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Ni(II) Complexes Bearing Pyrrolide-Imine Ligands with Pendant O- and S-donor Groups: Synthesis, Structural Characterization and use in Ethylene Oligomerization

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A series of new Ni(II) complexes of general formula {L}NiCl [**Ni1**, L = 2-(C_4H_3N-2′-CH=N)C_2H_4NHPh; **Ni2**, L = 5-*tert*-butyl-2-(C_4H_2N-2′-CH=N)C_2H_4NHPh; **Ni3**, L =2-(C_4H_3N-2′-CH=N)C_2H_4OPh; **Ni4**, L = 2-(C_4H_3N-2′-CH=N)C_6H_4-2′-OPh; **Ni5**, L = 2-(C_4H_3N-2′-CH=N)C_6H_4-2′-SPh; **Ni6**, L =2-(C_4H_3N-2′-CH=N)$CH_2C_6H_4$-2′-OMe] were prepared and fully characterized. All nickel precatalysts, activated with methylaluminoxane (MAO), exhibited moderate to good activities for ethylene oligomerization [TOF = 6.1–71.3 x 10^3 mol(C_2H_4)·(mol(Ni)$^{-1}$ h^{-1})] with high selectivities for 1-butene produced (68.3–94.0 wt.%). The catalytic performance was substantially affected by the ligand environment regarding the pendant oxygen- and sulfur-donor groups, and the substituents on the pyrrolide group. Activation of nickel precatalyst **Ni3** with ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC) instead of MAO produced a significantly more productive catalyst system than **Ni2**/MAO (TOF = 153,700 vs. 43,500 mol(C_2H_4)·(mol(Ni)$^{-1}$ h^{-1}); however, the 1-butene selectivity was drastically reduced, attaining only 53 wt.% with a concomitant production of larger amounts of internal butenes (38. wt.%). Under optimized conditions ([Ni] = 10 µmol, 30 °C, oligomerization time = 20 min, 20 bar ethylene, [Al]/[Ni] = 250), precatalyst **Ni3** led to TOF = 55,900 mol($_2H_4$)·(mol(Ni)$^{-1}$ h^{-1}) and 82.8 wt.% selectivity for 1-butene.

Introduction

The oligomerization of ethylene is one of the most important industrial processes to obtain linear α-olefins (LAOs).[1] LAOs are extensively used for preparing detergents, lubricants, plasticizers, and oil field chemicals or used as co-monomers, etc.[2] Among classes of catalysts used for the production of α-olefins, nickel complexes containing *P,P*-,[3] *P,N*-,[4] *P,O*-,[5] *N,N*-,[6] or *N,O*-[7] bidentate chelating ligands are the most frequently studied. More recently, nickel complexes bearing tridentate ligands have attracted much interest owing to their good to excellent performance towards the production of α-olefins.[8] In this context, many different classes of tridentate ligands bearing a variety of E-donor groups (E = N, O, P, and S) have been explored and used to support nickel complexes (Chart 1). In particular, Braunstein *et al.* reported the use of a tridentate *N,P,N*-type ligand in the synthesis of the pentacoordinated mononuclear nickel complex [$NiCl_2$(NOPONMe$_2$-*N,P,N*)] (NOPONMe$_2$ = bis(4,4-dimethyl- 2-oxazolyldimethylmethoxy)phenylphosphine), which is an effective precatalyst leading to selectivities in C_4 olefins higher than 90% when activated with ethylaluminum dichloride ($EtAlCl_2$).[9] Sun *et al.* described the synthesis of nickel complexes bearing 2-(benzimidazol-2-yl)-1,10-phenanthrolines; upon activation with diethylaluminum chloride (Et_2AlCl), high catalytic activity of up to 1.27 x 10^7 g·mol(Ni)$^{-1}$·h^{-1} and high selectivity for 1-butene (90.5 wt. %) could be achieved.[10] More recently, Olivier-Bourbigou *et al.* disclosed a new class of nickel complexes based on imino-imidazole ligands bearing a pendant donor group that are able to oligomerize ethylene in presence of $EtAlCl_2$ or methylaluminoxane (MAO), producing mostly dimers and trimers.[11]

In recent years our groups have been interested in exploring the potential applications of tridentate ligands in the oligomerization catalysis field.[12] Thus, we have previously reported on the use of nickel complexes based on tridentate nitrogen-, oxygen- or sulfur-bridged bis(pyrazolyl) ligands as highly selective and productive precatalysts for ethylene dimerization upon activation with MAO.[12a] Replacement of a pyrazole group by a pendant ether or thioether group on one side of the ether-bis(pyrazolyl) ligand led to more active systems.[12f]

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† Electronic Supplementary Information (ESI) available: Crystallographic data for **Ni1**, and typical GLC analyses of oligomerization mixtures. See DOI: 10.1039/x0xx00000x

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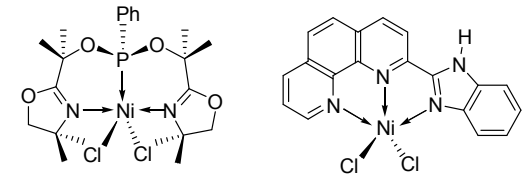
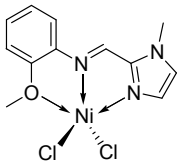
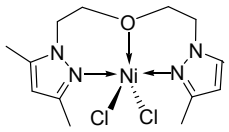


Braunstein et al.[9]

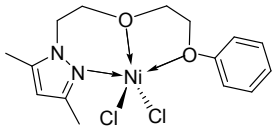
Sun *et al.*[10]



Olivier-Bourbigou *et al.*[11]



Carpentier *et al.*[12a]



Casagrande *et al.*[12f]

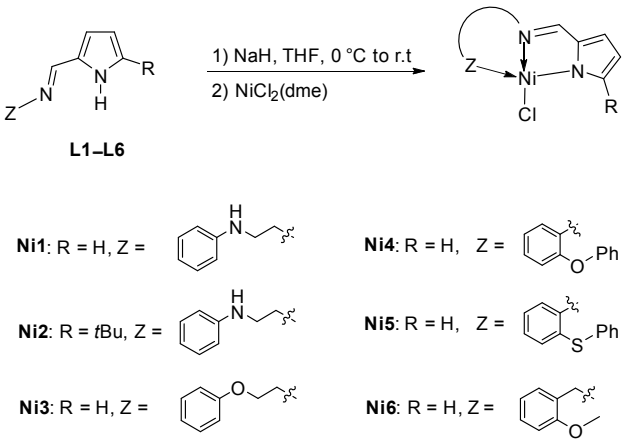
Chart 1. Examples of nickel complexes based on tridentate ligands applied in ethylene oligomerization.

As a continuation of the work outlined above, we report here the synthesis and structural characterization of a new family of Ni(II) complexes bearing pyrrole-imine ligands with pendant *O*- and *S*-donor groups and their catalytic behavior for ethylene oligomerization upon activation with MAO and ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC). We discuss the performance of these catalysts, evaluating the role of the ligand, and the experimental parameters on the activity and selectivity towards the production of 1-butene.

Results and discussion

Synthesis and Characterization of Ni(II) Complexes Bearing Pyrrolide-Imine Ligands with Pendant O- and S-donor Groups

The pyrrole-imino pro-ligands with pendant *O*- and *S*-donor groups were readily synthesized by Schiff base condensations between the corresponding primary amines and pyrrole-2-carboxaldehyde in refluxing methanol. The identity of this class of ligands was established by IR and NMR spectroscopy, elemental analysis, and by an X-ray diffraction study for ligands **L3, L4** and **L5** (see Electronic Supplementary Information). Treatment of **L1–L6** with 1.0 equiv. of NaH and then $NiCl_2$(dme) yielded the corresponding nickel complexes {L}NiCl (**Ni1–Ni6**), which were isolated as brown solids in moderate to good yields (63–90 wt.%) (Scheme 1). These nickel complexes show moderate solubility in acetonitrile or THF at room temperature. The ^{1}H NMR spectra of these complexes featured very broad resonances and proved uninformative. As complexes of Ni(II) with square-planar geometry are expected to be diamagnetic, this observation implies that these complexes are distorted from the ideal geometry in solution. Similar results have been found for salicylaldiminato nickel(II) halide complexes.[13] The identity of **Ni1-Ni6** was established on the basis of elemental analysis and single-crystal X-ray diffraction studies for **Ni1**.



Scheme 1

Single crystals of **Ni1** suitable for X-ray diffraction were grown from a concentrated acetonitrile/ether solution (80:20) at room temperature. In the solid state, this complex is monomeric with κ^3 coordination of the monoanionic pyrrolide-imine-amine ligand onto the nickel center. As shown in Figure 1, **Ni1** adopts a distorted square planar geometry around nickel(II). The N(1), N(7), N(10), and Cl(1) atoms are nearly coplanar, with Cl and N(7) occupying the *trans* positions (Cl(1)–Ni(1)–N(7) = 179.04(5)°, N(1) –Ni(1) –N(10): 168.77(6)°). The Ni(1)–N(1) and Ni(1)-N(7) bond distances [1.8715(4) Å, 1.8585(14) Å, respectively] are close to the values previously reported for Ni(II) complexes having pyrrole-imine ligands.[14]

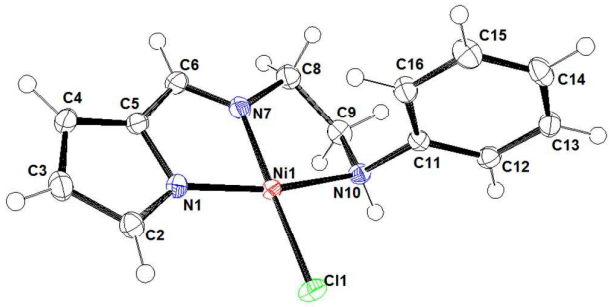


Fig. 1 ORTEP drawing of **Ni1**. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ni(1)–Cl(1) = 2.1774(4), Ni(1)–N(1) = 1.8715(14), Ni(1)–N(7)= 1.8585(14), Ni(1)–N(10) = 1.9335(14). N(7)–Ni(1)–Cl(1) = 179,04(5). N(1)–Ni(1)–N(10) = 168.77(6), N(7)–Ni(1)–N(1) = 83.74(6), N(7)–Ni(1)–N(10) = 85.37(6), Cl(1)–Ni(1)–N(10) = 94.04(4), N(1)–Ni(1)–Cl(1) = 96.81(4).

Ethylene Oligomerization Studies

The performance of nickel precatalysts **Ni1**–**Ni6** were explored in ethylene oligomerization using as cocatalyst methylaluminoxane (MAO) containing 20 wt.% $AlMe_3$, at 30 °C and 20 bar constant ethylene pressure. Table 1 summarizes the results of reactions carried out using 10 µmol of precatalyst in 40 mL of toluene. All experiments were at least duplicated, yielding reproducible results within ±10%. When activated with MAO, all the nickel complexes investigated were found to generate active systems for the production of short-chain olefins in the C_4–C_6 range with turnover frequencies (TOFs) varying from 6,100 to 71,300 mol (C_2H_4)· mol $(Ni)^{-1}$·h^{-1}. As shown in Table 1 (entries 1–6), the ligand environment regarding the pendant oxygen- and sulfur-donor groups, and the substituents on the pyrrolide group influenced the catalytic performance of the nickel precatalysts on ethylene oligomerization, as can be better visualized in Figure 2. It is should be pointed out that, taking into account the lower donor ability of the ether- and thio- groups as compared to the amine unit, we cannot rule out that **L3-L6** could act as bidentate and not tridentate ligands. In the absence of structural data for **Ni3-Ni6**, we can only speculate at this stage that the coordination of these pendant oxygen- and sulfur-donor groups onto the nickel center could stabilize the active catalytic species.

Table 1. Ethylene Oligomerization with **Ni1–Ni6** catalytic systems.[a]

entry	cat	[Al]/[Ni]	Olig. (g)	TOF[b] (x 10^3)	Selectivity (wt. %)	
					C_4 (α-C_4)	C_6 (α-C_6)
1	**Ni1**	250	1.10	11.6	97.2 (92)	2.8 (42)
2	**Ni2**	250	2.90	29.1	97.1 (83)	2.9 (43)
3	**Ni3**	250	4.00	43.5	97.4 (85)	2.6 (30)
4	**Ni4**	250	1.40	14.7	98.9 (84)	1.1 (30)
5	**Ni5**	250	7.10	71.3	94.8 (72)	5.2 (22)
6	**Ni6**	250	0.60	6.10	100 (94)	0.0
7	**Ni3**	500	1.00	11.0	97.7 (90.0)	2.3 (52)
8	**Ni3**	100	2.50	26.6	98.2 (90)	1.8 (44)
9	**Ni3**	50	0.50	2.10	97.7 (91.0)	2.3 (71)
10[c]	**Ni3**	250	2.50	27.3	97.4 (85)	2.6 (33)
11[d]	**Ni3**	250	1.40	55.9	96.4 (86)	3.6 (49)
12[e]	**Ni3**	250	3.50	18.9	94.5 (79)	5.5 (29)
13[f]	**Ni3**	50	15.3	153.7	91.5 (58)	8.5 (17)

[a] Reaction conditions: toluene = 40 mL, [Ni] = 10 µmol, oligomerization time = 20 min, P(ethylene) = 20 bar (kept constant), T_{pol} = 30 °C. The results shown are representative of at least duplicated experiments. [b] Mol of ethylene converted (mol of Ni)$^{-1}$·h^{-1} as determined by quantitative GLC. [c] T = 50 °C. [d] Oligomerization time = 5 min, [e] Oligomerization time = 40 min. [f] EASC as cocatalyst.

Precatalyst **Ni1**, when activated with 250 equiv of MAO, was found to give moderate activity [TOF = 11,600 mol (C_2H_4)· mol $(Ni)^{-1}$· h^{-1}] along with good selectivity towards 1-butene (89 wt.%). Increasing the steric hindrance on the pyrrolide unit, as in precatalyst **Ni2**, caused an increase in activity by a factor of 2.50 suggesting that the *tert*-butyl substituent acts as a protecting group of the active species, thereby increasing the catalytic productivity.[6b,15] Replacing the amine with an ether group as in precatalyst **Ni3** led to a much higher activity [TOF = 43,500 mol (C_2H_4)· mol $(Ni)^{-1}$·h^{-1}] as compared to the counterpart **Ni1** [TOF = 11,600 mol(C_2H_4) mol$(Ni)^{-1}$·h^{-1}]; however, a slight decreasing in 1-butene selectivity was found using **Ni3** [82.8 wt.% for **Ni3** vs. 89.4 wt.% for **Ni1**].

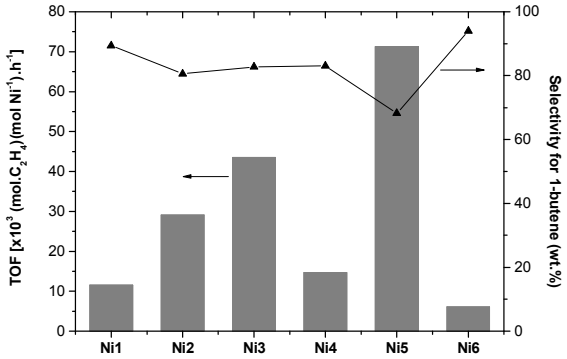


Fig. 2 Influence of the nature of nickel precatalyst on TOF and selectivity for 1-butene (T = 30 °C, 20 bar, time = 20 min, [Al]/[Ni] = 250).

The productivity for ethylene oligomerization is also substantially affected by the ligand framework. Hence, precatalyst **Ni3** that contains an ethylene bridge unit is ca. 3.0 times more active than **Ni4** that contains a more rigid phenyl moiety (compare entries 3 and 4). This result possibly arises from the presence of a electron-withdrawing group (phenyl unit) that decreases the Lewis base of the ether unit (OPh), and thus destabilizing the Ni(II) active species. On the other hand, the selectivity for butenes and especially 1-butene were similar (*ca*. 83.0 wt.%), indicating that this variation in the ligand structure had no influence on the product distribution.

Replacement of the ether by a thioether donor group (**Ni5**) led to a highly active oligomerization system (TOF = 71,300 mol(C_2H_4)· mol$(Ni)^{-1}$·h^{-1}] associated to a good selectivity for 1-butene production (68.3 wt.%). Under identical oligomerization conditions (10 µmol [Ni], 30 °C, 20 bar of ethylene, [Al]/[Ni] = 250, time = 20 min) **Ni5** is much more active than similar nickel complexes such as $NiCl_2${bis[2-(3,5-dimethylpyrazolyl)ethyl)]ether} [TOF = 7,100 mol(C_2H_4)· mol$(Ni)^{-1}$·h^{-1}][12a] and $NiCl_2${1-(2-(2-phenoxyethoxy)ethyl)-3,5-dimethyl-1H-pyrazole} [TOF = 35,800 mol(C_2H_4)· mol$(Ni)^{-1}$·h^{-1}].[12f] As suggested above we assume that this higher productivity may arise from the softer and greater donor ability of S (as compared to *O*-donor) leading to substantially improved catalyst lifetimes. Similar results have been found for the class of nickel precatalysts $NiCl_2$(NZN) based on nitrogen-, oxygen-,

or sulfur bridged ligands, whereas the replacement of O-bridged donor atom by S- promotes a much higher activity for $NiCl_2${bis[2-(3,5-dimethylpyrazolyl)ethyl)]sulfide} [TOF = 57,200 mol(C_2H_4)· mol(Ni)$^{-1}$·h^{-1}] as compared to $NiCl_2${bis[2-(3,5-dimethylpyrazolyl)ethyl)]ether} [TOF = 7,100 mol(C_2H_4)· mol(Ni)$^{-1}$·h^{-1}].[12a]

When the length of the spacer between the central imine and the ether donor group was increased by one carbon (compare complexes **Ni6** with **Ni3** and **Ni4**), the productivity decreased substantially [TOF = 6,100 mol(C_2H_4)· mol(Ni)$^{-1}$·h^{-1}]. In this case, we surmise a more difficult coordination of the OMe group onto the metal center to deliver a stable 6-membered-ring nickel complex.

The preliminary study was extended to investigate the effect of temperature, [Al]/[Ni] molar ratio, cocatalyst type, and oligomerization time on the catalytic performance of the more promising system, *i.e.* **Ni3**/MAO (Table 1, entries 7–13). Elevating the temperature from 30 °C to 50 °C led to a reduction in productivity [TOF = 27,300 mol(C_2H_4)· mol(Ni)$^{-1}$·h^{-1}], suggesting that a partial decomposition of the active catalytic species took place. However, it should be pointed out that even at higher temperature (50 °C), the **Ni3**/MAO still operates with high activity and good selectivity for 1-C_4 production (82.8 wt.%) when compared to similar nickel precatalysts bearing tridentate ligands.[8]

The catalyst selectivities and activities were monitored as a function of time in the ethylene oligomerization reaction promoted by the **Ni3**/MAO catalytic system (Figure 3). The oligomerization activity progressively decreased when the reaction time was prolonged from 5 to 20 min and finally to 40 min; this indicates that the catalyst lifetime is relatively short. Furthermore, it is important to note that **Ni3** undergoes almost complete deactivation after 20 min. On the other hand, the reaction time causes a minimum impact on the selectivity for 1-butene, varying from 82.9 wt.% (5 min) to 74.6 wt.% (40 min), indicating that a single species is operative in this system. These results also indicate that isomerization of butenes is a minor pathway in these reactions and that the observed selectivities directly reflect the dimerization abilities of the catalyst.

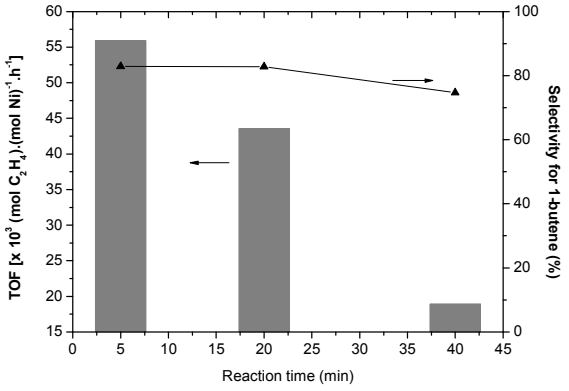


Fig. 3 Monitoring of selectivities and activities as a function of time in the ethylene oligomerization reaction promoted by the **Ni3**/MAO system (T = 30 °°C, 20 bar of ethylene, [MAO]/[Ni] = 250).

The influence of the MAO loading on the catalyst behavior was also studied. When activated with 50 equiv of MAO, precatalyst **Ni3** gave a lower activity [TOF = 2,100 mol(C_2H_4)· mol(Ni)$^{-1}$ h^{-1}, entry 9], which was increased upon using 100 equiv [TOF = 26,600 mol(C_2H_4)· mol(Ni)$^{-1}$ h^{-1}, entry 8] and even further with 250 equiv [TOF = 43,500 mol(C_2H_4)· mol(Ni)$^{-1}$·h^{-1}, entry 3]. On the other hand, a greater loading of MAO (500 equiv) led to lower activity (entry 7). In all cases, the use of different MAO loading ([Al]/[Ni] = 50–500) had little impact on the selectivity for α-C_4 that remained in the range of 82.8–88.4 wt.%.

Activation of the nickel precatalyst **Ni3** with 50 equiv of ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC) instead of MAO produced a significantly better catalyst system with TOF = 153,700 mol(C_2H_4)· mol(Ni)$^{-1}$·h^{-1}. This high activity eventually generated some exothermicity, so that the reaction with **Ni3**/EASC performed at an initial temperature of 30 °°C (entry 14) rapidly rose to 40–45 °C. Although the catalyst activity was improved by approximately 75-fold (compare entry 9 vs 13), the 1-butene selectivity was drastically reduced, dropping down to 58 wt.% with a concomitant production of larger amounts of internal butenes (33.5 wt.%) and hexenes (8.5 wt.%). The possibility of using small amounts of cocatalyst is obviously the most interesting feature of this catalyst system.

Conclusions

A new set of tetracoordinate nickel complexes bearing pyrrolide-imine ligands with pendant O- and S-donor groups were synthesized and structurally characterized. Upon activation with MAO or EASC co-catalysts, these Ni(II) complexes showed moderate to high catalytic activity for ethylene oligomerization with good selectivity towards 1-butene production. Variations of the ligand structure demonstrated that a dramatic change in catalytic behavior can be obtained upon a subtle modification in the ligand skeleton. For instance, with nickel complex chelated by **L2**, the increase in activity suggested the beneficial role of the *tert*-butyl group as sterically protecting group of the active species. On the other hand, an expansion of the imino-ether arm by introduction of one additional CH_2 unit in the spacer, generating a likely more flexible ligand **L6**, decreased substantially the activity of **Ni6**; this can be tentatively associated to the formation of a less stable 6-membered-ring nickel complex. Within the prepared series, the most active nickel catalyst (**Ni5**) is the one with a more rigid ligand bearing a soft donor-group (SPh). However, variation of the ligand structure does not play a significant role in the selectivity for butenes and especially 1-butene, attaining 72.0-94.0 wt.% of the total amount of olefins formed in the oligomerization reactions. The use of EASC instead of MAO afforded a highly active species; however the 1-butene selectivity was drastically reduced.

Experimental

General Procedures

All manipulations involving air- and/or water-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Solvents were dried from the appropriate drying agents under argon before use. The ligands

2-(C_4H_4N-2′-CH=N)C_2H_4(NH)Ph (**L1**), 5-*tert*-Butyl-2-(C_4H_3N-2′-CH=N)C_2H_4(NH)Ph (**L2**), and 2-(C_4H_4N-2′-CH=N)C_2H_4OPh (**L3**) were prepared by literature procedures.[16] 5-*tert*-Butyl-1H-pyrrole-2-carboxyaldehyde was prepared using the reported procedure.[17] $NiCl_2$(dme), pyrrole-2-carboxyaldehyde, 2-(phenylthio)aniline, 2-phenoxyaniline, and 2-methoxybenzylamine 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) was used as received. EASC (Akzo Nobel) was used with the previous dilution (2.1 wt.% Al solution in toluene). Infrared spectra were performed on neat products using a FT-IR Bruker Alpha Spectrometer operating in the ATR mode. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 25 °C on a Varian Inova 300 spectrometer operating at 300 MHz. Chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry-USP (Brazil) and are the average of two independent determinations. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on a Agilent 7890A instrument equipped with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and film thickness of 0.5 µm) (36 °C for 15 min, then heating at 5 °C·min^{-1} until 250 °C); cyclohexane was used as internal standard.

Synthesis of the pyrrol-imine ligands with O- and S-donor groups

2-(C_4H_4N-2′-CH=N)Ph-2-OPh (L4). To a stirred solution containing pyrrole-2-carboxyaldehyde (0.250 g, 2.63 mmol) in ethanol (75 mL), 2-phenoxyaniline (0.560 g, 2.63 mmol) was added. The reaction mixture was stirred for 72 h at 65 °C. The solvent was evaporated to give a pale brown solid that was recrystallized from ethanol/ether to give **L4** as an off-white solid (0.413 g, 87%). Mp: 110.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.21 (dd, ^2J = 2.6 and 3.6 Hz, 1H, H-pyrrole), 6.60 (dd, ^2J = 1.3 and 3.6 Hz, 1H, H-py), 6.79 (d, ^2J = 1.3 Hz, 1H, H-pyrrole), 6.90-7.27 (m, 9H, Ar-H), 8.23 (s, 1H, CH=N), 9.69 (br s, 1H, NH-pyrrole). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 110.38 (CH, 4-pyrrole), 116.68 (CH, 3-pyrrole), 117.89 (2CH, Ar-C), 120.98 (CH, 5-pyrrole), 121.20 (CH, Ar-C), 122.56 (CH, Ar-C), 123.31 (CH, Ar-C), 124.82 (CH, Ar-C), 126.25 (CH, Ar-C), 129.61 (2CH, Ar-C), 130.98 (C, 2-pyrrole), 144.04 (C, Ar-C), 149.21 (C, Ar-C), 150.88 (CH, N=C-H), 158.27 (C, Ar-C). IR (KBr, cm^{-1}) ν: 3238 (s), 3095 (w), 3063 (w), 2979 (w), 2896 (w), 1687 (m), 1631 (s), 1594 (m), 1488 (s), 1455 (m), 1418 (m), 1339 (w), 1319 (w), 1267 (w), 1237 (s), 1205 (m), 1184 (w), 1159 (s), 1134 (m), 1090 (m), 1069 (w), 969 (w), 940 (w), 878 (m), 845 (m), 795 (m), 751 (s), 693 (m), 603 (m), 490 (w), 460 (w). Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.26; H, 5.09; N, 10.69.

2-(C_4H_4N-2′-CH=N)CH_2Ph-2-SPh (L5). This product was prepared as described above for **L4**, starting from pyrrole-2-carboxyaldehyde (0.250 g, 2.63 mmol) and 2-(phenylthio)aniline (0.529 g, 2.63 mmol). **L5** was recovered as an off-white solid (0.219 g, 30%). Mp: 102.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.30 (dd, ^2J = 2.7 and 3.5 Hz, 1H, H-pyrrole), 6.67 (dd, ^2J = 1.1 and 3.6 Hz, 1H, H-pyrrole), 6.96-7.07 (m, 4H, H-Ar + H-pyrrole), 7.16-7.22 (m, 1H, H-Ar), 7.30-7.37 (m, 3H, H-Ar), 7.44-7.47 (m, 2H, H-Ar), 8.16 (s, 1H, CH=N), 9.55 (br s, 1H, NH-pyrrole). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 110.55 (CH, 4-pyrrole), 116.70 (CH, 3-pyrrole), 118.42 (CH, 5-pyrrole), 123.38 (CH, Ar-C), 125.88 (CH, Ar-C), 127.14 (CH, Ar-C), 127.84 (CH, Ar-C), 128.93 (2CH, Ar-C), 129.37 (2CH, Ar-C), 130.93 (CH, Ar-C), 132.46 (C, 2-pyrrole), 133.46 (C, Ar-C), 134.19 (C, Ar-C), 149.77 (CH, N=C-H), 149.87 (C, Ar-C). IR (KBr, cm^{-1}) ν: 3215 (m), 3165 (w), 3053 (w), 2975 (w), 2906 (w), 2864 (w), 1615 (s), 1562 (s), 1551 (m), 1463 (m), 1438 (m), 1405 (s), 1339 (m), 1315 (m), 1302 (w), 1262 (m), 1242 (w), 1198 (s), 1131 (s), 1088 (s), 1058 (m), 1032 (s), 962 (w), 935 (w), 912 (w), 879 (s), 848 (m), 831 (m), 785 (m), 741 (s), 718 (m), 688 (s), 679 (m), 601 (s), 582 (m), 522 (m), 495 (m). Anal. Calcd. for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.07; N, 10.06. Found: C, 73.05; H, 5.06; N, 10.02.

2-(C_4H_4N-2′-CH=N)CH_2Ph-2-OMe (L6). This product was prepared as described above for **L4**, starting from pyrrole-2-carboxyaldehyde (0.250 g, 2.63 mmol) and 2-methoxybenzylamine (0.358 g, 2.63 mmol). **L6** was recovered as pale brown needles (0.334 g, 60%). Mp: 62.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.80 (s, 3H, CH_3), 4.73 (s, 2H, CH_2), 6.19 (t, ^3J = 6.0 Hz, 1H, 4-pyrrole), 6.47 (d, ^2J = 3.0 Hz, 1H, 3-pyrrole), 6.74 (s, 1H, 5-pyrrole), 6.87-6.92 (m, 2H, Ar-H), 7.21-7.24 (m, 2H, Ar-H), 8.14 (s, 1H, CH=N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 55.40 (CH_3), 58.79 (CH_2), 109.58 (CH, 4-pyrrole), 110.30 (CH, 3-pyrrole), 114.37 (CH, Ar-C), 120.64 (CH,5-pyrrole), 122.00 (CH, Ar-C), 127.90 (C, Ar-C), 128.29 (CH, Ar-C), 129.41 (CH, Ar-C), 130.43 (C, 2-pyrrole), 153.04 (CH, N=C-H), 157.22 (C, Ar-C). IR (KBr, cm^{-1}) ν: 3424 (sh), 3170 (w), 3123 (w), 3063 (w), 2956 (w), 2832 (w), 1639 (s), 1601 (w), 1592 (w), 1490 (m), 1460 (m), 1441 (m), 1422 (m), 1353 (m), 1315 (w), 1283 (m), 1244 (s), 1166 (w), 1136 (m), 1110 (m), 1031 (s), 975 (w), 879 (w), 837 (w), 757 (s), 739 (s), 606 (w), 581 (w). Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.81; H, 6.68; N, 13.20.

Synthesis of the Ni(II) Complexes

[Ni{2-(C_4H_3N-2-CH=N)C_2H_4(NH)Ph}Cl] (**Ni1**). To a solution of **L1** (0.200 g, 0.94 mmol) in THF (5 mL) was added dropwise a suspension of NaH (0.034 g, 0.94 mmol) in THF (5 mL) at 0 °C. The resulting red solution was stirred for 4 h at room temperature and then added dropwise to a solution of $NiCl_2$(dme) (0.205 g, 0.94 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred overnight at room temperature and then volatiles were removed in vacuo. The brown crude solid was dissolved in toluene (15 mL), filtered by cannula and the resulting solution was concentrated (*ca.* 3 mL). Then, pentane (15 mL) was added to afford a pale brown solid which was washed with diethyl ether (2 × 10 mL) to give, after drying, **Ni1** as a brown solid (0.210 g, 73%). IR (ATR, cm^{-1}): ν 3048 (w), 2954 (w), 2845 (w), 1626 (w), 1597 (w), 1576 (s), 1490 (m), 1441 (m), 1387 (m), 1301 (s), 1246 (w), 1030 (s), 733 (s), 690 (s), 601 (m), 508 (m). Anal. Calcd. for $C_{13}H_{14}ClNiN_3$: C, 50.96; H, 4.61; N, 13.71. Found: C, 51.27; H, 4.94; N, 13.60.

[Ni{5-*tert*-butyl-2-(C_4H_2N-2-CH=N)C_2H_4(NH)Ph}Cl] (**Ni2**). This product was prepared as described above for **Ni1**, starting from **L2** (0.183 g, 0.68 mmol), NaH (0.025 g, 0.68 mmol), and $NiCl_2$(dme) (0.150 g, 0.68 mmol) in THF (10 mL) to give **Ni2** as a pale brown solid (0.221 g, 90%). IR (ATR, cm^{-1}): ν 3190 (w), 3102 (w), 2959 (w), 2899 (w), 1639 (m), 1593 (s), 1491 (m), 1441 (m), 1392 (m), 1341 (m), 1269 (m), 1231 (m), 1153 (w), 1093 (w), 1044 (s), 914 (m), 785 (m), 750 (s), 690 (s), 511 (m). Anal. Calcd. for $C_{17}H_{22}ClNiN_3$: C, 56.32; H, 6.12; N, 11.59. Found: C, 56.11; H, 5.87; N, 11.44.

[Ni{2-(C_4H_3N-2-CH=N)C_2H_4OPh}Cl] (**Ni3**). This product was prepared as described above for **Ni1**, starting from **L3** (0.199 g, 0.93 mmol), NaH (0.034 g, 0.93 mmol), and $NiCl_2$(dme) (0.190 g, 0.93 mmol) in THF (10 mL) to give **Ni3** as a pale brown solid (0.193 g, 67%). IR (ATR, cm^{-1}): ν 3011 (w), 2933 (w), 2924 (w), 2861 (w), 1586 (s),

1487 (m), 1487 (m), 1443 (w), 1391 (m), 1312 (m), 1231 (s), 1198 (w), 1172 (m), 1105 (w), 1079 (w), 1050 (m), 1034 (s), 1003 (w), 962 (w), 936 (w), 891 (w), 821 (w), 800 (w), 782 (w), 758 (s), 722 (s), 689 (w), 673 (m), 600 (m), 548 (w), 509 (m), 486 (w), 450 (s). Anal. Calcd. for $C_{13}H_{13}ClNiN_2O$: C, 50.79; H, 4.26; N, 9.11. Found: C, 51.15; H, 4.46; N, 8.88.

[Ni{2-(C_4H_3N-2-CH=N)Ph-2-OPh}Cl] (**Ni4**). This product was prepared as described above for **Ni1**, starting from **L4** (0.299 g, 1.14 mmol), NaH (0.042 g, 1.14 mmol), and $NiCl_2$(dme) (0.250 g, 1.14 mmol) in THF (10 mL) to give **Ni4** as a pale brown solid (0.280 g, 69%). IR (ATR, cm^{-1}): ν 3234 (w), 3065 (w), 2976 (w), 2899 (w), 1626 (s), 1573 (m), 1483 (s), 1452 (m), 1415 (s), 1332 (w), 1312 (w), 1268 (w), 1232 (s), 1182 (s), 1090 (s), 1036 (s), 968 (w), 874 (m), 835 (m), 795 (m), 746 (s), 690 (s), 601 (m), 490 (m). Anal. Calcd. for $C_{17}H_{13}ClNiN_2O$: C, 57.44; H, 3.69; N, 7.88. Found: C, 57.05; H, 3.44; N, 7.66.

[Ni{2-(C_4H_3N-2-CH=N)CH_2Ph-2-SPh}Cl] (**Ni5**). This product was prepared as described above for **Ni1**, starting from **L5** (0.326 g, 1.17 mmol), NaH (0.043 g, 1.17 mmol), and $NiCl_2$(dme) (0.255 g, 1.17 mmol) in THF (10 mL) to give **Ni5** as a pale brown solid (0.377 g, 87%). IR (ATR, cm^{-1}): ν 3054 (w), 1590 (m), 1556 (s), 1497 (s), 1474 (m), 1463(m), 1437 (m), 1379 (m), 1291 (s), 1225 (w), 1185 (m), 1164 (w), 1074 (w), 1030 (s), 996 (w), 943 (w), 902 (m), 889 (w), 836 (w), 748 (s), 723 (m), 685 (m), 667 (w), 625 (w), 597 (m). Anal. Calcd. for $C_{17}H_{13}ClNiN_2S$: C, 54.96; H, 3.53; N, 7.54. Found: C, 54.81; H, 3.94; N, 7.09.

[Ni{2-(C_4H_3N-2-CH=N)CH_2Ph-2-OMe}Cl] (**Ni6**). This product was prepared as described above for **Ni1**, starting from **L6** (0.300 g, 1.40 mmol), NaH (0.051 g, 1.40 mmol), and $NiCl_2$(dme) (0.307 g, 1.40 mmol) in THF (10 mL) to give **Ni6** as a pale brown solid (0.271 g, 63%). IR (ATR, cm^{-1}): ν 2999 (w), 2924 (w), 2835 (w), 1618 (w), 1600 (m), 1579 (s), 1490 (m), 1435 (m), 1378 (m), 1291 (m), 1241 (s), 1175 (w), 116 (m), 1026 (s), 805 (w), 730 (s), 601 (w). Anal. Calcd. for $C_{13}H_{13}ClNiN_2O$: C, 50.79; H, 4.26; N, 9.11. Found: C, 51.34; H, 4.96; N, 8.97.

General oligomerization procedure

Ethylene oligomerization reactions 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 cooled under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of co-catalyst (MAO or EASC) into the reactor under an ethylene atmosphere. After 20 min, the toluene catalyst solution (10 mL, [Ni] = 10 µmol) was injected into the reactor under a stream of ethylene and then the reactor was immediately pressurized. Ethylene was continuously fed in order to maintain the desired ethylene pressure. After 20 min, the reaction was stopped by cooling the system to −60 °C and depressurizing. An exact amount of cyclohexane was introduced (as an internal standard) and the mixture was analyzed by quantitative GLC.

X-ray Diffraction Analyses

A suitable single-crystal of **Ni1** was mounted onto a glass fiber using the ''oil-drop'' method. Diffraction data were collected at 150(2) K using an APEXII Bruker-AXS diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). A combination of ω and ϕ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97) with the aid of the WINGX program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. Crystal data and details of data collection and structure refinement can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 1407832).

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Notes and references

1 (a) M. Peuckert, W. Keim, *Organometallics*, 1983, **2**, 594. (b) M. Peuckert; W. Keim, S. Storp, R.S. Weber, *J. Mol. Catal. A: Chem*, 1983, **20**, 115. (c) W. Keim, *Angew. Chem. Int. Ed.*, 1990, **29**, 235. (d) S. M. Pillai, M. Ravindranathan, S. Sivaram, *Chem. Rev*., 1986, **86**, 353. (e) J. Skupinska, *Chem. Rev*., 1991, **91**, 613. (f) P.-A. R. Breuil, L. Magna, H. Olivier-Bourbigou, *Catal Le*tt., 2015, **145**,173–192.

2 (a) D. Vogt, in: B. Cornils, W. A. Herrmann, (Eds.), In *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley-VCH, Inc. Weinheim, 2000, pp. 245–258. (b) P. W. N. N. van Leeuwen, *Homogeneous Catalysis*, Kluwer Academic, Inc. Dordrecht, 2004, pp. 175–190.

3 (a) J. N. L. Dennett, A. L. Gillon, K. Heslop, D. J. Hyett, J. S. Fleming, C. E. Lloyd-Jones, A. G. Orpen, P. G. Pringle, D. F. Wass, *Organometallics*, 2004, **23**, 6077. (b) C. Bianchini, L. Gonsalvi, W. Oberhauser, D. Sémeril, P. Brüggeller, R. J. Gutmann, Chem. Soc., *Dalton Trans.*, 2003, 3869–3875. (c) T. M. J. Anselment, S. I. Vagin, B. Rieger, *Dalton Trans.*, 2008, 4537–4548. (d) Z. Guan, W. J. Marshall, *Organometallics*, 2002, **21**, () 3580–3586. (e) P. Boulens, M. Lutz, E. Jeanneau, H. Olivier-Bourbigou, J. N. H. Reek, P.-A. R. Breuil, *Eur. J. Inorg. Chem*., 2014, 3754–3762. (f) A. Ghisolfi , C. Fliedel, V. Rosa , K. Y. Monakhov, P. Braunstein, *Organometallics*, 2014, **33**, 2523–2534.

4 (a) F. Speiser, P. Braunstein, L. Saussine, R. Welter, *Organometallics,* 2004, **23**, () 2613–2624. (b) F. Speiser, P. Braunstein, L. Saussine, *Organometallics* 2004, **23**, 2625–2632.

(c) F. Speiser, P. Braunstein, L. Saussine, *Organometallics* 2004, 23, 2633–2640. (d) H. P. Chen, Y. H. Liu, S. M. Peng, S. T. Liu, *Organometallics*, 2003, **22**, 4893-4899. (e) E. K. van den Beuken, W. J. J. Smeets, A. L. Spek, B. L. Feringa, *Chem. Commun.*, 1998, 223–224. (f) P. Braunstein, J. Pietsch, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian, J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1996, 3571–3574. (g) J. Pietsch, P. Braunstein, Y. Chauvin, *New J. Chem.*, 1998, 467–472. (h) F. Speiser, P. Braunstein, L. Saussine, R. Welter, *Inorg. Chem.*, 2004, 43, 1649–1658. (i) X. Tang, D. Zhang, S. Jie, W.H. Sun, J. Chen, *J. Organomet. Chem.,* 2005, **690**, 3918–3928. (j) F. Speiser, P. Braunstein, L. Saussine, *Acc. Chem. Res.* 2005, **38**, 784–793. (k) W.-H. Sun, W. Zhang, T. Gao, X. Tang, L. Chen, Y. Li, X. Jin, *J. Organomet. Chem.,* 2004, **689**, 917–929. (l) M. E. Bluhm, C. Folli, O. Walter, M. Döring, *J. Mol. Catal. A: Chem.* 2005, **229**, 177–181. (m) Z. Weng, S. Teo, T. S. A. Hor, *Organometallics*, 2006, **25**, 4878–4882. (n) L. O. de la Tabla, I. Matas, P. Palma, E. Álvarez, J. Cámpora, *Organometallics*, 2012, **31**, 1006–1016. (o) S. Zhang, R.Pattacini, S. Jie, P. Braunstein, *Dalton Trans*., 2012, **41**, 379.

5 (a) W. Keim, *Angew. Chem., Int. Ed.* 1990, **29**, 235–244. (b) J. M. Malinoski, M. Brookhart, *Organometallics*, 2003, **22**, 5324–5335. (c) W. Liu, J. M. Malinoski, M. Brookhart, *Organometallics*, 2002, **21**, 2836–2838. (d) J. Heinicke, M. Köhler, N. Peulecke, W. Keim, *J. Catal.* 2004, **225**, 16–23. (e) P. Kuhn, D. Sémeril, D. Matt, M. J. Chetcutti, P. Lutz, *Dalton Trans.*, 2007, 515–528. (f) A. Kermagoret, P. Braunstein, *Dalton Trans.*, 2008, 822–831. (g) C.-Y. Guo, N. Peulecke, M. K. Kindermann, J.W. Heinicke, *J. Polym. Sci., A: Polym. Chem.* 2009, **47**, 258–266. (h) J. Flapper, H. Kooijman, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, C. J. Elsevier, P. C. J. Kamer, *Organometallics* 2009, **28**, 1180–1192.

6 (a) H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang, W.-H. Sun, *Organometallics,* 2011, **30**, 2418–2424. (b) R. Gao, L. Xiao, X. Hao, W.-H. Sun, F. Wang, *Dalton Trans.*, 2008, 5645–5651. (c) X. Tang,W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, *J. Organomet. Chem.,* 2005, **690**, 1570–1580. (d) S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng, W. Chen, *J. Organomet. Chem.,* 2005, **690**, 1739–1749. (e) E. Nelkenbaum, M. Kapon, M. S. Eisen, *J. Organomet. Chem.,* 2005, 690, 2297–2305. (f) J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez, P. Gómez-Sal, Organometallics, 2006, **25**, 3876–3887. (g) C.-L. Song, L.-M. Tang, Y.-G. Li, X.-F. Li, J. Chen, Y.-S. Li, *J. Polym. Sci., A: Polym. Chem.*, 2006, **44**, 1964–1974. (h) B. Y. Lee, X. Bu, G. C. Bazan, *Organometallics,* 2001, **20**, 5425–5431. (i) S. A. Sveida, M. Brookhart, *Organometallics*, 1999, **18**, 65–74. (j) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics,* 1997, **16**, 2005–2007. (k) A. J. Swarts, S. F. Mapolie, *Dalton Trans*., 2014, **43**, 9892–9900. (l) J. Canivet, S. Aguado, Y. Schuurman, D. Farrusseng, *J. Am. Chem. Soc*., 2013, **135**, 4195–4198. (m) S. Song, T. Xiao, T. Liang, F. Wang, C. Redshaw, W.-H. Sun, *Catal. Sci. Technol*., 2011, **1**, 69–75. (n) J. Yu, X. Hu, Y. Zeng, L. Zhang, C. Ni, X. Haoc, W.-H. Sun, *New J. Chem*., 2011, **35**, 178–183. (o) R. M. Bellabarba, P. T. Gomes, S. I. Pascu, *Dalton Trans*., 2003, 4431–4436. (p) J. Li, T. Gao, W. Zhang, W.-H Sun, *Inorg. Chem. Commun*., 2003, **6**, 1372–1374.

7 (a) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science*, 2000, **287**, 460–462. (b) C. Carlini, M. Isola, V. Liuzzo, A. M. R. Galletti, C. Sbrana, *Appl. Catal. A,* 2002, **231**, 307–320. (c) S. Wu, S. Lu, *Appl. Catal. A* 2003, **246**, 295–301. (d) F. Speiser, P. Braunstein, L. Saussine, *Inorg. Chem.,* 2004, **43**, 4234–4240. (e) Y. Chen, G. Wu, G. C. Bazan, *Angew. Chem. Int. Ed.,* 2005, **44**, 1108–1112. (f) A. Kermagoret, P. Braunstein, *Dalton Trans.*, 2008, 1564–1573. (g) N. A. Cooley, S. M. Green, D. F. Wass, *Organometallics,* 2001, 20, 4769–4771. (h) T. Hu, L.-M. Tang, X.-F. Li, Y.-S. Li, N.-H. Hu, *Organometallics*, 2005, **24**, 2628–2632. (i) T. Cheisson, T.-P.-A. Cao , X. F. Le Goff, A. Auffrant, *Organometallics*, 2014, **33**, 6193–6199.

8 (a) L. Xiao, M. Zhang, R. Gao, X. Cao, W.-H. Sun, *Aust. J. Chem*., 2010, **63**, 109. (b) Q.-Z. Yang, A. Kermagoret, M. Agostinho, O. Siri, P. Braunstein, *Organometallics*, 2006, **25**, 5518. (c) A. Kermagoret, F. Tomicki, P. Braunstein, *Dalton Trans*., 2008, 2945. (d) J. Hou, W.-H. Sun, S. Zhang, H. Ma,Y. Deng, X. Lu, *Organometallics*, 2006, **25**, 236. (e) C. Zhang, W.-H. Sun, Z.-X. Wang, *Eur. J. Inorg. Chem*., 2006, 4895. (f) W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, *J. Organomet. Chem*., 2006, **691**, 4196. (g) W.-H. Sun, K. Wang, K. Wedeking, D. Zhang, S. Zhang, J. Cai, Y. Li, *Organometallics*, 2007, **26**, 4781. (h) P. Hao, S. Zhang, W.-H. Sun, Q. Shi, S. Adewuyi, X. Lu, P. Li, *Organometallics*, 2007, **26**, 2439. (i) Y. Chen, P. Hao, W. Zuo, K. Gao, W.-H. Sun, *J. Organomet. Chem.*, 2008, **693**, 1829. (j) S. Adewuyi, G. Li, S. Zhang, W. Wang, P. Hao, W.-H. Sun, N. Tang, J. Yi, *J. Organomet. Chem*., 2007, **692**, 3532. (k) A. P. Armitage, Y. D. M. Champouret, H. Grigoli, J. D. A. Pelletier, K. Singh, G. A. Solan, *Eur. J. Inorg. Chem.*, 2008, 4597. (l) Y. Yang, P. Yang, C. Zhang, G. Li, X.-J. Yang, B. Wu, C. Janiak, *J. Mol. Catal. A: Chem*., 2008, **296**, 9. (m) R. Gao, M. Zhang, T. Liang, F. Wang, W.-H. Sun, *Organometallics*, 2008, **27**, 5641. (n) S. Jie, S. Zhang, W.-H. Sun, *Eur. J. Inorg. Chem*., 2007, **35**, 5584. (o) M. Zhang, P. Hao, W. Zuo, S. Jie, W.-H. Sun, *J. Organomet. Chem*., 2008, **693**, 483. (p) W.-H. Sun, P. Hao, S. Zhang, Q. Shi, W. Zuo, X. Tang, X. Lu, *Organometallics*, 2007, **26**, 2720. (q) R. Gao, Y. Li, F. Wang, W.-H. Sun, M. Bochmann, *Eur. J. Inorg. Chem*., 2009, **27**, 4149. (r) G. S. Nyamato, M. G. Alam, S. O. Ojwach, M. P. Akerman, *J. Organomet. Chem*., 2015, **783**, 64-72. (s) J. Lai, X. Hou, Y. Liu, C. Redshaw, W.-H. Sun, *J. Organomet. Chem.*, 2012, **702**, 52-58. (t) C. Obuaha, B. Omondia, K. Nozaki, J. Darkwa, *J. Mol. Cat. A: Chem*, 2014, **382**, 31–40.

9 F. Speiser, P. Braunstein, L. Saussine, *Dalton Trans*., 2004, 1539.

10 M. Zhang, S. Zhang, P. Hao, S. Jie, W.-H. Sun, P. Li, X. Lu, *Eur. J. Inorg. Chem*., 2007, 3816.

11 A. Boudier, P.-A. R. Breuil, L. Magna, H. Olivier-Bourbigou, P. Braunstein, *J. Organomet. Chem*., 2012, **718**, 31-37.

12 (a) N. Ajellal, M. C. A. Kuhn, A. D. G. Boff, M. Hoerner, C. M. Thomas, J.-F. Carpentier, O. L. Casagrande, *Organometallics*, 2006, **25**, 1213. (b) L. L. de Oliveira, R.R. Campedelli, A. L. Bergamo, A. H. D. P dos Santos, O. L. Casagrande, *J. Braz. Chem. Soc*., 2010, **21**, 1318. (c) F. A. Kunrath, R. F. de Souza, O. L. Casagrande, N. R. Brooks, V. G. Young, *Organometallics*, 2003, **22**, 4739. (d) F. Junges, M. C. A. Kuhn, A. H. P. Santos, C. R. K. Rabello, C. M. Thomas, J.-F. Carpentier, O. L. Casagrande Jr, *Organometallics*, 2007, **26**, 4010. (e) L.L. de Oliveira, R.R. Campedelli, M.C.A. Kuhn, J.-F. Carpentier, O.L. Casagrande Jr, *J. Mol. Catal. A: Chem.*, 2008, **288**, 58. (f) A. H. P. S. Ulbrich, A. L. Bergamo, O. L. Casagrande Jr., *Catal. Commun*., 2011, **16**, 245. (g) E. Kirillov, T. Roisnel, A. Razavi, J.-F. Carpentier, *Organometallics* 2009, **28**, 2401.

13 J. Wang, L. Wan, D. Zhang, Q. Wang, Z. Chen, *Eur. J. Inorg. Chem.* 2013, 2093.

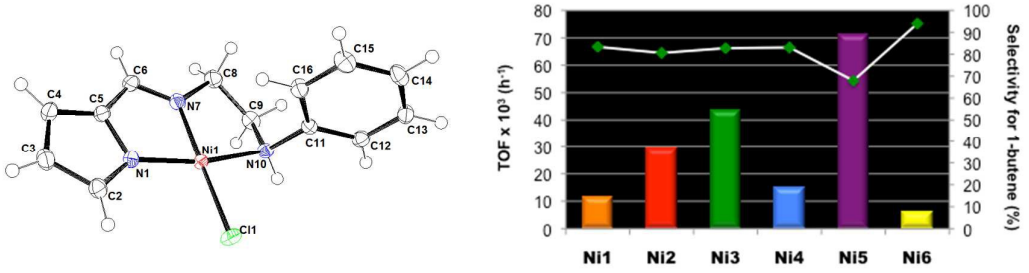
14 (a) X. Yang, Z.-X. Wang, *Organometallics*, 2014, **33**, 5863. (b)F.-B. Han, Y.-L. Zhang, X.-L. Sun, B.-G. Li, Y.-H. Guo, Y. Tang, *Organometallics*, 2008, **27**, 1924. (c) L.-C. Liang, P.-S. Chien, J.-M. Lin, M.-H. Huang, Y.-L. Huang, J.-H. Liao, *Organometallics*, 2006, **25**, 1399.

15 S. Wang, W.-H. Sun, C. Redshaw, *J. Organomet. Chem*., 2014, **751**, 717-741.

16 A. C. Pinheiro, E. Kirillov T. Roisnel, J.-F. Carpentier, O. L. Casagrande Jr, *Dalton Trans.*, 2015, **44**,16073.

17 H. J. Anderson, C. E. Loader, *Synthesis*, 1985, 353.

Graphical Contents Entry



Nickel complexes bearing pyrrolide-imine ligands with pendant O- and S-donor groups have been synthesized and their catalytic behavior in ethylene oligomerization has been investigated.