

N,N,N-Tridentate iron(II) and vanadium(III) complexes Part I. Synthesis and characterization

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Abstract

The synthesis of new iron(II) and vanadium(III) diiminepyridyl complexes is reported. The ligands were synthesized and characterized by GC/MS, ¹H and ¹³C NMR spectroscopy. The corresponding complexes are characterized by mass spectrometry and in part by elemental analyses. The activated vanadium complexes were found to be highly active and selective catalysts for the oligomerization of ethene to α -olefins.

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1. Introduction

The interest in new catalytic systems for various applications is vast. Organometallic chemistry has opened a gate to a wide variety of new processes and products. Metallocene and other organometallic complexes are used today worldwide to produce olefin polymers with new unique properties [1–12]. In addition, numerous other processes where transition metal complexes and their organic precursors are involved are changing the chemical industry.

New organometallic iron and vanadium complexes with diiminopyridyl ligand systems [13–22] have potential as olefin oligomerization and polymerization catalysts. Reardon et al. [22] along with others [13,14] have reported that certain of the vanadium complexes have proven to be active for ethene polymerization after activation with methylaluminoxane (MAO) [23–29].

We have discovered that there are many vanadium compounds with diiminopyridyl ligand systems that are highly active and selective catalysts for the oligomerization of ethene [21] when activated with MAO. This paper describes the synthesis and gives analytical data for a series of synthesized vanadium(III) and respective iron(II) complexes. Subsequent publications (paper II and III of this series) illustrate the catalytic performance (paper II [30]) and study the catalyst activation with methyl aluminoxane (MAO) via ultraviolet–visible spectroscopy (UV–vis (paper III [31])). We believe that this class of new compounds has great commercial potential for producing high purity α -olefin oligomers that are in high demand.

In this paper, we describe the synthesis and characterization of a series of new vanadium(III) diiminopyridyl complexes and their iron(II) counterparts. In part 2 of this series of papers [30] we will discuss the catalytic behavior of these compounds for the oligomerization and polymerization of ethene and the properties of the resulting products. Part 3 of this series [31] will focus on structural changes that occur after adding MAO to the vanadium or iron complexes.

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Their behavior towards other α -olefins is reported elsewhere [32].

The analytical data are consistent with the results reported by Reardon et al. [22].

2. Results and discussion

The discovery [21] that vanadium(III) diiminopyridyl complexes are highly active ethene oligomerization catalysts that are also highly selective for linear α -olefin production sparked our interest in synthesizing the complexes described below. Differently substituted anilines were selected as the ligand precursors based on their potential ability to alter the olefin polymerization and/or oligomerization behavior of the resulting, activated vanadium and iron complexes.

2.1. Synthesis of the ligands 1–19

Diacetylpyridine is reacted with suitable substituted aniline in a condensation reaction (Schiff's base reaction [15,33]) to give the corresponding diiminopyridyl ligands 1–19 (Fig. 1).

2.2. Characterization of the prepared ligands 1–19

The ligands 1–19 were prepared in accordance with the described procedure and analyzed via ^1H NMR, ^{13}C NMR spectroscopy and mass spectrometry (Table 1).

2.3. Preparation of the catalyst precursors 20–38 and 39–57

Complexes 20–38 were synthesized by combining the ligand and the metal in an addition reaction. Ligands 1–19 were added (Fig. 2) to the vanadium(III) chloride-THF adduct in diethyl ether. Compounds 39–57 are the corresponding

iron(II) chloride complexes some of which were already described elsewhere [20,33–36] and references therein).

2.4. Characterization of complexes 20–38 and 39–57

All prepared complexes were analyzed by mass spectrometry. In addition, some were analyzed by elemental analyses. Due to the paramagnetism of the used metals and their limited solubility in common deuterated solvents, no suitable NMR data were obtained.

The obtained data are listed in Table 2. Surprisingly, most of the vanadium(III) complexes lose one chloride during the MS-measurement. The highest molecular mass peaks are, therefore, lower than expected ($M^+ - \text{Cl}$) in the case of vanadium. This behavior is congruent with the observed formation of several different species after activation unlike the corresponding iron(II) complexes (part 3 of this series [31]).

2.4.1. Elemental analyses of selected catalysts

In addition to the NMR measurements of the ligands and MS data of the complexes, selected vanadium and iron complexes were also characterized by C, H, N combustion analyses (Table 3). The data shown are the average of two measurements.

Elemental analyses helped to confirm the structure of the complex. This was especially important in the case of the vanadium complexes as the MS data always indicated the loss of one chloride atom. The molecular ion was not detected for any of these complexes.

3. Discussion

In this publication (part I of III), we describe the synthesis and analysis of vanadium(III) and iron(II) compounds with diiminopyridyl ligand systems oligomerize ethene when activated with MAO.

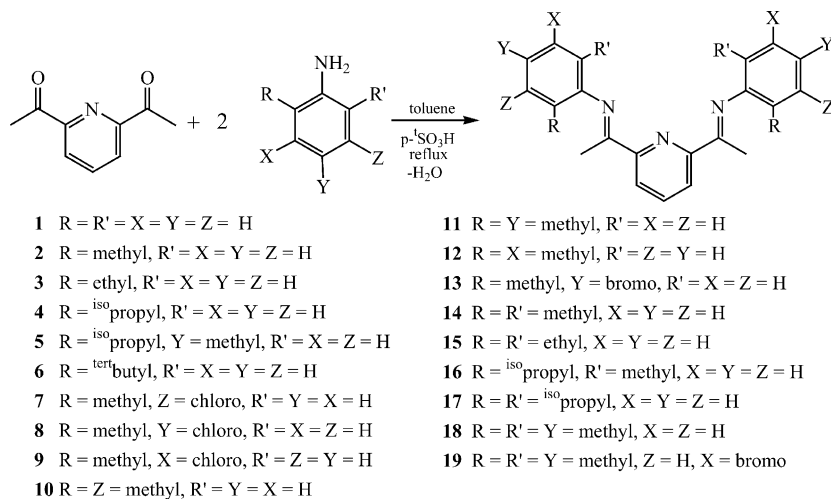


Fig. 1. Synthesis of the ligands 1–19.

Table 1
NMR spectroscopic and mass spectrometric data of the synthesized ligands

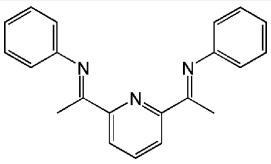
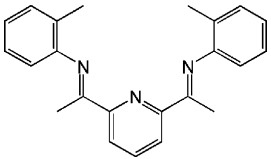
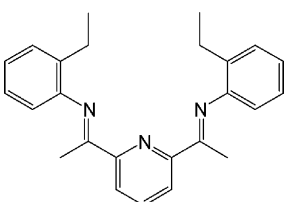
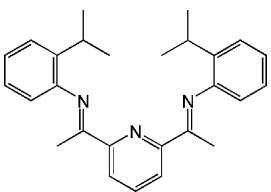
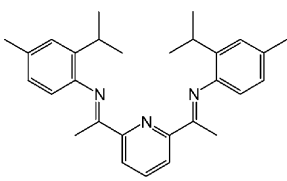
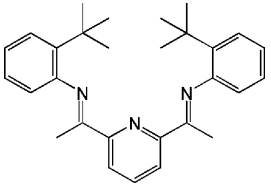
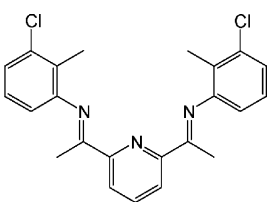
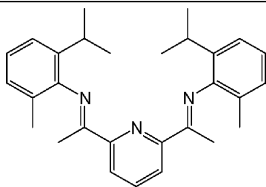
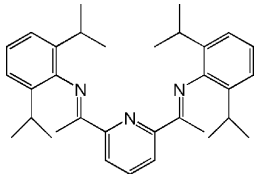
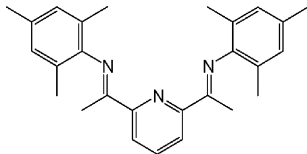
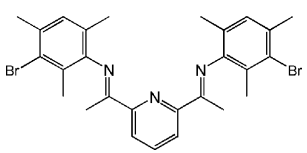
No.	Ligand	^1H NMR ^a	^{13}C NMR ^b	MS M^+ (m/e)
1		8.14 (d, 1H), 7.59 (t, 2H), 7.25–6.66 (m, 10H), 2.15 (s, 6H)	(C _q): 166.6, 160.8, 152.4 (CH): 138.7, 128.9, 124.1, 123.3, 119.7 (CH ₃): 16.5	313
2		8.13 (d, 1H), 7.86 (t, 2H), 7.22–6.69 (m, 8H), 2.31 (s, 6H), 2.13 (s, 6H)	(C _q): 164.6, 154.7, 148.7, 133.1 (CH): 138.5, 130.1, 125.5, 124.3, 123.2, 118.4 (CH ₃): 18.0, 16.4	341
3		8.40 (d, 2H), 7.89 (t, 1H), 7.27–7.05 (m, 8H), 6.67 (d, 2H), 2.51 (q, 4H), 2.37 (s, 6H), 1.18 (t, 6H)	(C _q): 165.5, 164.8, 146.6, 137.5 (CH): 138.9, 131.8, 131.0, 123.5, 121.7, 117.0 (CH ₃): 16.4, 12.8	369
4		8.14 (d, 1H), 7.59 (d, 2H), 7.26–6.67 (m, 8H), 3.00 (sept, 2H), 2.13 (s, 6H), 1.21 (d, 12H)	(C _q): 166.6, 155.5, 148.7, 138.1 (CH): 136.8, 126.1, 125.7, 124.0, 122.2, 118.4, 28.5 (CH ₃): 22.8, 16.4	397
5		8.49 (d, 2H), 7.92 (t, 1H), 7.19–6.99 (m, 6H), 2.82 (sept, 2H), 2.25 (s, 6H), 2.03 (s, 6H), 1.16 (d, 12H)	(C _q): 166.3, 155.1, 148.5, 136.3, 125.1, 121.9 (CH): 137.9, 123.5, 26.8 (CH ₃): 28.4, 22.8, 16.4	425
6		8.14 (d, 1H), 7.59 (d, 2H), 7.19–6.80 (m, 8H), 2.11 (s, 6H), 1.18 (s, 18H)	(C _q): 170.2, 158.5, 148.2, 139.0, 35.5 (CH): 138.0, 128.4, 125.3, 124.0, 123.8, 123.1 (CH ₃): 31.2, 16.2	425
7		8.39 (d, 1H), 7.90 (t, 2H), 7.16–7.09 (m, 2H), 6.92–6.81 (dt, 2H), 6.62–6.55 (m, 2H), 2.34 (s, 6H), 2.17 (s, 6H)	(C _q): 167.7, 155.1, 151.0, 131.6, 125.7 (CH): 137.1, 131.7, 131.4, 123.5, 122.6, 118.4, 114.6 (CH ₃): 17.4, 16.6	($M^+ - 1$): 409

Table 1 (Continued)

No.	Ligand	¹ H NMR ^a	¹³ C NMR ^b	MS M ⁺ (m/e)
8		8.37 (d, 2H), 7.88 (t, 1H), 7.14 (d, 2H), 6.99 (d, 2H), 6.70 (s, 2H), 2.34 (s, 6H), 2.06 (s, 6H)	(C _q): 164.9, 152.6, 151.1, 132.1, 129.3 (CH): 135.9, 131.9, 127.3, 126.4, 122.3 (CH ₃): 14.2, 12.3	410
9		8.38 (d, 1H), 7.89 (t, 2H), 7.25–6.64 (m, 6H), 2.34 (s, 6H), 2.12 (s, 6H)	(C _q): 167.5, 155.1, 151.2, 135.2, 125.4 (CH): 137.0, 127.0, 124.3, 122.5, 119.4, 116.7, 113.3 (CH ₃): 16.5, 14.7	(M ⁺ - 1): 409
10		8.40 (d, 1H), 7.87 (t, 2H), 7.12–6.52 (m, 6H), 2.30 (s, 12H), 2.04 (s, 6H)	(C _q): 164.9, 156.1, 149.4, 133.7, 121.1 (CH): 138.4, 131.0, 124.5, 124.0, 120.0 (CH ₃): 20.0, 16.0, 13.8	369
11		8.38 (d, 1H), 7.86 (t, 2H), 7.04–6.56 (m, 6H), 2.32 (s, 12H), 2.09 (s, 6H)	(C _q): 166.9, 155.1, 147.4, 132.9, 127.1 (CH): 136.7, 131.1, 126.9, 122.1, 118.1 (CH ₃): 20.8, 17.7, 16.2	369
12		8.36 (d, 2H), 7.86 (t, 1H), 7.10 (d, 2H), 6.84 (d, 2H), 6.50 (s, 2H), 2.32 (s, 6H), 2.31 (s, 6H), 2.05 (s, 6H)	(C _q): 168.5, 155.3, 149.8, 136.7, 123.7, 122.1 (CH): 135.9, 130.2, 124.2, 122.1, 118.6 (CH ₃): 21.0, 17.3, 16.3	369
13		8.39 (d, 2H), 7.91 (t, 1H), 7.28 (d, 2H), 7.24 (s, 2H), 6.55 (d, 2H), 2.32 (s, 6H), 2.08 (s, 6H)	(C _q): 167.6, 153.1, 151.2, 132.2, 129.4 (CH): 137.0, 125.0, 127.3, 124.5, 123.4 (CH ₃): 14.7, 12.1	499
14		8.23 (d, 1H), 7.86 (t, 2H), 7.04–6.52 (m, 6H), 2.13 (s, 6H)	(C _q): 167.2, 155.1, 148.7, 136.4, 125.4, 122.2 (CH): 127.9, 123.0 (CH ₃): 18.0, 16.5	369
15		8.36 (d, 1H), 7.90 (d, 2H), 7.12–6.70 (m, 4H), 2.63–2.25 (m, 8H), 2.22 (s, 6H), 1.22–1.05 (m, 12H)	(C _q): 166.9, 155.1, 136.9 (CH): 147.8, 131.2, 127.7, 126.0, 125.9, 123.3, 122.2 (CH ₂): 24.6, 24.3 (CH ₃): 16.8, 13.8, 13.0	425

Table 1 (Continued)

No.	Ligand	¹ H NMR ^a	¹³ C NMR ^b	MS <i>M</i> ⁺ (<i>m/e</i>)
16		8.30 (d, 1H), 7.88 (d, 2H), 7.10–6.65 (m, 6H), 2.90 (sept, 2H), 2.30 (s, 6H) 2.12 (s, 6H), 1.22 (dd, 12H)	(C _q): 166.0, 156.1, 142.6, 136.1 (CH): 145.8, 130.0, 126.8, 125.4, 125.0, 120.3 (CH ₃): 22.4, 16.8, 13.8, 13.0	425
17		7.85 (d, 1H), 7.20 (d, 2H), 6.88–6.72 (m, 6H), 2.88 (sept, 4H), 2.12 (s, 6H), 1.20 (dd, 24H)	(C _q): 167.1, 158.2, 145.6, 138.2 (CH): 138.8, 125.8, 123.9, 122.4 (CH ₃): 26.1, 23.3, 16.6	481
18		8.36 (d, 1H), 7.88 (t, 2H), 6.95–6.75 (m, 4H), 2.32 (s, 18H), 1.90 (s, 6H)	(C _q): 167.4, 155.2, 146.2, 132.2, 125.3 (CH): 136.8, 128.5, 122.1 (CH ₃): 20.7, 17.9, 16.4	397
19		8.45 (d, 1H), 7.90 (t, 2H), 6.98 (d, 2H), 2.39 (s, 6H), 2.22 (s, 6H), 2.15 (s, 6H), 1.97 (s, 6H)	(C _q): 167.9, 154.8, 147.1, 132.2, 125.2, 124.0 (CH): 136.7, 129.5, 122.2 (CH ₃): 23.3, 18.3, 17.5, 16.4	556

^a 25 °C, in chloroform-*d*₁, δ (ppm) rel. chloroform-*d*₁ (7.24).

^b 25 °C, in chloroform-*d*₁, δ (ppm) rel. chloroform-*d*₁ (77.0).

MS-data revealed that most vanadium(III) complexes lose one chloride during the measurement whereas the respective iron(II) complexes are stable. The highest molecular mass peaks are, therefore, lower than expected (*M*⁺ – Cl) in the case of vanadium.

Table 2
Analytical data of the V(III) and Fe(II) complexes, respectively

V(III) complex no.	MS <i>M</i> ⁺ (<i>m/e</i>)	Fe(II) complex no.	MS <i>M</i> ⁺ (<i>m/e</i>)
20	Inconclusive	39	439 (<i>M</i> ⁺ – H) (see C, H, N analysis)
21	464/462 (<i>M</i> ⁺ – Cl)	40	467 (<i>M</i> ⁺ – H)
22	491 (<i>M</i> ⁺ – Cl)	41	496 (<i>M</i> ⁺)
23	519 (<i>M</i> ⁺ – Cl)	42	524 (<i>M</i> ⁺)
24	546 (<i>M</i> ⁺ – HCl)	43	551 (<i>M</i> ⁺ – H)
25	545 (<i>M</i> ⁺ – HCl)	44	552 (<i>M</i> ⁺)
26	532 (<i>M</i> ⁺ – Cl)	45	537 (<i>M</i> ⁺)
27	532 (<i>M</i> ⁺ – Cl)	46	537 (<i>M</i> ⁺)
28	Inconclusive (<i>M</i> ⁺ – Cl)	47	537 (<i>M</i> ⁺)
29	491 (<i>M</i> ⁺ – Cl)	48	495 (<i>M</i> ⁺ – H)
30	490 (<i>M</i> ⁺ – HCl)	49	495 (<i>M</i> ⁺ – H)
31	491 (<i>M</i> ⁺ – Cl)	50	496 (<i>M</i> ⁺)
32	605 (inconclusive)	51	626 (<i>M</i> ⁺)
33	491 (<i>M</i> ⁺ – Cl)	52	495 (<i>M</i> ⁺ – H)
34	547 (<i>M</i> ⁺ – Cl)	53	551 (<i>M</i> ⁺ – H)
35	547 (<i>M</i> ⁺ – Cl)	54	551 (<i>M</i> ⁺ – H)
36	603 (<i>M</i> ⁺ – Cl)	55	607 (<i>M</i> ⁺ – H)
37	519 (<i>M</i> ⁺ – Cl)	56	523 (<i>M</i> ⁺ – H)
38	677 (<i>M</i> ⁺ – Cl)	57	682 (<i>M</i> ⁺)

The unsubstituted iron(II) complex, **39**, behaved differently from all the others [13,17,37,38] after activation with MAO and during polymerization/oligomerization experiments (as will be shown in part II [30]). In this case, the chlorine content was determined in order to obtain information as to why only this complex showed no oligomerization or polymerization activity after adding MAO. Due to the lack of steric hindrance, it might be conceivable that complex **39** forms a chlorine-bridged dimer, which would have resulted in a change in the chlorine content, but elemental analysis eliminated this possibility. Or, it could be speculated that it forms a salt-like structure of the following formula [Fe(ligand)₂][FeCl₄] similar to the corresponding terpyridine complex [39–41].

In an attempt to further investigate this behavior we synthesized the isostructural complexes of Ligand 39 with iron bromide and iron iodide (not shown). The obtained complexes showed activity after activation with MAO.

Reiff et al. synthesized the (terpyridine)FeBr₂ and (terpyridine)FeI₂ complexes and showed that these compounds are monomeric [39]. The corresponding CoCl₂ complex was isolated and analyzed by X-ray crystallography [42]. It was determined that the cobalt complex was monomeric as well.

At this point, we have not been able to derive conclusively from the available data what renders complex **39** inactive towards olefins after the addition of MAO.

20	R = R' = X = Y = Z = H; M = V (III);	39	M = Fe (II);
21	R = methyl; R' = X = Y = Z = H; M = V (III);	40	M = Fe (II);
22	R = ethyl; R' = X = Y = Z = H; M = V (III);	41	M = Fe (II);
23	R = ^{iso} propyl; R' = X = Y = Z = H; M = V (III);	42	M = Fe (II);
24	R = ^{iso} propyl; R' = X = Z = H; Y = methyl; M = V (III);	43	M = Fe (II);
25	R = ^{tert} butyl; R' = X = Y = Z = H; M = V (III);	44	M = Fe (II);
26	R = methyl; Z = chloro; R' = X = Y = H; M = V (III);	45	M = Fe (II);
27	R = methyl; Y = chloro; R' = X = Z = H; M = V (III);	46	M = Fe (II);
28	R = methyl; X = chloro; R' = Y = Z = H;	47	M = Fe (II);

	M = V (III);		
29	R = Z = methyl; R' = X = Y = H; M = V (III);	48	M = Fe (II);
30	R = Y = methyl; R' = X = Z = H; M = V (III);	49	M = Fe (II);
31	R = X = methyl; R' = Y = Z = H; M = V (III);	50	M = Fe (II);
32	R = methyl; Y = bromo; R' = X = Z = H; M = V (III);	51	M = Fe (II);
33	R = R' = methyl; X = Y = Z = H; M = V (III);	52	M = Fe (II);
34	R = R' = ethyl; X = Y = Z = H; M = V (III);	53	M = Fe (II);
35	R = ^{iso} propyl; R' = methyl; X = Y = Z = H; M = V (III);	54	M = Fe (II);
36	R = R' = ^{iso} propyl; X = Y = Z = H; M = V (III);	55	M = Fe (II);
37	R = R' = Y = methyl; X = Z = H; M = V (III);	56	M = Fe (II);
38	R = R' = Y = methyl; Z = H; X = bromo; M = V (III);	57	M = Fe (II)

Fig. 2. Synthesis of the catalyst precursors 20–38 and 39–57.

4. Experimental

Ligand syntheses were carried out in air. All complex preparations were performed under inert gas conditions, in the absence of moisture and oxygen, using standard Schlenk or glove box techniques. Purified and dried nitrogen was used as the inert gas.

All solvents were purchased as technical grade and purified by distillation over Na/K alloy under a nitrogen atmosphere. All other chemicals were purchased commercially or were synthesized according to literature procedures.

NMR spectra of the ligands were recorded in CDCl₃ at 25 °C on a Bruker ARX 250 instrument. The chemical shifts of ¹H NMR spectra were referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for CHCl₃); the carbon resonances in ¹³C NMR spectra were

Table 3
Elemental analyses data of selected V(III) and Fe(II) complexes

No.	Measured (%)	Calculated (%)
Fe: 39 ^a	C: 54.70 H: 4.35 Cl: 16.11	C: 54.13 H: 4.37 Cl: 16.10
V: 21	C: 55.34 H: 5.19 N: 7.61	C: 55.39 H: 4.95 N: 8.03
V: 31 ^a	C: 57.01 H: 5.20	C: 56.99 H: 5.16
V: 26	C: 46.93 H: 3.82 N: 6.92	C: 48.67 H: 3.73 N: 7.40
Fe: 42	C: 60.61 H: 6.30 N: 7.53	C: 61.85 H: 5.96 N: 8.01
V: 33	C: 59.61 H: 6.02 N: 7.25	C: 58.80 H: 5.57 N: 7.98
Fe: 52	C: 60.87 H: 5.95 N: 7.77	C: 60.49 H: 5.68 N: 8.17
V: 36	C: 57.76 H: 6.07 N: 6.99	C: 61.03 H: 6.28 N: 6.58
Fe: 55	C: 65.26 H: 7.22 N: 7.13	C: 65.14 H: 7.12 N: 6.91
Fe: 37	C: 60.80 H: 6.09 N: 7.81	C: 61.85 H: 5.96 N: 8.01

^a N not available.

also referenced to the solvent signal ($\delta = 77.0$ ppm for CDCl₃).

Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV).

Elemental analyses were performed using a Carlo Erba elemental analyzer EA-1108. Determination of C, H, N is based on the quantitative 'dynamic flash combustion' method. Samples were enclosed in a tin container and purged with a continuous flow of helium. After dropping the tin container in the combustion furnace (1020 °C), the helium is enriched with pure oxygen. In the resulting flash combustion, the container and sample are entirely oxidized. The obtained gas mixture is then passed over copper to remove excess oxygen and to reduce nitrogen oxides to elemental nitrogen. In a chromatographic column (Porapak PQS), the individual components are separated and quantitatively analyzed by a thermal conductivity detector connected to a workstation (EAGER 200).

4.1. General procedure for the preparation of the ligands (condensation reaction)

To a stirred solution of the corresponding diketopyridine in toluene 0.05 g of *p*-toluenesulfonic acid was added. The

aniline compound was added in excess. The mixture was refluxed and the water formed was separated via a Dean–Stark trap. Refluxing was continued for, at least, 3 h and up to 25 h (depending on the aniline added). The length of reflux time for the reaction was controlled via GC or GC/MS analysis.

After cooling to room temperature the mixture was washed twice with a diluted solution of Na₂CO₃ in water and twice with water. The organic layer was separated and the water phase was extracted twice with diethyl ether. The combined organic layers were dried over Na₂SO₄ and evaporated to dryness.

Ethanol was added to the residue. If crystallization did not occur immediately the solution was stored at –20 °C overnight.

The resulting crystals were filtered off, washed with cold ethanol and dried in air. The liquid residue was reduced in volume to about 30–40% of the original volume. A second crop of crystals was obtained after storing at –20 °C overnight.

Overall yield was 80–90%.

4.2. General procedure for the preparation of the vanadium(III) complexes

To a stirred solution of the corresponding ligand in either diethyl ether or a mixture of diethyl ether/tetrahydrofuran a stoichiometric amount of vanadium trichloride-tetrahydrofuran adduct was added at room temperature. Stirring was continued overnight. Filtration of the formed solids under inert conditions, washing with diethyl ether and drying of the solids in vacuo gave an overall yield of 50–75%.

4.3. General procedure for the preparation of the iron(II) complexes

To a stirred solution of the corresponding ligand in diethyl ether a stoichiometric amount of iron dichloride was added at room temperature. Stirring was continued overnight. The precipitated blue solids were filtered under inert conditions and washed with diethyl ether. Drying of the solids in vacuo gave an overall yield of 65–80%.

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