## Titanium and vanadium catalysts with 2-hydroxyphenyloxazoline and oxazine ligands for ethylene-norbornene (co)polymerization

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	(L1)2VCl2 (■), (L2)2VCl2 (●), (L3)2VCl2 (♦)	

## Nomenclature of ligands:

a) 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol,

b) 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol.

c) 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol,

## Materials:

Ethylene (Linde AG Gas) was dried using sodium metal supported on alumina. Nitrogen (Polgaz, Poland) was earlier dried over sodium hydroxide and phosphorus pentoxide. Hexane (Avantor, Poland) was purified by concentrated sulfuric acid (VI) 95 wt%, dried by sodium hydroxide and distilled to obtain fraction 65-70 °C. The hexane was stored over sodium metal and distilled over benzophenone shortly before reaction. Toluene (Avantor, Poland) and tetrahydrofuran (Chempur, Poland) were distilled over sodium metal. Methylene dichloride (Avantor, Poland) was distilled over phosphorus pentoxide. Argon (Linde AG Gas), methanol, salicylic acid, sodium bicarbonate, phosphorus pentoxide- $P_2O_5$  (Avantor, Poland), (±)-2-amino-1-propanol, 3-amino-1-propanol, ethanolamine, thionyl chloride, aluminium chloride-AlCl<sub>3</sub>, diethylaluminum chloride-AlEt<sub>2</sub>Cl (1 M in hexane), NaH (60%)(Sigma-Aldrich), ethyl trichloroacetate-ETA, vanadium(IV) chloride-VCl<sub>4</sub> (Acros Organics), titanium(IV) chloride-TiCl<sub>4</sub> (1 M in CH<sub>2</sub>Cl<sub>2</sub>), 1,2-dichlorobenzene-d4 (Alfa Aesar), DMSO-d6, CDCl<sub>3</sub>-d (Armar AG) were applied as purchased.



Figure 1S. Scheme of synthesis of studied ligands and catalysts.



**Figure 2S.** Example of changes of chemical shifts in <sup>13</sup>C NMR spectra in DMSO-d6 for the ligand molecule L1 and its complexes: (a) ligand L1, (b) L1 titanium complex, (c) L1 vanadium complex.



**Figure 3S.** <sup>1</sup>H NMR spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (L1) in DMSO-d6.



Figure 4S. <sup>13</sup>C NMR spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (L1) in DMSO-d6.



**Figure 5S.** <sup>1</sup>H NMR spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (**L1**) titanium complex in DMSO-d6.



**Figure 6S.** <sup>13</sup>C NMR spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (**L1**) titanium complex in DMSO-d6.



**Figure 7S.** <sup>1</sup>H NMR spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (**L1**) vanadium complex in DMSO-d6.



ppm 120 110 100 

**Figure 8S.** <sup>13</sup>C NMR spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (**L1**) vanadium complex in DMSO-d6.









**Figure 12S.** <sup>13</sup>C NMR spectrum of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol (**L2**) titanium complex in DMSO-d6.



**Figure 13S.** <sup>1</sup>H NMR spectrum of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol (**L2**) vanadium complex in DMSO-d6.



**Figure 14S.** <sup>13</sup>C NMR spectrum of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol (**L2**) vanadium complex in DMSO-d6.





**Figure 18S.** <sup>13</sup>C NMR spectrum of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol (**L3**) titanium complex in DMSO-d6.



**Figure 19S.** <sup>1</sup>H NMR spectrum of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol vanadium complex (L3) in DMSO-d6.



**Figure 20S.** <sup>13</sup>C NMR spectrum of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol (**L3**) vanadium complex in DMSO-d6.



**Figure 21S.** Schematic presentation of the similarity of the fragmentation pattern in the mass spectra of vanadium complexes; (a)  $(L1)_2VCl_2$ , (b)  $(L2)_2VCl_2$ , (c)  $(L3)_2VCl_2$ .



Figure 22S. Mass spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (L1).



Figure 23S. Mass spectrum of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol (L2).



Figure 24S. Mass spectrum of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol (L3).



191008\_sample2 #115-131 RT: 1.43-1.62 AV: 17 NL: 4.03E2 T: + c Full ms [50.00-900.00]



Figure 25S. Mass spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol vanadium complex ((L1)<sub>2</sub>VCl<sub>2</sub>).



191008\_sample11 #277-299 RT: 3.22-3.47 AV: 23 NL: 6.77E3 T: + c Full ms [50.00-900.00]



**Figure 26S.** Mass spectrum of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol vanadium complex (**(L2)**<sub>2</sub>**VCl**<sub>2</sub>).



191008\_sample10 #145-148 RT: 1.70-1.74 AV: 4 NL: 2.51E5 T: + c Full ms [50.00-900.00]



**Figure 27S.** Mass spectrum of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol vanadium complex (**(L3)**<sub>2</sub>**VCl**<sub>2</sub>).



Figure 28S. Schematic presentation of the similarity of the fragmentation pattern in the mass spectra of titanium complexes; (a)  $(L1)_2TiCl_2$ , (b)  $(L2)_2TiCl_2$ , (c)  $(L3)_2TiCl_2$ .



191008\_sample2 #115-131 RT: 1.43-1.62 AV: 17 NL: 4.03E2 T: + c Full ms [50.00-900.00]



Figure 29S. Mass spectrum of 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol titanium complex ((L1)<sub>2</sub>TiCl<sub>2</sub>).



191008\_sample4 #121-134 RT: 1.52-1.68 AV: 14 NL: 7.14 T: + c Full ms [50.00-900.00]



**Figure 30S.** Mass spectrum of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol titanium complex (**(L2)**<sub>2</sub>**TiCl**<sub>2</sub>).



191008\_sample5+ACN #223-264 RT: 2.61-3.09 AV: 42 NL: 1.53E3 T: + c Full ms [50.00-900.00]



Figure 31S. Mass spectrum of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol titanium complex ((L3)<sub>2</sub>TiCl<sub>2</sub>).



**Figure 32S.** <sup>13</sup>C NMR spectrum of E-NB copolymer (12 mol% NB incorporation) at 0.5 mol/L initial NB concentration obtained with 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (L1) vanadium complex in *o*-dichlorobenzene-d4.



**Figure 33S.** <sup>13</sup>C NMR spectrum of E-NB copolymer (22 mol% NB incorporation) at 1.0 mol/L initial NB concentration obtained using 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (L1) vanadium complex in *o*-dichlorobenzene-d4.



**Figure 34S.** <sup>13</sup>C NMR spectrum of E-NB copolymer (28 mol% norbornene incorporation) at 1.5 mol/L initial NB concentration obtained using 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (**L1**) vanadium complex in *o*-dichlorobenzene-d4.



**Figure 35S.** <sup>13</sup>C NMR spectrum of E-NB copolymer (17 mol% NB incorporation) at 0.5 mol/L initial NB concentration obtained using of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol (**L2**) vanadium complex in *o*-dichlorobenzene-d4.



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**Figure 375.** <sup>13</sup>C NMR spectrum of E-NB copolymer (27 mol% NB incorporation) at 1.5 mol/L initial NB concentration obtained using of 2-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl)phenol (**L2**) vanadium complex in *o*-dichlorobenzene-d4.



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**Figure 40S.** <sup>13</sup>C NMR spectrum of E-NB copolymer (30 mol% NB incorporation) at 1.5 mol/L initial NB concentration obtained using of 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol (L3) vanadium complex in *o*-dichlorobenzene-d4.



**Figure 41S.** Plot of NB incorporated in the copolymers versus the copolymers  $T_g$  using complex:  $(L1)_2VCl_2 (\blacksquare), (L2)_2VCl_2 (\bullet), (L3)_2VCl_2 (\bullet)$