexes of late and middle-late transition metals.<sup>14</sup>

## Results and discussion

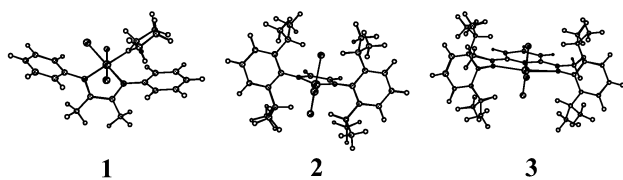
### Synthesis and characterization of the vanadium complexes 1–3

The  $\alpha$ -diimine ligands  $[\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{Ph}]^{15}$  and  $\{[2,6-(i\text{-Pr})_2\text{Ph}]_2\text{N}=\text{CH}-\text{CH}=\text{N}[2,6-(i\text{-Pr})_2\text{Ph}]\}^{16}$  were synthesized according to the literature by reaction of two equivalents of the appropriate aniline with one equivalent of the  $\alpha$ -diketone in methanol at  $0^\circ\text{C}$ . The **bie-py** ligand was obtained through a modification of the published procedure<sup>17</sup> in higher yields and purity (see Experimental and Scheme 2). Ligands were fully characterized by NMR and FT-IR spectroscopy.



**Scheme 2** Synthesis of the bidentate  $[\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NPh}]$  and  $\{[2,6-(i\text{-Pr})_2\text{Ph}]_2\text{N}=\text{CH}-\text{CH}=\text{N}[2,6-(i\text{-Pr})_2\text{Ph}]\}$  ligands.

The vanadium complexes  $[\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NPh}]\text{V}(\text{THF})\text{Cl}_3$  (**1**),  $\{[2,6-(i\text{-Pr})_2\text{Ph}]_2\text{N}=\text{CH}-\text{CH}=\text{N}[2,6-(i\text{-Pr})_2\text{Ph}]\}\text{VCl}_3$  (**2**) and  $\{2,6\text{-bis}[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{Me})_2(\text{C}_5\text{H}_3\text{N})]\}\text{VCl}_3$  (**3**) were isolated in good yields from reaction of  $\text{VCl}_3(\text{THF})_3$  with the appropriate ligand in toluene at room temperature (see Scheme 3), using a 1 : 1 metal to ligand molar ratio. Attempts to



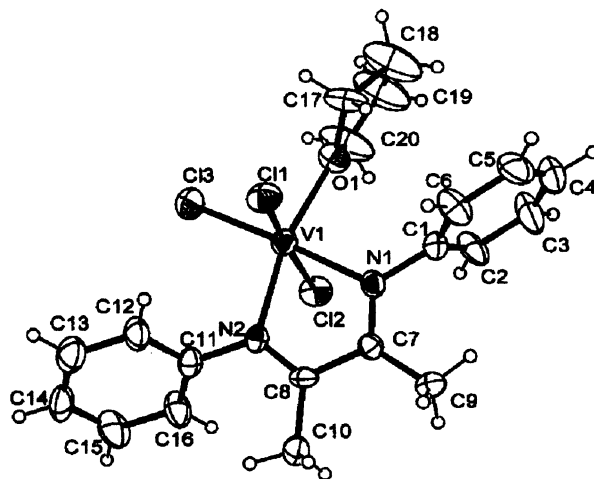
**Scheme 3**  $\alpha$ -Diimine vanadium(III) complexes 1–3.

synthesize the same compounds under different conditions were unsuccessful. In particular, when the reaction was conducted in THF or in toluene at higher temperature ( $100\text{--}110^\circ\text{C}$ ) the expected products were recovered from the reaction mixture in lower yields.

Complexes **1–3** have been characterized using a variety of techniques including elemental analysis, FT-IR and NMR spectroscopy. Dark red crystals of **1** suitable for the X-ray diffraction analysis were grown from toluene at room temperature. The molecular structure of the complex **1** is shown in Fig. 1 and the corresponding selected interatomic distances and angles are reported in Table 1. Disordered solvated toluene molecules (0.5 per V atom) were also found in the crystal structure. The coordination environment of the vanadium is distorted octahedral with two axial chlorine atoms where the oxygen atom of the THF ligand and the third chlorine atom lie in the same

**Table 1** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1**

V(1)–Cl(1)	2.324(3)	V(1)–Cl(2)	2.342(3)
V(1)–Cl(3)	2.297(3)	V(1)–O(1)	2.123(6)
V(1)–N(1)	2.132(7)	V(1)–N(2)	2.128(7)
N(1)–C(1)	1.463(10)	N(1)–C(7)	1.284(9)
N(2)–C(11)	1.435(9)	N(2)–C(8)	1.287(9)
C(7)–C(8)	1.482(10)		
N(1)–V(1)–N(2)	74.6(2)	N(2)–V(1)–Cl(3)	102.6(2)
Cl(3)–V(1)–O(1)	91.0(2)	N(1)–V(1)–O(1)	91.8(2)
N(1)–V(1)–Cl(1)	85.8(2)	N(2)–V(1)–Cl(1)	90.5(2)
Cl(1)–V(1)–Cl(3)	94.46(11)	Cl(1)–V(1)–O(1)	91.9(2)
N(1)–V(1)–Cl(2)	85.1(2)	N(2)–V(1)–Cl(2)	86.0(2)
Cl(2)–V(1)–Cl(3)	94.57(14)	Cl(2)–V(1)–O(1)	89.5(2)
N(1)–C(7)–C(8)	114.9(7)	N(2)–C(8)–C(7)	115.7(7)
C(1)–N(1)–V(1)	121.7(5)	C(11)–N(2)–V(1)	121.1(5)



**Fig. 1** X-Ray molecular structure of  $[\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NPh}]\text{V}(\text{THF})\text{Cl}_3$  (**1**). Thermal ellipsoids are drawn at 30% probability level.

plane as the two nitrogen atoms of the bidentate ligand (root mean square deviation (rmsd)  $\text{V}(1)\text{--Cl}(3)\text{--N}(1)\text{--N}(2)\text{--O}(1)$  plane: 0.030). The  $\text{V}(1)\text{--N}(1)$  and  $\text{V}(1)\text{--N}(2)$  distances are practically equivalent (2.132(7) and 2.128(7)  $\text{\AA}$ , respectively) as well as the  $\text{C}(7)\text{--N}(1)$  and  $\text{C}(8)\text{--N}(2)$  distances (1.284(9) and 1.287(9)  $\text{\AA}$ ) suggesting a symmetric coordination of the ligand to the metal center. The two aromatic rings of the bidentate ligand are planar ( $\text{C}(1)\text{--C}(6)$  rmsd 0.007 and  $\text{C}(11)\text{--C}(16)$  rmsd 0.002), the former plane is almost perpendicular to the vanadium equatorial plane ( $86.9(3)^\circ$ ) while the latter forms an angle of  $68.0(2)^\circ$ . The X-ray structure of **3** was reported by Gambarotta *et al.* when this work was in progress.<sup>12</sup> The coordination geometry around the metal center is distorted octahedral: the diimine-pyridyl ligand acts as *N,N,N*-tridentate and the three nitrogen atoms and one chlorine atom share the same plane. The  $\text{V}\text{--Cl}$ ,  $\text{V}\text{--N}$  and  $\text{C}=\text{N}$  bond lengths found for **1** and **3** are similar. To date we are unable to obtain crystals of **2** suitable for X-ray analysis. However spectroscopic data, elemental analysis and mass spectroscopy data (see *infra*) suggest that the structure of **2** corresponds to the THF free complex  $\{[2,6-(i\text{-Pr})_2\text{Ph}]_2\text{N}=\text{CH}-\text{CH}=\text{N}[2,6-(i\text{-Pr})_2\text{Ph}]\}\text{VCl}_3$ .

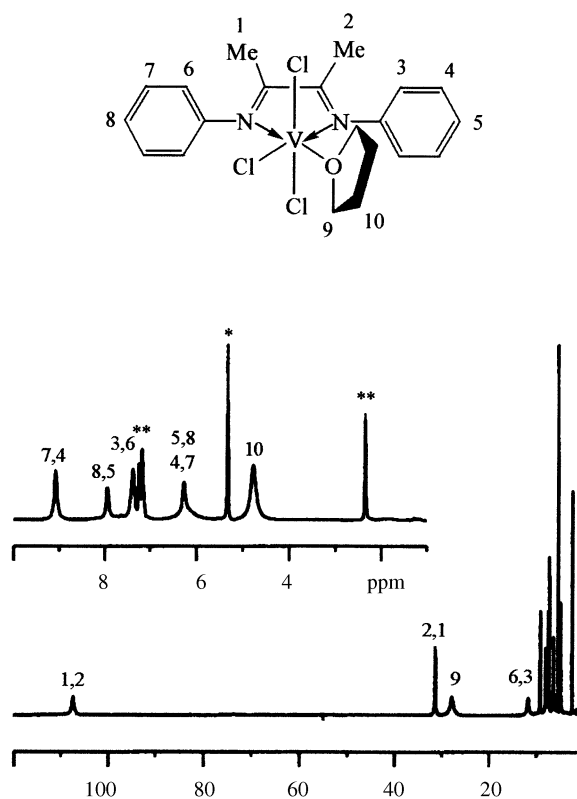
Elemental analysis of the complexes **1–3** is in agreement with the proposed molecular structures. In particular the  $\text{V} : \text{N}$  and  $\text{V} : \text{Cl}$  molar ratios are in agreement with most of vanadium in the oxidation state +3 and a metal : ligand ratio equal to 1. These values were further confirmed by titration of the chlorides and gravimetric determination of the ligand isolated after hydrolysis of the complexes (see Experimental).

The FT-IR spectrum of **1** in  $\text{CH}_2\text{Cl}_2$  solution exhibits the  $\text{C}=\text{N}$  stretching at  $1590\text{ cm}^{-1}$ , not resolved from  $\text{C}=\text{C}$  stretching of the aromatic rings, and shifted at wavenumber lower than in the free ligand ( $1648\text{ cm}^{-1}$ ). Analogous results were observed in

Cu(II) diimine complexes  $[\text{RN}=\text{C}(\text{R}')_2\text{Cu}-\text{X}]$ , ( $\text{R} = \text{alkyl}$ ;  $\text{R}' = \text{H}$ ,  $\text{Me}$ ;  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ) where the *N,N*-chelation of the diimine ligand to the metal center was similarly observed.<sup>18</sup> Signals at  $890\text{--}1015\text{ cm}^{-1}$  account for the presence of coordinated THF. In the FT-IR spectrum of **2** the C=N stretching was observed at  $1580\text{ cm}^{-1}$  ( $1625\text{ cm}^{-1}$  in the free ligand) and signals due to coordinated THF were not detected. In **3**, the stretching of the C=N groups and coordinated pyridyl ring were observed at  $1575\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$ , respectively: these values are very similar to those observed in  $\{2,6\text{-bis}[2,6\text{-}(\text{i-Pr})_2\text{PhN}=\text{C}(\text{Me})_2\text{-}(\text{C}_5\text{H}_3\text{N})\}\text{FeCl}_2$ <sup>14,17</sup> and suggest that the solid state structure of **3**, including the coordinated pyridyl group, is retained in  $\text{CH}_2\text{Cl}_2$  solution.

Complexes **1–3** are paramagnetic and the effective magnetic moments  $\mu_{\text{eff}}$ , determined using the Evans method<sup>19</sup> in  $\text{CH}_2\text{Cl}_2$  solution, were found to be equal to 2.7 (**1**), 2.5 (**2**) and 2.6  $\mu_{\text{B}}$  (**3**), respectively. These values fall in the range expected for a  $d^2$  configuration and for V(III) compounds in the solid state ( $2.5\text{--}3\mu_{\text{B}}$ ).<sup>20</sup> The  $\mu_{\text{eff}}$  measured for **3** in the solid state ( $2.8\mu_{\text{B}}$ )<sup>12</sup> is greater than that found in  $\text{CH}_2\text{Cl}_2$  solution and suggests the presence of V(IV) by-products in traces. Actually EPR measurements carried out on  $\text{CH}_2\text{Cl}_2$  solutions of **1–3** show signals at  $g_{\text{ISO}} = 1.977$  with hyperfine coupling constant  $a = 106\text{ G}$  indicative of the presence of V(IV) species.

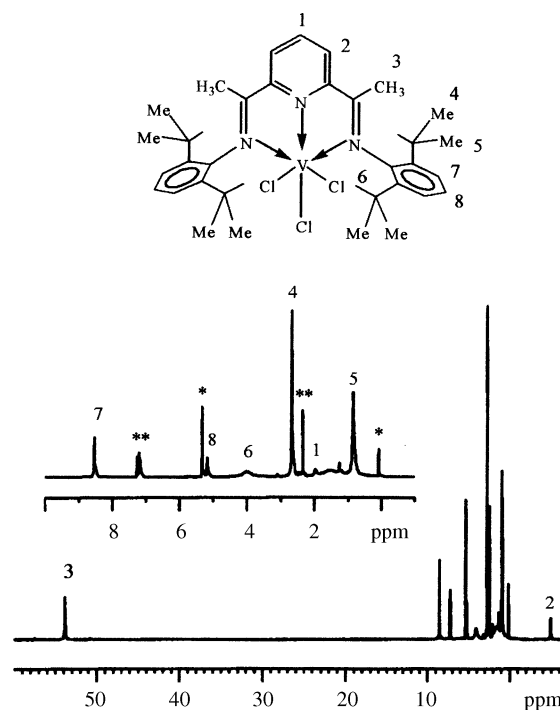
Despite their paramagnetism, complexes **1** and **3** yield well-resolved  $^1\text{H}$  NMR spectra. The room temperature  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  exhibits sharp and well resolved peaks in the range  $0\text{--}110\text{ ppm}$ , assigned on the basis of the integral values (see Fig. 2) using the area of the  $^1\text{H}$ -signals due to the



**Fig. 2**  $^1\text{H}$  NMR spectrum of **1** ( $\text{CD}_2\text{Cl}_2$ ,  $25\text{ }^\circ\text{C}$ ,  $\delta$  in ppm). The signals labeled with an asterisk are due to the isotopic impurities of the solvent and TMS. Those labeled with a double asterisk are due to the clathrated toluene molecules.

clathrated toluene as reference. Coordination of THF to vanadium produces the non equivalence of the aryl and methyl groups of the diimine ligand. The most downfield shifted peaks at  $105.2$  and  $30.5\text{ ppm}$  were attributed to the protons of the two methyl groups of the diimine bridge whereas signals due to the

aryl groups are detected in the region  $6\text{--}12\text{ ppm}$  (see Fig. 2). The *ortho*, *meta* and *para* protons of one aryl are observed at  $11.4$ ,  $9.0$  and  $7.9\text{ ppm}$  respectively; the *meta* and *para* protons of the other aryl are observed at  $6.3\text{ ppm}$  while the *ortho* protons are at  $7.2\text{ ppm}$ . Variable temperature  $^1\text{H}$  NMR experiments carried out in the range  $25\text{--}100\text{ }^\circ\text{C}$  on tetrachloroethane- $d_2$  solutions of **1** show at  $100\text{ }^\circ\text{C}$  the coalescence of the aromatic protons signals producing a unique broad resonance centered at  $7.7\text{ ppm}$ . The temperature dependent behavior of **1** is completely reversible and the same room temperature NMR spectrum was observed by cooling the tetrachloroethane solution to room temperature. The  $^1\text{H}$  signals observed at  $27.1$  and  $4.6\text{ ppm}$  were attributed to the  $\alpha$  and  $\beta$  protons of coordinated THF: after addition of  $\text{THF-}d_8$  these signals are replaced by resonances at  $3.6\text{ ppm}$  and  $1.8\text{ ppm}$  due to uncoordinated THF molecules. The room temperature  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CD}_2\text{Cl}_2$  solution exhibits sharp and well resolved peaks in the region  $60\text{--}10\text{ ppm}$  (see Fig. 3). The high symmetry of complex **3**



**Fig. 3**  $^1\text{H}$  NMR spectrum of **3** ( $\text{CD}_2\text{Cl}_2$ ,  $25\text{ }^\circ\text{C}$ ,  $\delta$  in ppm). The signals labeled with an asterisk are due to the isotopic impurities of the solvent and TMS. Those labeled with a double asterisk are due to the clathrated toluene molecules.

produces the equivalence of the two aryl groups and of the methyl of the ketimine bridge. Thus the signal assignment can be simply accomplished on the basis of the integral values and proximity to the paramagnetic center. The methyl protons of the ketimine groups are assigned to the most downfield shifted signals at  $53.8\text{ ppm}$  and the *meta* pyridyl protons to the upfield shifted signal at  $-5.0\text{ ppm}$ . The *para* protons cannot be unequivocally assigned and are tentatively attributed to the low intensity signal at  $2.3\text{ ppm}$  on the basis of the integral values of the spectral lines. The two most intense signals at  $2.6$  and  $0.8\text{ ppm}$  were attributed to two non equivalent methyls of the isopropyl groups whereas the corresponding methine protons are at  $3.9\text{ ppm}$ . The *meta* and *para* aromatic protons are quite far from the paramagnetic center and, as a result, are assigned to the poorly shifted signals at  $8.5$  and  $5.1\text{ ppm}$ , respectively: the coupling between these protons is clearly detected in the spectrum confirming the proposed assignment. Variable temperature  $^1\text{H}$  NMR experiments run in tetrachloroethane solutions of **1** and **3** show a linear dependence of the chemical shifts vs. reciprocal temperature ( $T^{-1}$ ) in agreement with the Curie law.

**Table 2** Polymerisation results for 1–3–AlEt<sub>2</sub>Cl catalysts at –40 °C and 50 °C<sup>a</sup>

Entry	Catalyst precursor	Al/V molar ratio	T/°C	A <sup>b</sup>
1	1 [PhN=C(Me)–C(Me)=NPh]V(THF)Cl <sub>3</sub>	5	–40	1.0
2	2 {[2,6-(i-Pr) <sub>2</sub> Ph]N=CH–CH=N[2,6-(i-Pr) <sub>2</sub> Ph]}VCl <sub>3</sub>	5	–40	13
3	3 {2,6-bis[2,6-(i-Pr) <sub>2</sub> Ph]N=C(Me) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)}VCl <sub>3</sub>	5	–40	1.2
4	1 [PhN=C(Me)–C(Me)=NPh]V(THF)Cl <sub>3</sub>	20	–40	3.5
5	2 {[2,6-(i-Pr) <sub>2</sub> Ph]N=CH–CH=N[2,6-(i-Pr) <sub>2</sub> Ph]}VCl <sub>3</sub>	20	–40	39
6	3 {2,6-bis[2,6-(i-Pr) <sub>2</sub> Ph]N=C(Me) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)}VCl <sub>3</sub>	20	–40	5.5
7 <sup>c</sup>	1 [PhN=C(Me)–C(Me)=NPh]V(THF)Cl <sub>3</sub>	5	50	29
8 <sup>c</sup>	2 {[2,6-(i-Pr) <sub>2</sub> Ph]N=CH–CH=N[2,6-(i-Pr) <sub>2</sub> Ph]}VCl <sub>3</sub>	5	50	40
9 <sup>c</sup>	3 {2,6-bis[2,6-(i-Pr) <sub>2</sub> Ph]N=C(Me) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)}VCl <sub>3</sub>	5	50	17
10 <sup>c</sup>	1 [PhN=C(Me)–C(Me)=NPh]V(THF)Cl <sub>3</sub>	20	50	54
11 <sup>c</sup>	2 {[2,6-(i-Pr) <sub>2</sub> Ph]N=CH–CH=N[2,6-(i-Pr) <sub>2</sub> Ph]}VCl <sub>3</sub>	20	50	44
12 <sup>c</sup>	3 {2,6-bis[2,6-(i-Pr) <sub>2</sub> Ph]N=C(Me) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)}VCl <sub>3</sub>	20	50	25

<sup>a</sup> Polymerisation conditions: 40 ml of toluene; ethylene pressure = 1 bar; amount of organometallic precursor =  $4.0 \times 10^{-5}$  mol ([V] =  $1 \times 10^{-3}$  M); polymerisation time: 1 h. <sup>b</sup> Activity =  $\text{kg}_{\text{PE}} \times \text{mol V}^{-1} \times \text{h}^{-1}$ . <sup>c</sup> Amount of organometallic precursor =  $4.0 \times 10^{-6}$  mol ([V] =  $1 \times 10^{-4}$  M).

**Table 3** Polymerisation results for 1–3 catalysts activated with MAO at –40 °C and 50 °C<sup>a</sup>

Entry	Catalyst precursor	Al/V molar ratio	T/°C	A <sup>b</sup>
1	1 [PhN=C(Me)–C(Me)=NPh]V(THF)Cl <sub>3</sub>	100	–40	12
2	2 {[2,6-(i-Pr) <sub>2</sub> Ph]N=CH–CH=N[2,6-(i-Pr) <sub>2</sub> Ph]}VCl <sub>3</sub>	100	–40	11
3	3 {2,6-bis[2,6-(i-Pr) <sub>2</sub> Ph]N=C(Me) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)}VCl <sub>3</sub>	100	–40	0.6
4 <sup>c</sup>	1 [PhN=C(Me)–C(Me)=NPh]V(THF)Cl <sub>3</sub>	100	50	10
5 <sup>c</sup>	2 {[2,6-(i-Pr) <sub>2</sub> Ph]N=CH–CH=N[2,6-(i-Pr) <sub>2</sub> Ph]}VCl <sub>3</sub>	100	50	33
6 <sup>c</sup>	3 {2,6-bis[2,6-(i-Pr) <sub>2</sub> Ph]N=C(Me) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)}VCl <sub>3</sub>	100	50	186

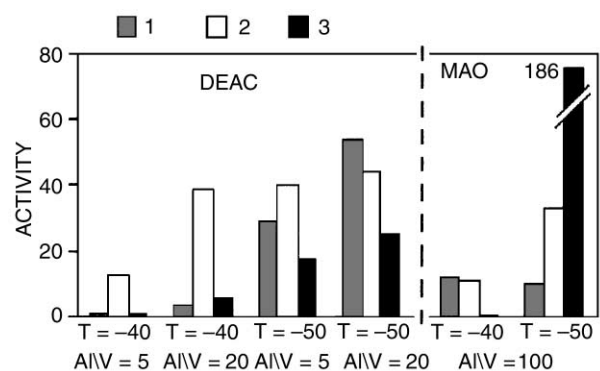
<sup>a</sup> Polymerisation conditions: 40 mL of toluene; ethylene pressure = 1 bar; amount of organometallic precursor =  $4.0 \times 10^{-5}$  mol ([V] =  $1 \times 10^{-3}$  M); polymerisation time: 1 h. <sup>b</sup> Activity =  $\text{kg}_{\text{PE}} \times \text{mol V}^{-1} \times \text{h}^{-1}$ . <sup>c</sup> Amount of organometallic precursor =  $4.0 \times 10^{-6}$  mol ([V] =  $1 \times 10^{-4}$  M).

In the case of complex **1** this behavior suggests that the solid structure determined by X-ray diffraction is retained in tetrachloroethane solution and coordinated THF is not involved in a dissociative exchange reaction with the solvent. In striking contrast with **1** and **3**, the <sup>1</sup>H NMR spectrum of **2** exhibits broad featureless signals in the region between –85–10 ppm and only tentative attributions were carried out (see Experimental). Addition of THF does not produce any modification of the <sup>1</sup>H NMR spectrum and only signals due to free THF are detected. To confirm the proposed structure of **2** the mass spectrum of this sample was recorded and the molecular ion corresponding to {[2,6-(i-Pr)<sub>2</sub>Ph]N=CH–CH=N[2,6-(i-Pr)<sub>2</sub>Ph]}VCl<sub>3</sub><sup>+</sup> actually found at 532 amu.

### Ethylene polymerisation catalysed by 1–3

*In situ* alkylation of 1–3 with MAO or AlEt<sub>2</sub>Cl produces active ethylene polymerisation catalysts: the polymerisation activities of 1–3 were preliminarily investigated under different experimental conditions (Tables 2 and 3).

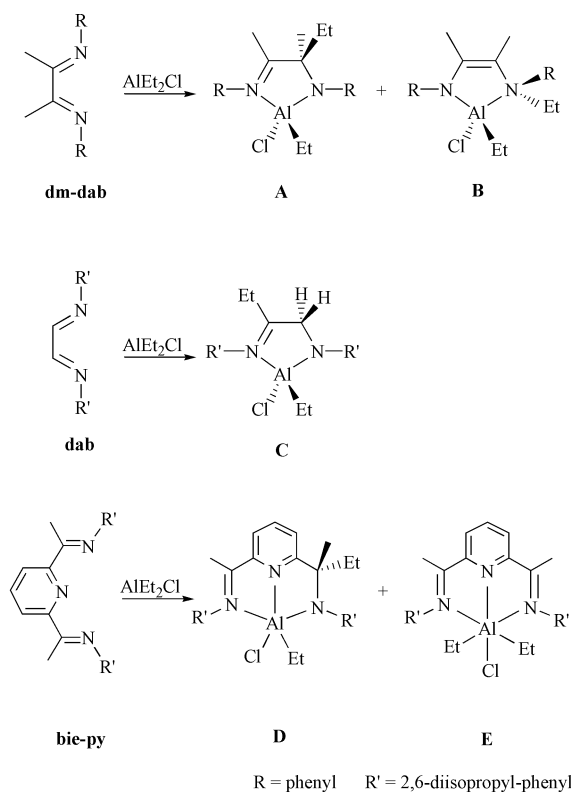
Treatment of 1–3 with AlEt<sub>2</sub>Cl (Al/V molar ratio = 5 or 20) produces fairly active catalysts (A = 1–40  $\text{kg}_{\text{PE}} \times \text{mol cat}^{-1} \times \text{h}^{-1}$ ) at –40 °C (see Fig. 4 and Table 2). The increase of the Al/V molar ratio from 5 to 20 and of temperature from –40 °C to 50 °C produces an increase of the polymerisation activities. The productivity of **2** is almost constant and found to be temperature independent (entries 5, 11; Table 2) whereas those of **1** and **3** increase significantly as polymerisation temperature and co-catalyst molar concentration increase (Table 2, entries 1, 3, 10, 12). The trend of the polymerisation activities at Al/V = 20 and T<sub>p</sub> = 50 °C appears to follow the steric hindrance at the metal center, in the order **1** > **2** > **3**. Activation of 1–3 with MAO at –40 °C produces ethylene polymerisation catalysts with activity values lower than corresponding AlEt<sub>2</sub>Cl activated catalysts. When polymerisation temperature is increased to 50 °C the activities of **1** and **2**-MAO are still lower than the corresponding AlEt<sub>2</sub>Cl activated catalysts whereas the **3**-MAO exhibits a surprisingly high activity in ethylene polymerisation. The latter finding was similarly observed by Gambarotta *et al.*



**Fig. 4** Ethylene polymerisation activity values ( $A = \text{g}_{\text{PE}} \times \text{mmol V}^{-1} \times \text{h}^{-1}$ ) of complexes 1–3 activated with AlEt<sub>2</sub>Cl and MAO under different polymerisation conditions.

and attributed to the conversion of the neutral pyridyl group of the **bie-py** ligand into the corresponding amido form resulting from MAO promoted methylation at the *ortho*-pyridine position.<sup>12</sup> The trend of the ethylene polymerisation activities suggests that activation of the complexes 1–3 with AlEt<sub>2</sub>Cl is low and requires drastic conditions, namely high reaction temperature or high Al/V molar ratios but preserves ligand structure (see *infra*). The low productivity values found for 1–3 could result from i) low molar concentrations of the active sites; ii) deactivation processes involving alkylation of the ligand–ligand transfer from vanadium to aluminium, reduction of the vanadium oxidation state to inactive species; iii) slow ethylene polyinsertion rate determined by the ligand environment. We roughly evaluated the molar concentration of the active species, C\*, from the  $\text{g}_{\text{PE}}/M_n$  ratio at –40 °C: under this condition the chain transfer reaction rate is expected to be slow as well as the deactivation processes determining a variation of C\* with time. The C\* values found are  $1.2 \times 10^{-4}$  (**1**),  $1.8 \times 10^{-4}$  (**2**) and  $5.5 \times 10^{-5}$  M (**3**) at –40 °C, corresponding to 12, 18 and 5% of the total vanadium, respectively. To assess if alkylation of the diimine ligand and/or ligand transfer from vanadium to

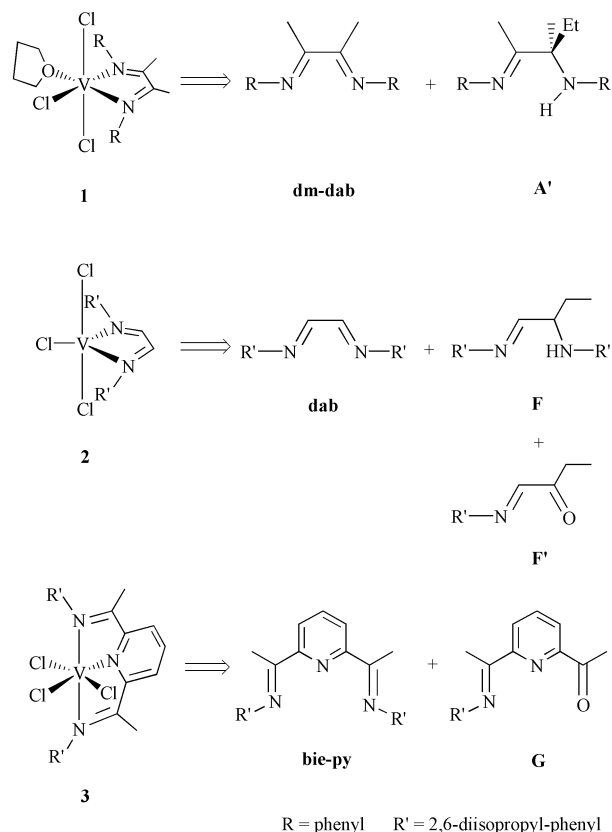
aluminium occur during polymerisation we investigated the reaction of  $\text{AlEt}_2\text{Cl}$  with complexes **1–3**. The reactivity of the  $\alpha$ -diimine ligands with  $\text{AlR}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) was studied in detail in the past.<sup>21</sup> Reaction of the  $\alpha$ -diimine compounds with  $\text{AlEt}_3$  affords a mixture of products resulting from the ethyl transfer from aluminium to either the imine nitrogen atom (N-alkylation) or the imine carbon atom (C-alkylation) with formation of the enamine aluminium compound (in some cases followed by a 1,2-hydrogen shift of the  $\text{N}=\text{C}=\text{N}$  skeleton) or the imino-amide aluminium compound, respectively (for the corresponding structures see *e.g.* **A** and **B** in Scheme 4).<sup>22</sup> Data



**Scheme 4** Reaction scheme of the diimine ligands **dab**, **dm-dab** and **bie-py** with  $\text{AlEt}_2\text{Cl}$  (toluene, 50 °C, 1 h).

concerning the same reaction with  $\text{AlEt}_2\text{Cl}$  are not available: thus we decided first to investigate the extent of this reaction in toluene at 50 °C. Treatment of **dm-dab** with  $\text{AlEt}_2\text{Cl}$  in 1 : 1 molar ratio produces ethyl transfer to both the imine carbon and imine nitrogen atoms producing the imino-amide **A** or the enamine **B** aluminium compounds in 60 mol% and 40 mol% yields, respectively. The selectivity of the alkylation reaction is temperature dependent and the kinetic product **B** could be obtained in 100% yield at –80 °C in hexane. The ligand **dab** quantitatively reacts with  $\text{AlEt}_2\text{Cl}$  to afford the product **C**, resulting from the C-alkylation followed by a 1,2-hydrogen shift. The ligand **bie-py** slowly reacts with  $\text{AlEt}_2\text{Cl}$ : the adduct **E** and the C-alkylated compound **D**, resulting from nucleophilic attack at the imine functionality, were recovered in 44 and 56 mol% yields, respectively.

Reaction of **1–3** with  $\text{AlEt}_2\text{Cl}$  was thus monitored under the polymerisation conditions (1 h, Al/V molar ratio = 20, 50 °C, see Scheme 5). The reaction mixtures were hydrolyzed at 0 °C and the products characterized by  $^1\text{H-NMR}$  spectroscopy. Hydrolysis of **1-AlEt<sub>2</sub>Cl** produces the ligand **dm-dab** in 35 mol% yield in mixture with the **A'** compound (75 mol%), resulting from the C-alkylation followed by hydrolysis of the N–Al bond. Hydrolysis of **2-AlEt<sub>2</sub>Cl** produces three different compounds: the **dab** ligand and **F–F'**, resulting from the C-alkylation followed partly by hydrolysis of one imino group. The three products were identified by  $^1\text{H}$  NMR spectroscopy



**Scheme 5** Reaction products isolated after hydrolysis of the reaction mixture of **1–3** with  $\text{AlEt}_2\text{Cl}$  (molar ratio Al/V = 20, toluene, 50 °C, 1 h).

and determined in 12, 37 and 51 mol% yields, respectively. The ligand **bie-py** was recovered quantitatively not alkylated after the hydrolysis of **3-AlEt<sub>2</sub>Cl**: an aliquot of the ligand (10 mol% of the total mixture) was found as **G**, resulting from the hydrolysis of one imino group.

The above results suggest that the coordination to vanadium partially preserves the diimine ligand structure during the activation reaction of the **1–3** pre-catalysts with  $\text{AlEt}_2\text{Cl}$  and an aliquot of the vanadium catalyst is still present at the end of the polymerisation. On the contrary MAO activation of **1** and **2** affords fast degradation of the active species structures at both high and low polymerisation temperature.<sup>23</sup> The peculiar behavior of the **3-MAO** catalyst at 50 °C can be explained on the basis of the particular modification of the ligand framework.<sup>12</sup>

Moreover other factors appear to determine the productivity of the **1–3** catalysts and the molar concentration of the active sites. Addition at –40 °C of  $\text{AlEt}_2\text{Cl}$  to **1–3** in  $\text{CH}_2\text{Cl}_2$  solution produces a rapid increase of  $\mu_{\text{eff}}$  from 2.6–2.7 to 3.0  $\mu_{\text{B}}$  indicating fast reduction of part of the vanadium V(III) to V(II) (see Experimental for more details). Under the same conditions, the  $^1\text{H}$  resonances corresponding to the V(III) complexes disappear in the  $^1\text{H}$  NMR spectrum and only low intensity  $^1\text{H}$  signals, due to impurities, are actually detected. The reduction of the V(III) active species to V(II) species is fast and occurs in a few minutes under the polymerisation conditions: attempts to re-oxidize the V(II) to V(III) using trichloroethylacetate were unsuccessful.

## Conclusions

Two novel  $\alpha$ -diimine V(III) complexes **1** and **2** have been synthesized and characterized, and their ethylene polymerisation activity explored after activation with MAO or  $\text{AlEt}_2\text{Cl}$ . The productivity values were compared with that of the diimine-pyridine catalyst **3** reported by Gambarotta *et al.* *In situ* alkylation of **1–3** with  $\text{AlEt}_2\text{Cl}$  produces active ethylene polymerisation catalysts whose activities increase with polymerisation

temperature and molar concentration of the aluminium co-catalyst. At 50 °C and Al/V molar ratio = 20 short lived catalysts were obtained but the observed productivities follow the trend expected on the basis of the steric hindrance at the metal center. Investigation of the reaction of **1** and **2** with AlEt<sub>2</sub>Cl shows that the **1** and **2** ligand structures are only partially alkylated by the aluminium co-catalyst. The extent of the alkylation reaction at the C and N imine sites of the diimine ligand skeleton depends on the type of ligand. The **bie-py** ligand was recovered unmodified after hydrolysis of the **3**-AlEt<sub>2</sub>Cl mixture treated under polymerisation conditions. MAO-activation produces chemical modification of the ligand frameworks and scarcely active ethylene polymerisation catalysts in the presence of **1** and **2** were correspondingly obtained. The results herein reported confirm that the surprisingly high activity observed for the **3**-MAO catalyst at 50 °C arises from a chemical transformation of the diimino-pyridyl ligand of this catalyst.

## Experimental

### General procedures

All manipulations involving moisture and air sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk-type techniques or a MBraun glovebox. Solvents were distilled from the appropriate drying agents (sodium-benzophenone for ethyl ether and THF; sodium-potassium alloy for the hydrocarbon solvents). Thiophene-free toluene was obtained after treatment with concentrated sulfuric acid followed by washing with saturated bicarbonate solution and water, in that order. The solvent was dried with calcium chloride and distilled over sodium before use. VCl<sub>3</sub>(THF)<sub>3</sub>,<sup>24</sup> 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene<sup>15</sup> and 1,4-bis-2,6-diisopropylphenyl-1,4-diazabuta-1,3-diene<sup>16</sup> were synthesized according to the literature. Volatiles (toluene and unreacted AlMe<sub>3</sub>) were removed from MAO (AZKO, 30% w/w toluene solution) by distillation *in vacuo* at 50 °C. The purity of AlEt<sub>2</sub>Cl (Aldrich) was checked by <sup>1</sup>H NMR spectroscopy before use. Ethylene (SON; polymerisation grade) was dried by passing over 4 Å molecular sieves.

NMR spectra were recorded on a Bruker AM250 and Bruker AVANCE 400 operating at 250 MHz and 400 MHz for <sup>1</sup>H, respectively. The chemical shifts are referenced to TMS using the residual protio impurities of the deuterated solvents as standard reference. Elemental analyses were carried out at the Analytische Laboratorien (Prof. Dr. H. Malissa und G. Reuter GmbH) and Universidad de Alcalá de Henares, Madrid (Spain). Electron Impact mass spectra were obtained using a Finnigan Thermoquest GLQ Plus 2000 spectrometer equipped with direct exposure probe. Data for X-ray crystal structure determination were collected on a Rigaku AFC7S diffractometer. Infrared spectra were recorded on a FT-IR Bruker Vector 22.

The GPC analysis of the polymer was performed in dichlorobenzene at 120 °C using a Waters 150-C instrument calibrated with polystyrene standards.

X-Band electron spin resonance (ESR) spectra were recorded with an ER 200 D-SRC Bruker spectrometer equipped with a HS Bruker rectangular cavity operating at  $\nu = 9.62$  GHz and Bruker ER 4111 VT device ( $\pm 1$  K) to monitor temperature. The operational frequency was controlled with a Hewlett-Packard X5-32 B wavemeter and the magnetic field was calibrated with the diphenylpicrylhydrazyl free radical (DPPH) as field marker.

### Syntheses

**Preparation of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (bie-py).** 2,6-Bis[1-(2,6-dimethylphenylimino)ethyl]pyridine was obtained through a modification of the published procedure.<sup>17</sup> 2,6-Diacetylpyridine (6.19 g,  $3.5 \times 10^{-2}$  mol) was

reacted with 2,6-diisopropylaniline (20 ml,  $10.6 \times 10^{-2}$  mol) at 70 °C in isopropanol (750 ml) containing a few drops of concentrated formic acid. The warm reaction mixture was filtered with a pre-heated Buckner filter and the diimine-pyridyl ligand isolated as a yellow solid. The filtrate containing the reagents was concentrated and left to react for an additional 12 h; a second fraction was isolated by filtration as described above. The procedure was repeated several times, yielding 14.7 g of the pure ligand (yield = 87%).

**Preparation of [PhN=C(Me)-C(Me)=NPh]VCl<sub>3</sub>(THF) (1).** A bright yellow toluene solution (20 ml) of 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene (0.68 g, 2.89 mmol) was added dropwise to a slurry of VCl<sub>3</sub>(THF)<sub>3</sub> (1.08 g, 2.89 mmol) in toluene (15 ml) at room temperature and left to react overnight under stirring. Dark red crystals were filtered off from the red solution. The filtrate was concentrated to half of its initial volume, layered with petroleum ether (bp 40–60 °C) (20 ml) and kept overnight at –20 °C. A second portion of the crystalline compound was thus recovered by filtration. Yield (both fractions): 68%. (Found: C, 54.98; H, 5.20; N, 5.57; V, 9.75; Cl, 20.98. C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>3</sub>V requires C, 55.15; H, 5.51; N, 5.47; V, 9.95; Cl, 20.78%).  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub> solution): 3057m, 3051m, 2982br, 1592s, 1486s, 1451m, 1419w, 1380m, 1237s, 1140w, 1072w, 1015m.  $\delta_{\text{H}}$  (400 MHz; CD<sub>2</sub>Cl<sub>2</sub>; standard SiMe<sub>4</sub>) 4.7 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 6.3 (s, 3H, H'<sub>m</sub> + H'<sub>p</sub>), 7.2 (s, 2H, H'<sub>o</sub>), 7.9 (s, 1H, H<sub>p</sub>), 9.0 (s, 2H, H<sub>m</sub>), 11.4 (s, 2H, H<sub>o</sub>), 27.1 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 30.5 (s, 3H, N=C(CH'<sub>3</sub>)), 105.3 (s, 3H, N=C(CH<sub>3</sub>)).  $\mu_{\text{eff}} = 2.7 \pm 0.1 \mu_{\text{B}}$ .

**Preparation of {[2,6-(i-Pr)<sub>2</sub>Ph]N=CH-CH=N[2,6-(i-Pr)<sub>2</sub>Ph]}VCl<sub>3</sub> (2).** A toluene solution (15 ml) of 1,4-bis-2,6-diisopropylphenyl-1,4-diazabuta-1,3-diene (0.79 g, 2.09 mmol) was added dropwise to a slurry of VCl<sub>3</sub>(THF)<sub>3</sub> (0.78 g, 2.09 mmol) in toluene (10 ml) at room temperature and the resulting brown solution was stirred overnight at this temperature. The reaction solution was concentrated to 10 ml, layered with petroleum ether (45 ml) and kept at –20 °C overnight. Complex **2** was isolated by filtration as brown powder (0.66 g, yield 59%). (Found: C, 59.01; H, 6.92; N, 5.11; V, 9.40; Cl, 20.07. C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>3</sub>V requires C, 58.49; H, 6.80; N, 5.25; V, 9.54; Cl, 19.92%).  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub> solution): 2972s, 2926m, 2875m, 1580w, 1490m, 1461m, 1384w, 1364w, 1333w, 1174w, 1097m, 1056m, 1041m, 1010m.  $\delta_{\text{H}}$  (400 MHz; C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>; TMS Scale): –82.3 (s, 2H, NCH), –32.7 (s, 4H, CHMe<sub>2</sub>), 1.6 (s, 12H, CHMe'<sub>2</sub>), 1.9 (s, 12H, CHMe<sub>2</sub>), 6.3 (s, 4H, H<sub>m</sub>), 9.8 (s, 2H, H<sub>p</sub>).  $\mu_{\text{eff}} = 2.6 \pm 0.1 \mu_{\text{B}}$ .

**Preparation of {[2,6-bis[2,6-(i-Pr)<sub>2</sub>Ph]N=C(Me)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)]VCl<sub>3</sub> (3).** A toluene solution (130 ml) of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (1.0 g, 2.09 mmol) was added dropwise to a slurry of VCl<sub>3</sub>(THF)<sub>3</sub> (0.78 g, 2.09 mmol) in toluene (20 ml) at room temperature and left to react overnight under stirring. Complex **3** was isolated by filtration as dark red powder (1.12 g, yield 83%). (Found: C, 61.93; H, 6.63; N, 6.92; V, 7.85; Cl, 16.47. Calc. for C<sub>33</sub>H<sub>43</sub>N<sub>3</sub>Cl<sub>3</sub>: C, 62.03; H, 6.78; N, 6.58; V, 7.97; Cl, 16.64%).  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub> solution): 3055sp, 2963s, 2927m, 2869m, 1575m, 1495m, 1466w, 1384m, 1373m, 1327m, 1205m, 1179w, 1105m, 1056m, 1037m.  $\delta_{\text{H}}$  NMR (400 MHz; CD<sub>2</sub>Cl<sub>2</sub>; standard SiMe<sub>4</sub>): –5.0 (s, 2H, H<sub>py-m</sub>), –0.9 (s, 12H, CHMe<sub>2</sub>), 2.0 (s, 1H, H<sub>py-p</sub>), 2.7 (s, 12H, CHMe'<sub>2</sub>), 4.0 (s, 4H, CHMe<sub>2</sub>), 5.2 (s, 2H, H<sub>p</sub>), 8.5 (s, 4H, H<sub>m</sub>), 53.8 (s, 6H, MeC=N).  $\mu_{\text{eff}} = 2.5 \pm 0.1 \mu_{\text{B}}$ .

### Hydrolysis of 1–3

A weighed amount of **1–3** was dissolved in 10 ml of toluene and treated with an aqueous solution of formic acid (15 ml; 0.5 M). The aqueous layer was separated and extracted four times with 15 ml of petroleum ether each. The combined organic solutions

were dried over CaSO<sub>4</sub> and the solvent was distilled *in vacuo* producing a yellow solid, identified by <sup>1</sup>H NMR spectroscopy as the ligand of the starting complex. The concentration of chloride anions was determined in the aqueous layer by titration according to the Volhard method.

### Reaction of the diimine ligands (**dab**; **dm-dab**; **bie-py**) with AlEt<sub>2</sub>Cl

A toluene solution of AlEt<sub>2</sub>Cl (0.80 mmol, 2 ml, 0.4 M) was added by syringe to a stirred toluene solution of the diimine ligand (0.80 mmol in 20 ml, 0.04 M) kept at 50 °C. The mixture was stirred for 1 h at this temperature and subsequently the solvent was removed *in vacuo* to yield an air and moisture sensitive oily material.

$\delta_{\text{H}}$  for **A** (400 MHz; toluene-d<sub>8</sub>; standard SiMe<sub>4</sub>): 0.20 (m, 2H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.63 (t, 3H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.98 (t, 3H, C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.13 (s, 3H, C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.15 (s, 3H, N=C(CH<sub>3</sub>)), 2.56 (m, 2H, C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 7.00 (m, 10H, N(C<sub>6</sub>H<sub>5</sub>)).  $\delta_{\text{H}}$  for **B** (400 MHz; toluene-d<sub>8</sub>; standard SiMe<sub>4</sub>): -0.26 (m, 2H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.74 (t, 3H, AlCH<sub>2</sub>CH<sub>3</sub>), 1.27 (s, 3H, C(CH<sub>3</sub>)=C(CH<sub>3</sub>)NEtPh), 1.39 (t, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.68 (s, 3H, C(CH<sub>3</sub>)=C(CH<sub>3</sub>)NEtPh), 2.66 (m, 1H, NC(H)HCH<sub>3</sub>), 3.76 (m, 1H, NC(H)HCH<sub>3</sub>), 7.00 (m, 10H, N(C<sub>6</sub>H<sub>5</sub>)).  $\delta_{\text{H}}$  for **C** (400 MHz; toluene-d<sub>8</sub>; standard SiMe<sub>4</sub>): 0.08 (m, 2H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.95 (t, 3H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.84 (dd, 6H, CHMe<sub>2</sub>), 0.45 (t, 3H, =CCH<sub>2</sub>CH<sub>3</sub>), 1.25 (m, 18H, CHMe<sub>2</sub>), 1.72 (m, 2H, =CCH<sub>2</sub>CH<sub>3</sub>), 2.92 (m, 1H, CHMe<sub>2</sub>), 2.99 (m, 1H, CHMe<sub>2</sub>), 3.46 (m, 1H, CHMe<sub>2</sub>), 4.09 (m, 1H, CHMe<sub>2</sub>), 4.11 (dd, 2H, N=C(Et)CH<sub>2</sub>N), 6.99 (m, 6H, C<sub>6</sub>H<sub>5</sub>(i-Pr)<sub>2</sub>).  $\delta_{\text{H}}$  for **D** (400 MHz; toluene-d<sub>8</sub>; standard SiMe<sub>4</sub>): 0.19 (q, 2H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.84 (t, 3H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.94 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.04 (dd, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (t, 3H, C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.37 (dd, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (s, 3H, C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.68 (s, 3H, N=C(CH<sub>3</sub>)), 2.74 (s, 2H, C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 3.15 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.35 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.45 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>).  $\delta_{\text{H}}$  for **E** (400 MHz; toluene-d<sub>8</sub>; standard SiMe<sub>4</sub>): 0.12 (q, 4H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.28 (t, 6H, AlCH<sub>2</sub>CH<sub>3</sub>), 1.19 (dd, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.28 (s, 6H, N=C(CH<sub>3</sub>)), 2.92 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.15 (m, 6H, H<sub>m+p</sub>), 7.28 (t, 1H, H<sub>py-p</sub>), 8.50 (d, 2H, H<sub>py-m</sub>).

### Reaction of 1–3 with AlEt<sub>2</sub>Cl followed by hydrolysis

A toluene solution of AlEt<sub>2</sub>Cl (3.2 mmol, 0.4 ml) was added to a toluene solution of **1–3** (0.16 mmol, 40 ml) at 50 °C: a rapid change of the color of the solution was soon observed. The reaction mixture was kept at 50 °C for 1 h under stirring, cooled at 0 °C and hydrolyzed with few drops of methanol and 10 ml of water, in that order. The organic layer was separated, washed two times with 10 ml of water and dried over Na<sub>2</sub>SO<sub>4</sub>. <sup>1</sup>H NMR of solid residue indicated the presence of **dm-dab** (35 mol% yield) and **A'** (65 mol% yield) for **1**-AlEt<sub>2</sub>Cl system, the presence of **dab** (about 12 mol% yield), **F** (about 51 mol% yield) and **F'** (about 37 mol% yield) for the **2**-AlEt<sub>2</sub>Cl system and the presence of **bie-py** and **G** in quantitative yield for **3**-AlEt<sub>2</sub>Cl system.

### Polymerisation procedure. General procedure

In a 100 mL round bottom flask the required amount of catalyst precursor was dissolved in toluene (40 ml) and the solution kept for 10 min at the desired temperature. The reactor was evacuated and filled with ethylene: this procedure was repeated three times in order to remove nitrogen from the solution. Finally ethylene at atmospheric pressure was equilibrated with the toluene solution and the polymerisation run started by injection of the aluminium co-catalyst. Ethylene polymerisation was stopped by treatment of the solution with plenty of acidic (HCl) ethanol and the polymer recovered by filtration and dried at 80 °C *in vacuo*.

### Magnetic moment measurements

A coaxial NMR tube (10 mm o.d.) was filled in the external section with a dichloromethane-d<sub>2</sub> solution of tetramethylsilane (TMS) and in the internal section (5 mm o.d.) with the same solution containing the paramagnetic complex (5 × 10<sup>-3</sup> M). The <sup>1</sup>H chemical shift difference observed for TMS in the external and internal sections provides, according to the Evans method, the  $\mu_{\text{eff}}$  value of the compound.<sup>19</sup> To evaluate the extent of the reduction after treatment with the aluminium co-catalyst, 20 equivalents of AlEt<sub>2</sub>Cl were added by syringe to the internal section of the NMR tube at -40 °C: the color of the 1–3 dichloromethane solutions soon turned from dark red to green. The following increases of the magnetic moments were measured: from 2.7 to 3.1  $\mu_{\text{B}}$  (**1**); from 2.5 to 3.6  $\mu_{\text{B}}$  (**2**); from 2.6 to 2.8  $\mu_{\text{B}}$  (**3**). The experimental error affecting these values is about ±10% due to low accuracy in determining the weight of the small amount of paramagnetic complex needed to prepare the standard solutions.

### X-Ray crystallography

A suitable crystal of **1** (0.3 × 0.4 × 0.7 mm) was selected and sealed in a Lindemann capillary under a nitrogen atmosphere. Diffraction measurements were performed at room temperature using a Rigaku AFC7S diffractometer (graphite monochromated MoK $\alpha$  radiation,  $\lambda = 0.71069$  Å). Lattice constants and crystal orientation were obtained from the setting angles of 23 centered reflections in the range 20° < 2 $\theta$  < 28°. Diffracted intensities were collected within 4° < 2 $\theta$  < 50°, using  $\omega$ -2 $\theta$  scan method, scan width (1.63 + 0.35 tg $\theta$ )°, scan speed 4° min<sup>-1</sup>. Intensity data were corrected for Lorentz and polarization, no decay correction was applied.

The structure was solved by direct methods using SIR92<sup>25</sup> and refined on  $F^2$  including all diffraction data by means of SHELXL97.<sup>26</sup> From the beginning the electron density map showed the presence of a disordered toluene molecule in an inversion center. A rigid body refinement was performed for the solvent molecule, assuming that two distinct molecules equally share the same site with opposite orientation. Hydrogen atoms were positioned geometrically and refined using a rigid model. The hydrogen atoms of the methyl groups were assumed to be disordered over two sites rotated at 60° to each other. Anisotropic displacement parameters were used for all non-hydrogen atoms except those belonging to the solvent molecule: in this case a unique isotropic displacement parameter was refined. The carbon atoms of the THF ligand were markedly anisotropic: different disorder models were tried to account for this effect, but none was completely satisfactory. Two alternative locations were considered for THF carbon atoms and relative occupancies refined, but any attempt to refine the ligand moiety anisotropically was unsuccessful. Finally a total of 257 parameters were refined considering 4343 intensity data. Maximum and minimum residual density were 0.44 and -0.42 eÅ<sup>-3</sup>, respectively. Final disagreement indices:  $R_1 = 0.052$  for 1647 reflections with  $F_o > 4\sigma(F_o)$ ,  $R_1 = 0.2047$  and  $wR_2 = 0.2192$  for all 4343 data.

ORTEP drawings were prepared by means of the program ORTEP32.<sup>27</sup> Crystallographic data for **1**: formula VCl<sub>3</sub>ON<sub>2</sub>-C<sub>20</sub>H<sub>24</sub>0.5C<sub>7</sub>H<sub>8</sub>,  $M = 511.79$ , monoclinic, space group  $P2_1/n$ ,  $Z = 4$ ,  $a = 11.024(9)$ ,  $b = 16.299(4)$ ,  $c = 13.722(3)$  Å,  $\beta = 90.47(5)^\circ$ ,  $V = 2465(1)$  Å<sup>3</sup>,  $D_x = 1.38$  g cm<sup>-3</sup>,  $\mu_{\text{calc}} = 0.74$  mm<sup>-1</sup>.

CCDC reference number 176858.

See <http://www.rsc.org/suppdata/dt/b1/b105931a/> for crystallographic data in CIF or other electronic format.

### Acknowledgements

This work was supported by the Italian Ministry of University (MURST), National Research Council (CNR) and MURST

(PRIN 1998 – “Polimerizzazione stereoselettiva: nuovi catalizzatori e nuovi materiali polimerici”). The authors wish to thank Prof. F. Laschi (Università di Siena) for the characterization of the 1–3 complexes by ESR spectroscopy and dott. Ines Mingozzi (Basell-Ferrara) for the GPC measurements.

## References and notes

- 1 G. Natta, I. Pasquon and A. Zambelli, *J. Am. Chem. Soc.*, 1962, **84**, 1448; A. Zambelli, G. Natta and I. Pasquon, *J. Polym. Sci., Part C*, 1963, **4**, 411.
- 2 A. Zambelli, I. Pasquon, R. Signorini and G. Natta, *Makromol. Chem.*, 1968, **112**, 160; A. Zambelli, G. Natta, I. Pasquon and R. Signorini, *J. Polym. Sci., Part C*, 1967, **16**, 2485; Y. Doi, J. Kinoshita, A. Morinaga and T. Keii, *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13**, 2491.
- 3 A. Zambelli, A. Cety, C. Tosi and I. Pasquon, *Makromol. Chem.*, 1968, **115**, 73; Y. Doi, N. Tokuhira, S. Suzuki and K. Soga, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 285.
- 4 A. Zambelli, C. Tosi and M. C. Sacchi, *Macromolecules*, 1972, **5**, 649; F. A. Bovey, M. C. Sacchi and A. Zambelli, *Macromolecules*, 1974, **7**, 752; A. Zambelli, C. Wolfsgruber and G. Zannoni, *Macromolecules*, 1974, **7**, 752.
- 5 G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre and P. Centola, *Makromol. Chem.*, 1965, **81**, 161.
- 6 Y. Doi, S. Suzuki and K. Soga, *Makromol. Chem., Rapid Commun.*, 1985, **6**, 639.
- 7 S. Cesca, *Macromol. Rev.*, 1975, **10**, 1; Y. Doi, S. Suzuki and K. Soga, *Macromolecules*, 1986, **19**, 2896; T. Ouzumi and K. Soga, *Makromol. Chem.*, 1992, **193**, 823; E. Adisson, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 1033; S. C. Davis, W. Von Hellens and H. Zahalka, *Polymer Material Encyclopedia*, ed. J. C. Salamone, CRC Press Inc., Boca Raton, FL, 1996, vol. 3.
- 8 A. Zambelli and G. Allegra, *Macromolecules*, 1980, **13**, 42.
- 9 P. Corradini, G. Guerra and R. Pucciariello, *Macromolecules*, 1985, **18**, 2030.
- 10 M. Vivanco, J. Ruiz, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1993, **12**, 1794; E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 1998, **17**, 4090; M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Eur. J. Inorg. Chem.*, 1998, 1867; M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1997, **16**, 5183; J. Barker, M. Cameron, M. Kilner, M. M. Mahound and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 1986, 1359.
- 11 C. P. Gerlach and J. Arnold, *Organometallics*, 1997, **16**, 5148; C. P. Gerlach and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1997, 4795; N. Desmangles, S. Gambarotta, C. Bensimon, S. Davis and H. Zahalka, *J. Organomet. Chem.*, 1998, **562**, 53; P. Bero and S. Gambarotta, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 822; P. Bero and S. Gambarotta, *Organometallics*, 1994, **13**, 1052.
- 12 D. Reardon, F. Conan, S. Gambarotta, G. Yap and Q. Wang, *J. Am. Chem. Soc.*, 1999, **121**, 9318.
- 13 A. Michalak and T. Ziegler, *Organometallics*, 2000, **19**, 1850; A. Michalak and T. Ziegler, *Organometallics*, 1999, **18**, 3998.
- 14 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664; D. Pappalardo, M. Mazzeo and C. Pellecchia, *Macromol. Rapid Commun.*, 1997, **18**, 1017; B. L. Small, M. Brookhart and A. M. A. Bennet, *J. Am. Chem. Soc.*, 1998, **120**, 4049; G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Stromberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728.
- 15 A. T. T. Hsieh and B. O. West, *J. Organomet. Chem.*, 1976, **112**, 285.
- 16 T. H. Dieck, M. Svoboda and Z. Greiser, *Z. Naturforsch., Teil B*, 1981, **36**, 823.
- 17 B. L. Small, M. Brookhart and A. M. A. Bennet, *J. Am. Chem. Soc.*, 1998, **120**, 4049.
- 18 H. T. Dieck and I. W. Renk, *Chem. Ber.*, 1971, **104**, 92.
- 19 D. F. Evans, *J. Chem. Soc.*, 1959, 2003; D. H. Grant, *J. Chem. Ed.*, 1995, **72**, 39.
- 20 F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman Hall, New York, 1973.
- 21 J. M. Klerks, D. J. Stufkens, G. van Koten and K. Vrieze, *J. Organomet. Chem.*, 1979, **181**, 271–283.
- 22 E. T. Wissing, J. Jastrzebski, J. Boersma and G. van Koten, *J. Organomet. Chem.*, 1993, **459**, 11–16.
- 23 The polydispersity of PE samples by 1–2/MAO catalysts is very broad:  $M_w/M_n = 183$  ( $M_w = 1.4 \times 10^6$ ; entry 4, Table 3);  $M_w/M_n = 11$  ( $M_w = 6 \times 10^5$ ; entry 5, Table 3).
- 24 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 138.
- 25 A. Altomare, G. Cascarano, C. Giacobozzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
- 26 G. M. Sheldrick, SHELXL97, A program for refining crystal structures, University of Göttingen, Germany, 1997.
- 27 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.