FULL PAPER

Vanadium(III) complexes containing phenoxy-imine-thiophene ligands: Synthesis, characterization and application to homo- and copolymerization of ethylene

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Osvaldo de L. Casagrande Jr, Laboratory of Molecular Catalysis, Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Porto Alegre, RS, 91501-970, Brazil. Email: osvaldo.casagrande@ufrgs.br A set of vanadium(III) complexes, namely $\{SNO\}VCl_2(THF)_2$ (2a, SNO = thiophene-(N=CH)-phenol; 2b, SNO = 5-phenylthiophene-(N=CH)-phenol; 2c, SNO = 5-phenylthiophene-(N=CH)-4-tert-butylphenol; 2d, SNO = 5-methylthiophene-(N=CH)-phenol; 2e, SNO = 5-methylthiophene-(N=CH)-4-tert-butyl-SNO 5-methylthiophene-(N=CH)-2-methylphenol; phenol; 2f, = 2g. SNO = 5-methylthiophene-(N=CH)-4-fluorophenol), were synthesized by reaction of VCl₃(THF)₃ with phenoxy-imine-thiophene proligands (1a-g). All vanadium (III) complexes were characterized using elemental analysis and infrared and electron paramagnetic resonance spectroscopies. Upon activation with methylaluminoxane (MAO), vanadium precatalysts 2a-g proved active in the polymerization of ethylene (213.6–887.2 kg polyethylene $(mol[V])^{-1} \cdot h^{-1}$), yielding high-density polyethylenes with melting temperatures in the range 133-136 °C and crystallinities varying from 28 to 41%. The 2e/MAO catalyst system was able to copolymerize ethylene with 1-hexene affording poly(ethylene-co-1-hexene)s with melting temperatures varying from 126 to 102 °C and co-monomer incorporation in the range 3.60-4.00%.

KEYWORDS

ethylene polymerization, ethylene–1-hexene copolymerization, phenoxyimine ligands, vanadium(III) complexes

1 | INTRODUCTION

Polyolefin materials are used in a wide variety of applications, including grocery bags, containers, toys, adhesives, home appliances, engineering plastics, automotive parts, medical applications and prosthetic implants, and account for about 60% of the global thermoplastic polymer market.^[1] Besides the homopolymers of ethylene and propylene, copolymerization of ethylene with α -olefins generates an important class of commodity plastics (linear low-density polyethylene). In this context, the design and synthesis of efficient non-metallocene catalysts for olefin polymerization have grown considerably over the past few decades largely due to the remarkable variety of non-cyclopentadienyl ligands

available and their high performance in the production of polyolefin products.^[2] Among the variety of catalysts that have been used for this purpose, vanadium-based complexes have been extensively investigated for the production of high-molecular-weight polyethylene (PE) as well as ethylene– α -olefin with high co-monomer incorporations.^[3] However, one deficiency associated with the use of vanadium catalysts is the loss of activity at elevated temperatures due to the reduction of catalytically active vanadium species to inactive species (typically to V(II)).^[3c,4] In order to overcome this problem, several classes of neutral and anionic ligands have been employed to generate more robust and thermally stable vanadium catalysts. In particular, many well-defined and highly active homogeneous vanadium(III) catalysts with bi-

and tridentate ligands have been described in the literature and their polymerization activity investigated.^[5] Selected examples are presented in Chart 1. For instance, Gambarotta and co-workers found that bis(imino)pyridine vanadium(III) complexes showed high catalytic activity towards ethylene polymerization and produced bimodal molecular weight distribution PEs.^[5a] In 2003, Fujita and co-workers described a highly active (65 100 kg of PE (mol[V])⁻¹·h⁻¹ at 75 °C) and thermally robust vanadium catalyst bearing two phenoxyimines for ethylene polymerization (Chart 1).^[5b]

Li and co-workers described the synthesis and characterization of vanadium(III) complexes bearing salicylaldiminato ligands. In the presence of Et₂AlCl, these salicyladiminato vanadium complexes were highly active catalysts for ethylene polymerization at 25 °C (up to 22 300 kg of PE $(mol[V])^{-1} \cdot h^{-1} \cdot bar^{-1}$, and afforded highmolecular-weight polymers ($M_{\rm w} > 100 \text{ kg mol}^{-1}$) with unimodal molecular weight distributions.^[5c] More recently, Golisz and Bercaw reported that a vanadium(III) complex containing bis(phenoxy)pyridine ligand showed remarkable catalytic activity for propylene polymerization in the presence of methylaluminoxane (MAO) (803 kg of polypropyl- $(mol[V])^{-1} \cdot h^{-1})$ affording high-molecular-weight ene polypropylene with uniform molecular weight distribution $(M_{\rm w} = 1.17 \times 10^6 \text{ g mol}^{-1}; M_{\rm w}/M_{\rm n} = 2.03).^{[5d]}$

As part of our investigation of tridentate chelating ligands in oligomerization and polymerization catalysis,^[6] we have been interested in preparing a new set of vanadium(III) complexes containing phenoxyimine ligands with pendant thiophene group. Herein, we report the synthesis and characterization of a series of vanadium(III) complexes supported by phenoxy–imine–thiophene ligands and investigate the catalytic performance in polymerization of ethylene and copolymerization of ethylene with 1-hexene using MAO as co-catalyst. We anticipated that the nature of the ligand would significantly affect polymerization behavior as well as polymer properties. Furthermore, we discuss the performance of these vanadium precatalysts,



CHART 1 Selected examples of vanadium(III) complexes successfully applied in homo- and copolymerization of ethylene with α -olefins

evaluating the influence of some experimental parameters on catalyst activity and polymer properties.

2 | EXPERIMENTAL

2.1 | General considerations

All manipulations involving air- and/or water-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Toluene, tetrahydrofuran (THF), pentane and hexane (Et₂O) were dried using a Braun MB-SPS-800 solvent purification system. Others solvents were dried using the appropriate drying agents under argon before use. VCl₃(THF)₃, 2.4-di-*tert*-butylsalicylaldehyde, 2-thiophenecarbaldehyde, 5-phenylthiophene-2-carboxaldehyde, 2-aminophenol, 2amino-4-tert-butylphenol and 2-amino-4-fluorophenol were purchased from Sigma-Aldrich and used as received. Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated molecular sieves prior to use. MAO (Witco, 5.21 wt% Al solution in toluene, 20% TMA) was used as received. Infrared (IR) spectra were obtained with a Bruker FT-IR Alpha spectrometer. NMR spectra were recorded with a Varian Inova 300 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm versus SiMe₄ and were determined by reference to the residual solvent peaks. ¹³C NMR spectra of the copolymers were recorded with a Varian Inova 300 NMR spectrometer at 125 °C with $C_6D_6-o-C_6H_4Cl_2$ as the solvent. Electron paramagnetic resonance (EPR) experiments were performed at X-band using a Bruker EMX micro-X spectrometer. Elemental analysis was performed by the Analytical Central Service of the Institute of Chemistry-USP (Brazil) and is the average of two independent determinations. Melting temperatures were determined using differential scanning calorimetry (DSC) with a TA Instruments DSC-Q20 at a heating rate of 10 °C min⁻¹ after twice previous heating to 180 °C and cooling to 40 °C at 10 °C min⁻¹.

2.2 | Synthesis of phenoxy-imine-thiophene ligands

2.2.1 | Thiophene-(N=CH)-phenol (1a)^[7]

To a stirred solution of 2-thiophenecarbaldehyde (0.4486 g, 4.00 mmol) in ethanol, 2-aminophenol (0.4365 g, 4.00 mmol) and formic acid (3 drops) were added. The reaction mixture was stirred for 72 h at 35 °C. The final reaction mixture was evaporated to dryness, and recrystallized from THF–hexane to give **1a** as yellow crystals (0.5500 g, 68%); m.p. 79.0 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.79 (s, 1H), 7.52 (2H, m), 7.28 (1H, m), 7.16 (3H, m), 7.00 (1H, dd), 6.89 (1H, td). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 115.00; 115.74, 120.01, 127.96, 128.72, 130.64, 132.45, 135.02, 142.81, 149.62, 152.19. IR (ATR, cm⁻¹): 3337 (w), 1608 (s), 1591 (s), 1577 (s), 1480 (s), 1417 (m), 1376 (m),

1354(m), 1295 (m), 1255 (s), 1218 (s), 1176 (s), 1149 (m), 1101 (m), 1048 (m), 1036 (m), 969 (m), 925 (w), 880 (w), 864 (w), 813 (s), 743 (s), 734 (s), 717 (s), 578 (m), 499 (m). Anal. Calcd for $C_{11}H_9NOS$ (%): C, 65.00; H, 4.46; N, 6.89. Found (%): C, 65.12; H, 4.53; N, 7.16.

2.2.2 | 5-Phenylthiophene-(N=CH)-phenol (1b)

Ligand 1b was prepared as described above for 1a, starting 5-phenylthiophene-2-carboxaldehyde from (0.1883)g, 1.00 mmol) and 2-aminophenol (0.1091 g, 1.00 mmol). The reaction mixture was stirred for 24 h at 35 °C. Ligand 1b was obtained as a yellow solid after recrystallization from THF-hexane (0.2400 g, 87%); m.p. 133.9 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.75 (1H, s), 7.69 (2H, m), 7.36 (5H, m), 7.19 (2H, m), 7.01 (1H, dd), 6.90 (1H, td). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 115.13, 115.81, 120.22, 123.96, 126.29, 128.81, 128.93, 129.25, 133.74, 133.78, 135.23, 142.07, 149.65, 149.72, 152.48. IR (ATR, cm⁻¹): 3410 (w), 1605 (w), 1583 (m), 1571 (m), 1495 (w), 1482 (m), 1453 (m), 1438 (m), 1361 (w), 1349 (w), 1319 (w), 1292 (w), 1250 (m), 1203 (m), 1172 (m), 1146 (m), 1057 (m), 1033 (m), 958 (m), 907 (w), 812 (s), 750 (s), 686 (s), 579 (s), 539 (m), 483 (s), 437 (m). Anal. Calcd for C₁₇H₁₃NOS (%): C, 73.09; H, 4.69; N, 5.01. Found (%): C, 72.76; H, 4.50; N, 4.60.

2.2.3 | 5-Phenylthiophene-(N=CH)-4-tert-butyl-phenol (1c)

Ligand 1c was prepared as described above for 1a, starting from 5-phenylthiophene-2-carboxaldehyde (0.1883 g, 1.00 mmol) and 2-amino-4-tert-butylphenol (0.1652 g, 1.00 mmol). The reaction mixture was stirred for 72 h at 35 °C. Ligand 1c was obtained as a yellow solid after recrystallization from THF-hexane (0.2600 g, 78%); m.p. 120.9 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.76 (1H, s), 7.69 (2H, m), 7.48 (1H, d), 7.43 (2H, m), 7.36 (2H, m), 7.29 (1H, d), 7.23 (1H, dd), 7.04 (1H, s), 6.94 (1H, d), 1.34 (9H, s). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 31.61, 34.47, 112.45, 114.49, 123.81, 125.92, 126.16, 128.62, 129.10, 133.30, 133.71, 134.33, 142.07, 143.00, 148.99, 149.30, 149.91. IR (ATR, cm⁻¹): 3453 (w), 2955 (m), 2861 (w), 1610 (m), 1584 (s), 1501 (m), 1455 (s), 1440 (m), 1362 (m), 1342 (w), 1280 (m), 1245 (m), 1214 (s), 1168 (m), 1095 (w), 1060 (m), 1025 (w), 958 (m), 927 (m), 877 (m), 821 (s), 807 (m), 754 (s), 687 (s), 634 (m), 588 (m), 529 (s), 479 (s), 427 (m). Anal. Calcd for C₂₁H₂₁NOS (%): C, 75.19; H, 6.31; N, 4.18. Found (%): C, 74.82; H, 6.42; N, 4.04.

2.2.4 | 5-Methylthiophene-(N=CH)-phenol (1d)^[8]

Ligand **1d** was prepared as described above for **1a**, starting from 5-methylthiophene-2-carboxaldehyde (0.5047 g, 4.00 mmol) and 2-aminophenol (0.4365 g, 4.00 mmol). The reaction mixture was stirred for 48 h at 35 °C. Ligand **1d** was obtained as a yellow solid after recrystallization from THF–hexane (0.6400 g, 74%); m.p. 70.5 °C. ¹H NMR

(300 MHz, CDCl₃, δ , ppm): 8.67 (1H, s), 7.35 (1H, m), 7.24 (1H, d), 7.16 (1H, td), 6.99 (1H, dd), 6.88 (1H, td), 6.82 (1H, d), 2.56 (3H, s). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 16.23, 115.08, 115.72, 120.18, 126.60, 128.68, 133.33, 135.47, 140.85, 146.77, 149.92, 152.20. IR (ATR, cm⁻¹): 3341 (w), 3064 (w), 3039 (w), 2910 (w), 1615 (s), 1586 (s), 1490 (w), 1461 (s), 1366 (s), 1286 (w), 1250 (s), 1230 (s), 1145 (m), 1046 (m), 1025 (m), 953 (m), 927 (m), 810 (m), 790 (s), 739 (s), 606 (s), 575 (m), 507 (s), 478 (m), 424 (m). Anal. Calcd for C₁₂H₁₁NOS (%): C, 66.13; H, 5.10; N, 6.45. Found (%): C, 65.89; H, 5.07; N, 6.37.

2.2.5 | 5-Methylthiophene-(N=CH)-4-tert-butyl-phenol (1e)

Ligand 1e was prepared as described above for 1a, starting from 5-methylthiophene-2-carboxaldehyde (0.5047 g, 4.00 mmol) and 2-amino-4-tert-butylphenol (0.6609 g, 4.00 mmol). The reaction mixture was stirred for 72 h at 35 °C. Ligand 1e was obtained as a yellow solid after recrystallization from THF-hexane (0.7500 g, 69%); m.p. 99.3 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.58 (1H, s), 7.15 (2H, m), 7.10 (1H, m), 6.83 (1H, d), 6.72 (1H, d), 2.46 (3H, s), 1.23 (9H, s). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 16.20, 31.72, 34.53, 112.61, 114.42, 125.64, 126.61, 133.09, 134.60, 143.07, 149.54, 149.83. IR (ATR, cm⁻¹): 3419 (m), 2953 (m), 2862 (w), 1611 (m), 1588 (s), 1499 (m), 1466 (s), 1440 (m), 1363 (m), 1276 (m), 1219 (s), 1167 (m), 1053 (m), 966 (m), 929 (m), 876 (m), 813 (s), 749 (w), 705 (w), 638 (m), 584 (s), 570 (s), 559 (s), 509 (s), 420 (m). Anal. Calcd for C₁₆H₁₉NOS (%): C, 70.29; H, 7.00; N, 5.12. Found (%): C, 69.64; H, 6.57; N, 5.06.

2.2.6 | 5-Methylthiophene-(N=CH)-2-methylphenol (1f)

Ligand 1f was prepared as described above for 1a, starting from 5-methylthiophene-2-carboxaldehyde (0.5047 g, 4.00 mmol) and 2-amino-2-methylphenol (0.4926 g, 4.00 mmol). The reaction mixture was stirred for 72 h at 35 °C. Ligand 1f was obtained as a yellow solid after recrystallization from THF-hexane (0.7500 g, 69%); m.p. 82.0 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.66 (1H, s), 7.29 (1H, d), 7.09 (1H, d), 7.01 (1H, d), 6.79 (2H, m), 2.55 (3H, s), 2.29 (3H, s). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 15.69, 16.05, 112.99, 119.22, 124.28, 126.45, 129.59, 132.90, 134.66, 140.92, 146.30, 149.52, 150.45. IR (ATR, cm⁻¹): 3332 (m), 2908 (w), 2844 (w), 1620 (m), 1595 (s), 1456 (s), 1360 (m), 1314 (m), 1281 (w), 1248 (s), 1210 (s), 1158 (s), 1083 (m), 1043 (m), 1010 (m), 965 (m), 940 (w), 830 (m), 802 (s), 788 (s), 711 (s), 734 (s), 695 (w), 634 (s), 559 (m), 506 (m), 490 (s), 435 (m). Anal. Calcd for C₁₃H₁₃NOS (%): C, 67.50; H, 5.66; N, 6.06. Found (%): C, 67.22; H, 5.52; N. 6.02.

2.2.7 | 5-Methylthiophene-(N=CH)-4-fluorophenol (1g)

Ligand **1g** was prepared as described above for **1a**, starting from 5-methylthiophene-2-carboxaldehyde (0.5047 g,

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4.00 mmol) and 2-amino-4-fluorophenol (0.5085 g, 4.00 mmol). The reaction mixture was stirred for 96 h at 35 °C. Ligand 1 g was obtained as yellow crystals after recrystallization from THF-hexane (0.6800 g, 72%); m.p. 72.7 °C. Crystals suitable for X-ray diffraction analysis were obtained from this batch. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.61(1H, s), 7.35 (1H, d), 6.98 (1H, dd), 6.89 (2H, m), 6.82 (1H, m), 2.56 (3H, s). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 15.58, 111.23, 115.12, 118.43, 126.04, 127.11, 138.33, 139.08, 142.07, 147.22, 152.24, 156.81. IR (ATR, cm⁻¹): 3347 (m), 3066 (w), 2969 (w), 2919 (w), 2857 (w), 1625 (m), 1595 (s), 1535 (m), 1494 (s), 1464 (s), 1371 (m), 1250 (s), 1226 (s), 1132 (s), 1093 (m), 1051 (m), 970 (m), 957 (m), 856 (s), 817 (m), 793 (s), 764 (m), 732 (m), 705 (w), 626 (w), 596 (w), 567 (m), 529 (m), 502 (s), 453 (m), 425 (m). Anal. Calcd for C13H13NOS (%): C, 61.26; H, 4.28; N, 5.95. Found (%): C, 61.21; H, 4.11; N, 5.94.

2.3 | Synthesis of vanadium(III) complexes

2.3.1 | [V{thiophene-(N=CH)-OC₆H₄}(THF)₂Cl₂] (2a)

A solution of **1a** (0.0381 g, 0.187 mmol) in THF (10 ml) was added dropwise to a stirring solution of $[V(THF)_3Cl_3]$ (0.070 g, 0.187 mmol) in THF (15 ml), and the resulting solution was allowed to stir for 24 h at 35 °C. The solvent was removed until about one-third remained and 10 ml of pentane added to complete the precipitation. The product was collected by filtration, washed with pentane (3 × 10 ml) and dried *in vacuo*. Complex **2a** was obtained as an orange solid (0.0500 g, 57%). IR (ATR, cm⁻¹): 1638 (s), 1589 (m), 1480 (s), 1409 (s), 1350 (m), 1318 (m), 1253 (s), 1184 (w), 1155 (w), 1103 (w), 1058 (m), 1040 (m), 997 (s), 861 (F), 823 (m), 749 (s), 564 (m), 516 (w), 469 (w). Anal. Calcd for C₁₉H₂₄Cl₂NO₃SV (%): C: 48.73, H: 5.17, N: 2.99. Found (%): C: 47.04, H: 4.88, N: 2.66.

This complex was prepared as described above for **2a**, starting from **1b** (0.0523 g, 0.187 mmol) and VCl₃(THF)₃ (0.070 g, 0.187 mmol) in THF (10 ml) to give **2b** as a red solid (0.0600 g, 59%). IR (ATR, cm⁻¹): 1635 (s), 1588 (m), 1491 (m), 1480 (m), 1434 (s), 1359 (m), 1325 (w), 1256 (s), 1187 (m), 1156 (w), 1106 (w), 1073 (m), 1000 (m), 869 (m), 809 (m), 755 (s), 687 (m), 599 (w), 572 (w), 463 (m), 441 (m). Anal. Calcd for $C_{25}H_{28}Cl_2NO_3SV$ (%): C: 55.15, H: 5.18, N: 2.57. Found (%): C: 54.67, H: 4.56, N: 2.44.

2.3.3 | [V{5-phenylthiophene-(N=CH)-4-tert-butyl-(OC₆H₃)} (THF)₂Cl₂] (2c)

This complex was prepared as described above for 2a, starting from 1c (0.0627 g, 0.187 mmol) and VCl₃(THF)₃ (0.070 g, 0.187 mmol) in THF (10 ml) to give 2c as a red solid (0.0800 g, 71%). IR (ATR, cm⁻¹): 2956 (w), 2868

(w), 1637 (s), 1596 (m), 1499 (m), 1434 (s), 1362 (m), 1322 (w), 1265 (s), 1189 (m), 1126 (m), 1072 (m), 999 (m), 828 (s), 757 (s), 684 (s), 525 (m), 474 (m). Anal. Calcd for $C_{29}H_{36}Cl_2NO_3SV$ (%): C: 58.00, H: 6.04, N: 2.33. Found (%): C: 57.67, H: 5.78, N: 2.21.

This complex was prepared as described above for **2a**, starting from **1d** (0.0406 g, 0.187 mmol) and VCl₃(THF)₃ (0.070 g, 0.187 mmol) in THF (10 ml) to give **2d** as an orange solid (0.0700 g, 78%). IR (ATR, cm⁻¹): 1638 (s), 1590 (m), 1485 (m), 1445 (s), 1357 (m), 1317 (m), 1225 (s), 1163 (m), 1105 (w), 1062 (m), 998 (m), 867 (m), 807 (m), 758 (F), 578 (m), 502 (m), 481 (m), 434 (m). Anal. Calcd for $C_{20}H_{26}Cl_2NO_3SV$ (%): C: 49.80, H: 5.43, N: 2.90. Found (%): C: 49.11, H: 4.87, N: 2.23.

This complex was prepared as described above for **2a**, starting from **1e** (0.0511 g, 0.187 mmol) and VCl₃(THF)₃ (0.070 g, 0.187 mmol) in THF (10 ml) to give **2e** as an orange solid (0.0700 g, 70%). IR (ATR, cm⁻¹): 2959 (m), 2869 (f), 1640 (F), 1599 (m), 1496 (m), 1445 (F), 1362 (m), 1266 (F), 1163 (f), 1129 (m), 1063 (f), 1005 (f), 830 (F), 735 (f), 684 (f), 626 (f), 499 (F). Anal. Calcd for C₂₄H₃₄Cl₂NO₃SV (%): C: 53.54, H: 6.36, N: 2.60. Found (%): C: 52.77, H: 5.88, N: 2.44.

This complex was prepared as described above for **2a**, starting from **1f** (0.0433 g, 0.187 mmol) and VCl₃(THF)₃ (0.070 g, 0.187 mmol) in THF (10 ml) to give **2f** as an orange solid (0.0600 g, 65%). IR (ATR, cm⁻¹): 1636 (s), 1593 (m), 1476 (m), 1441 (s), 1357 (m), 1312 (m), 1274 (m), 1209 (m), 1161 (m), 1099 (w), 1060 (w), 999 (m), 923 (w), 850 (s), 805 (m), 743 (s), 487 (s), 432 (m). Anal. Calcd for $C_{21}H_{28}Cl_2NO_3SV$ (%): C: 50.81, H: 5.69, N: 2.82. Found (%): C: 50.04, H: 5.43, N: 2.67.

2.3.7 \mid [V{5-methylthiophene-(N=CH)-4-fluoro-(OC_6H_3)} (THF)_2Cl_2] (2g)

This complex was prepared as described above for **2a**, starting from **1g** (0.0440 g, 0.187 mmol) and VCl₃(THF)₃ (0.070 g, 0.187 mmol) in THF (10 ml) to give **2g** as an orange solid (0.0640 g, 69%). IR (ATR, cm⁻¹): 1640 (s), 1598 (s), 1491 (s), 1445 (s), 1358 (m), 1310 (m), 1259 (s), 1199 (s), 1167 (m), 1144 (m), 1097 (w), 1065 (m), 1004 (m), 972 (m), 852 (s), 815 (s), 724 (m), 494 (s), 447 (m), 429 (m). Anal. Calcd for C₂₀H₂₅Cl₂NO₃SV (%): C: 48.01, H: 5.04, N: 2.80. Found (%): C: 47.65, H: 4.56, N: 2.55.

2.4 | EPR spectroscopy

Solid samples of the vanadium complexes were dissolved in THF for solution studies at 25 and -78 °C. Signal channel field modulation amplitude was adjusted to less than 10% of the smallest line width to safely improve signal-to-noise ratio, while signal channel time constant was set to less than 10% of the conversion time to avoid distortion effects. Microwave power was set below saturation.

2.5 | Procedures for polymerization of ethylene and copolymerization of ethylene with 1-hexene

All ethylene oligomerization tests were performed in a 100 ml double-walled stainless Parr reactor equipped with mechanical stirring, internal temperature control and continuous feed of ethylene. The Parr reactor was dried in an oven at 120 °C for 5 h prior to each run, and then placed under vacuum for 30 min. In a typical reaction, toluene (with 1-hexene) and MAO solution were canulla-transferred into the reactor under an ethylene atmosphere. After complete thermal equilibration (20 min), the toluene catalyst solution was injected into the reactor under a stream of ethylene and then the reactor was immediately pressurized, and stirred at 500 rpm for 15 min. The total pressure (5 bar) was kept constant by a continuous feed of ethylene. Afterwards, the reactor was depressurized and cooled to 25 °C. The polymer was precipitated using 20 ml of ethanol acidified with hydrochloric acid, under stirring for 30 min. After filtration and washing with small portions of acidic ethanol, then ethanol and water, the resulting polymeric material was dried in a vacuum oven at 60 °C for 12 h.

3 | **RESULTS AND DISCUSSION**

3.1 | Synthesis and characterization of V(III) complexes bearing phenoxy–imine–thiophene ligands

The phenoxy-imine-thiophene proligands (1a-1g) were readily synthesized by Schiff base condensations between the 2-thiophenecarbaldehyde and the corresponding phenolamine. The identity of this class of ligands was established using elemental analysis, IR and NMR spectroscopies, and an X-ray diffraction study for 1g. The ¹H NMR spectra of **1a-1g** in CDCl₃ at room temperature exhibit resonances in the region 8.79-8.58 ppm assigned to the imine proton (HC=N), with the corresponding ¹³C NMR resonances for the carbons of the imine moieties at ca 149 ppm. Single crystals of 1g suitable for crystal X-ray diffraction analysis were obtained by slow evaporation from pentane solution. The molecular geometry and atom-labeling scheme are shown in Figure 1.

The molecular structure of **1g** shows that the geometry around the C=N bond is essentially co-planar, with phenoxy group *trans* to the thiophene unit, and C(8)-N(7)-C(6)-C(5)



FIGURE 1 Molecular structure of 1g (thermal ellipsoids drawn at 30% probability level)

torsion angle of $179.7(3)^{\circ}$. The N(7)—C(7) (1.278 Å) and N(7)—C(8) (1.408 Å) bond distances are comparable to those found in similar Schiff base ligands bearing thiophene group.^[9]

The reaction of 1a-1g with 1 equiv. of VCl₃(THF)₃ in THF at 35 °C yielded the corresponding vanadium complexes (2a-2g) as orange or red moisture-sensitive solids in moderate to good yields (57-78%) (Scheme 1). The identity of 2a-2g was established on the basis of elemental analysis and IR and EPR spectroscopies. Due to the high sensitivity of these vanadium complexes to air and moisture, all manipulations were performed either using standard Schlenk-line techniques or in a glovebox under an inert atmosphere of argon. Elemental analyses of 2a-2g are in agreement with the formation of vanadium complexes of general formula {SNO}VCl₂(THF)₂ having two molecules of THF coordinated to the vanadium metal center. These complexes are paramagnetic and show very broad peaks in the ¹H NMR spectra. All attempts to recrystallize the precatalysts 2a-2g using various crystallization procedures failed resulting in amorphous materials, unfortunately not suitable for a single-crystal X-ray diffraction analysis.

The IR spectra of the vanadium complexes show the characteristic absorption bands related to the phenoxy-iminethiophene ligands. Particularly, the IR spectra of 2a-2g show the absence of O–H stretching bands in the range 3332–3453 cm⁻¹ indicating the coordination of the phenoxy



SCHEME 1 Synthesis of {SNO}VCl₂(THF)₂ complexes

group to the vanadium metal center. Furthermore, the IR spectra of the these complexes show absorption bands at $1592-1619 \text{ cm}^{-1}$ corresponding to the coordinated HC=N unit of the ligands (**1a-1g**).^[10,11]

Powdered solids and THF solutions of **2a**, **2c**, **2d**, **2e** and **2g** in nitrogen atmosphere were analyzed using EPR spectroscopy at 77 K before and after air exposure. EPR spectra are very consistent among all samples and the typical responses are illustrated for sample **2e** in Figure 2. The results are consistent with an EPR-silent vanadium(III) species being oxidized to a detectable vanadium(IV) species.^[12]

Before exposure to air, powder and solution samples already show a low-intensity vanadium(IV) spectrum due to some degree of oxidation during sample preparation and/or manipulation (Figure 2, black). However, after air exposure, the signal intensity greatly increases, indicating the oxidation of the vanadium(III) (Figure 2, red). Moreover, the great increase in the signal indicates the majority of vanadium species in the solid and solution samples being in the +3 oxidation state before air exposure.



FIGURE 2 EPR spectra (77 K) of **2e** before and after air exposure. (a) Powdered solid and (b) frozen THF solution. The solid-state spectrum is broad due to magnetic interactions among paramagnetic vanadium(IV) centers

3.2 | Ethylene polymerization

The performance of vanadium complexes 2a-2g was explored in homopolymerization of ethylene in toluene and using MAO as co-catalyst. The typical results are collected in Table 1. Initial studies carried out at 30 °C show that these catalyst systems are able to produce high-density PE with melting temperatures (T_m) in the range 133–136 °C, and crystallinities varying from 28 to 41%. The resulting PEs are insoluble for ordinary gel permeation chromatography analysis (in *o*-dichlororbenzene at 140 °C) probably due to their ultrahigh molecular weights.^[13]

As shown in Figure 3, the presence of substituents (Me, ^tBu) on the phenoxy unit promotes higher activities in comparison with the unsubstituted catalysts. For instance, the precatalysts 2c and 2e containing p^{-t} Bu group are ca 2.0 times more active than 2b and 2d (compare runs 2 versus 3 and 4 versus 5). In this case, we assume that the introduction of these electron-donating group at the R^2 position in the phenoxy moiety strengthens the vanadium-oxygen bond, improving the stability of the active species as already reported for zirconium complexes bearing phenoxy-imine chelate ligands.^[14] On the other hand, the presence of substituents (Me, Ph) on the thiophene unit show less of an influence on the activity as result of no interaction of this pendant group with the vanadium metal center; however, we cannot rule out the beneficial role of thiophene moiety for stabilizing catalytically active species, and thus improving the catalyst performance.^[15]

The replacement of *p*-'Bu group by a fluorine atom as in precatalyst **2** g leads to a higher activity (887.2 kg of PE $(mol[V])^{-1} \cdot h^{-1}$) as compared to the counterpart **2e** (664.8 kg of PE $(mol[V])^{-1} \cdot h^{-1}$). In this case, we speculate that the introduction of electron-withdrawing group into a phenoxy moiety decreases the electron density on oxygen atom, which decreases the electron density of the vanadium metal center. Accordingly, it will make ethylene monomer coordination to the vanadium much easier and enhance catalytic activity. A similar effect has been reported for titanium complexes containing β -enaminoketonato and phenoxyimine ligands.^[16,17]

To gain a more detailed understanding of ethylene polymerization behavior of this class of precatalysts, we decided to explore the effect of reaction parameters such as temperature, MAO loading and reaction time using some selected vanadium complexes. As presented in Figure 4, increasing the polymerization temperature from 30 to 50 °C does not significantly affect the catalytic activity of **2d** and **2e**, which are comparable considering an average error of $\pm 10\%$. However, on further increasing the temperature (80 °C), the catalytic activity dropped substantially suggesting the thermal deactivation of the catalytically active vanadium species to low-valent, less active or inactive species.^[2b,5q,18] Furthermore, the comparable polymerization performance of **2d** and **2e** at 80 °C (219.2 kg of PE (mol[V])⁻¹·h⁻¹ (**2d**);

TABLE 1 Ethylene polymerization reactions using 2a-2g^a

Run	Catalyst	[Al]/[V]	Temp. (°C)	$m_{\rm pol}~({\rm g})$	Activity ^b	$T_{\rm m}$ (°C)	$\chi(\%)^{c}$
1	2a	500	30	0.267	213.6	135	34
2	2b	500	30	0.320	256.0	134	30
3	2c	500	30	0.678	542.4	133	31
4	2d	500	30	0.450	360.0	134	30
5	2d	500	50	0.543	434.4	133	21
6	2d	500	80	0.274	219.2	134	33
7	2e	500	30	0.831	664.8	136	41
8	2f	500	30	0.508	406.4	135	28
9	2g	500	30	1.109	887.2	134	40
10 ^d	2g	500	30	0.617	1486.7	133	46
11 ^e	2g	500	30	1.219	487.6	131	42
12	2e	500	50	0.733	586.4	137	50
13	2e	500	80	0.330	264.0	137	43
14	2e	100	30	0.314	251.2	136	31
15	2e	250	30	0.829	663.2	135	35
16	2e	1000	30	0.776	620.8	136	37
17	2e	2000	30	0.931	744.8	135	33
18	2e	4000	30	0.941	752.8	135	34

^aReaction conditions unless specified otherwise: toluene =100 ml, $[V] = 5 \mu\mu$ mol, polymerization time = 15 min, *P*(ethylene) = 5 bar (kept constant), MAO as co-catlyst. The results shown are representative of at least duplicated experiments, yielding reproducible results within ±10%.

^bkg of PE $(mol[V])^{-1} \cdot h^{-1}$.

^cCrystallinity calculated as $(\Delta H_{\rm f} / \Delta H_{\rm f\alpha}) \times 100$, $\Delta H_{\rm f\alpha} = 286.6 \text{ J g}^{-1}$.

^dReaction time = 5 min.

^eReaction time = 30 min.



FIGURE 3 Influence of nature of vanadium complex on activity (30 °C, 5 µmol of catalyst, $P_{C2H4} = 5$ bar, molar ratio [Al]/[V] = 500)

264.0 kg of PE (mol[V])⁻¹·h⁻¹ (**2e**)) suggests the formation of similar active species, which the presence of *tert*-butyl group in **2e** did not induce any additional thermal stability as compared with **2d**.

To examine the role of the MAO loading in the polymerization, we carried out several runs using **2e** in which the [Al]/[V] molar ratio was systematically varied from 100 to 4000 equiv. Upon activation with 100 equiv. of MAO, the precatalyst **2e** shows moderate activity of



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FIGURE 4 Influence of temperature on activity using the precatalysts 2d and 2e (30 °C, 15 min, 5 μ mol of catalyst, $P_{C2H4} = 5$ bar, molar ratio [Al]/[V] = 500)

251.2 kg of PE $(mol[V])^{-1} \cdot h^{-1}$ which is increased 2.6 times upon using 250 equiv. (663.2 kg of PE $(mol[V])^{-1} \cdot h^{-1}$). However, further increase of the [Al]/[V] molar ratio from 500 to 4000 shows only slight variations in the activity attaining values in the range 664.8–752.8 kg of PE $(mol[V])^{-1} \cdot h^{-1}$. Thus, the [Al]/[V] molar ratio of 250 appears as a good tradeoff between activity and cost of co-catalyst.



FIGURE 5 Lifetime graph of ethylene polymerization for precatalyst **2g** (30 °C, 5 μ mol of catalyst, $P_{C2H4} = 5$ bar, molar ratio [Al]/[V] = 500)

Lifetime study of the 2g/MAO catalytic system was conducted for 5, 15 and 30 min at 30 °C in order to verify the deactivation process (runs 9–11 in Table 1). As can be seen in Figure 5, the relationship between reaction time and polymer yield indicates that 2g undergoes almost complete deactivation after 15 min. At 30 min a net 67% of catalytic activity is reduced in contrast with that at 5 min.

3.3 | Copolymerization of ethylene with 1-hexene

The ethylene–1-hexene copolymerization reactions were performed using complex **2e** as precatalyst at 30 °C, in toluene– 1-hexene mixture with an overpressure of ethylene (5 bar), and using MAO as co-catalyst ([A1]/[V] =500). Representative copolymerization results are summarized in Table 2.

The catalytic activities and $T_{\rm m}$ of the ethylene–1-hexene copolymers are substantially influenced by 1-hexene concentration. Thus, it is found that the activity decreases on increasing the 1-hexene concentration from 0.32 to 0.97 mol 1^{-1} as result of a 'negative co-monomer effect'.^[19] In this case, the chain propagation rate ($R_{\rm p}$) of the ethylene–hexene copolymerization is smaller than that for ethylene homopolymerization (compare run 1 with runs 2–5). As

 TABLE 2
 Copolymerization of ethylene with 1-hexene using 2e/MAO catalytic system^a

Run	$[1-hexene] (mol l^{-1})$	$m_{\rm pol}~({\rm g})$	Activity ^b	$T_{\mathbf{m}}$ (°C)	$\chi(\%)^{c}$
1	0.00	0.831	664.8	136	41
2	0.32	0.574	459.0	123	19
3	0.64	0.496	397.0	117	12
4	0.97	0.664	531.2	115	24
5	1.29	0.772	617.6	113	18
6	1.61	0.953	762.4	102	18

^aReaction conditions: toluene =100 ml, $[V] = 5 \mu mol$, polymerization time = 15 min, *P*(ethylene) = 5 bar (kept constant), *T* = 30 °C, MAO as cocatalyst ([A1][V] = 500). The results shown are representative of at least duplicated experiments yielding reproducible results within ±15%.

^bkg of PE $(mol[V])^{-1} \cdot h^{-1}$.

^cCrystallinity calculated as $(\Delta H_f / \Delta H_{f\alpha}) \times 100$, $\Delta H_{f\alpha} = 286.6 \text{ J g}^{-1}$.



FIGURE 6 Effect of 1-hexene concentration on activity and $T_{\rm m}$ using precatalyst **2e** (30 °C, 5 µmol of catalyst, $P_{\rm C2H4} = 5$ bar, molar ratio [Al]/ [V] = 500)

shown in Figure 6, the catalytic activity reaches the minimum value with a 1-hexene feed concentration of 0.64 mol l^{-1} . A greater loading of 1-hexene (1.61 mol l^{-1}) leads to an improvement in the activity (762.4 kg of PE (mol[V])⁻¹·h⁻¹) that can be tentatively associated with the hexene homopolymerization process that occurs in parallel with the ethylene–hexene copolymerization reaction.^[19a]

The DSC curves of ethylene–1-hexene copolymer produced at different co-monomer concentrations are presented in Figure 7. The ethylene–1-hexene copolymers produced using **2e**/MAO are found to exhibit $T_{\rm m}$ between 102 and 123 °C with crystallinities varying from 12 to 24%. As can be seen in Figure 7, the melting temperatures of the resulting copolymers decrease with an increase of 1-hexene feed as result of higher co-monomer incorporation into the main polymer chain.

The microstructure of ethylene-1-hexene copolymers produced using the 2e/MAO catalyst system was analyzed



FIGURE 7 DSC thermograms of PE and ethylene–1-hexene copolymers produced using the **2e/MAO** system (30 °C, 5 μ mol of catalyst, $P_{C2H4} = 5$ bar, molar ratio [Al]/[V] = 500)

TABLE 3 Monomer sequence distributions for poly(ethylene-co-1-hexene)s obtained with 2e/MAO catalyst system^a

		Sequence distribution (%) ^b					1-
Run	[HHH]	[EHH]	[EHE]	[EEE]	[HEH]	[HEE]	Hexene content (mol%)'
5	0.0	0.5	3.1	89.5	0.7	6.3	3.6
6	0.0	0.0	4.0	87.5	0.4	8.0	4.0

^aPolymerization conditions: see Table 2.

^bCalculated by analysis of ¹³C NMR spectra.

^c1-Hexene content estimated on the basis of ¹³C NMR spectra.



FIGURE 8 Typical ¹³C{¹H} NMR spectrum (*o*-C₆D₄Cl₂, 408 K) of poly(ethylene-*co*-1-hexene) produced with **2e**/MAO ([V] = 5 µmol; toluene =100 ml; MAO as co-catalyst; [Al]/[V] = 500; T = 30 °C; $P_{C2H4} = 5$ bar; [1-hexene] = 1.61 mol l⁻¹; time = 15 min)

by ¹³C NMR in o-C₆D₄Cl₂ at 135 °C. Table 3 summarizes the ¹³C NMR analysis results for ethylene–1-hexene copolymers produced using 1-hexene concentrations of 1.29 and 1.61 mol 1⁻¹. A typical ¹³C NMR spectrum for resultant poly(ethylene-*co*-1-hexene) is shown in Figure 8. The absence of resonances in the range 40–42 ppm in the ¹³C NMR spectrum related to α,α -carbon in the HH dyad sequence^[20] indicates that 1-hexene units are essentially isolated by ethylene units in the polymer chains. In addition, no [EHH] or [HHH] sequences are observed.

The co-monomer content of the ethylene–1-hexene copolymers was calculated based on ¹³C NMR analysis,^[20] and the results are given in Table 3. It is observed that on varying the 1-hexene concentration from 1.20 to 1.61 mol 1^{-1} the co-monomer content remains almost unchanged indicating the low co-monomer incorporation ability of precatalyst **2e**. This result can be associated with the steric hindrance and electron effect of the phenoxy–imine–thiophene ligand hampering the coordination of the co-monomer to the vanadium metal center.

The highest 1-hexene incorporation (4.0%) is found for copolymerization reaction carried out using 1.61 mol l⁻¹ (run 6) which is much lower as compared with other similar vanadium(III) complexes having phenoxy bidentate ligands.^[5n,5p]

4 | CONCLUSIONS

A new set of vanadium(III) complexes bearing phenoxyimine ligands with pendant thiophene group has been prepared and evaluated for homo- and copolymerization of ethylene under MAO activation. EPR results indicate that the vast majority of vanadium species in the solid and solution samples were in the +3 oxidation state before air exposure. Upon activation with MAO, these vanadium(III) precatalysts showed moderate catalytic activity for ethylene polymerization producing highdensity PE. The impossibility of dissolving these PEs in a common solvent for gel permeation chromatography analysis suggests that such polymers might present very high molecular weights. The presence of electron-donating group (Me, ^tBu) at the *para* position in the phenoxy moiety strengthens the vanadium-oxygen bond, improving the stability and activity of the active species as compared with the unsubstituted moiety. However, much higher activity was obtained using phenoxyimine bearing an electron-withdrawing group (fluorine) in 2g that can be tentatively associated with easier coordination of ethylene monomer to the vanadium metal center. As expected, the presence of substituents (Me, Ph) on the thiophene unit showed less of an influence on the activity; however, we cannot rule out the beneficial role of thiophene moiety for stabilizing catalytically active species. The optimization results showed that 2e/MAO operates with good activity at low MAO loading (250 equiv.) and moderate polymerization temperature (50 °C). Lifetime study of the 2g/MAO catalytic system showed that polymerization activity progressively decreased when the reaction time was prolonged from 5 to 30 min. In this case, the relationship between reaction time and polymer yield indicates that 2 g undergoes almost complete deactivation after 15 min. Precatalyst 2e was able to copolymerize ethylene with 1-hexene producing ethylene-1-hexene copolymers with low co-monomer incorporation. Furthermore, this catalyst system showed lower activities as compared with the ethylene homopolymerization results that might be attributed to the steric and electronic effects of the ligand on the metal center.

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SUPPORTING INFORMATION

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