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Nickel Complexes Based on Tridentate Pyrazolyl Ligands for Highly Efficient Dimerization of Ethylene to 1-Butene

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A series of new pentacoordinated nickel complexes $NiCl_2$(NZN) based on nitrogen-, oxygen-, or sulfur-bridged bis(pyrazolyl) ligands (NZN) were synthesized and characterized by elemental analysis and an X-ray diffraction study for $NiCl_2$\{bis[2-(3,5-dimethylpyrazolyl)ethyl)]amine\} (**1**). Upon activation with methylaluminoxane (MAO), these complexes show high activity in ethylene oligomerization (TOF $= 7-80 \times 10^3\ h^{-1}$), which varies according to the ligand environment. Up to 92% selectivity for 1-butene, combined with a TOF of $60 \times 10^3\ h^{-1}$, has been obtained under moderate conditions (30 °C, 40 bar, MAO-to-Ni = 250) using $NiCl_2$\{bis[2-(5-phenylpyrazolyl)ethyl)]ether\} (**3**) as the catalyst precursor.

Introduction

Olefin oligomerization is a major industrial process.[1] Linear α-olefin oligomers with relatively short chain lengths (C_4-C_{12}), commonly produced with nickel catalysts in the Shell's SHOP process,[2] are used as comonomers in the polymerization of ethylene to give linear low-density polyethylene (LLDPE). These oligomers are also used for the preparation of a variety of economically important compounds, e.g., detergents, synthetic lubricants, and fuel powering components.[1] Many efforts are still devoted to the development of highly selective ethylene oligomerization catalysts, and among classes of catalysts used for production of α-olefins, nickel complexes are the most frequently studied. The vast majority of single-site nickel catalyst precursors reported for homogeneous oligomerization of ethylene are tetracoordinated and contain P,P-,[3] P,N-,[4] P,O-,[5] N,N-,[6] or N,O-[7] as bidentate chelating ligands. On the other hand, very few examples of pentacoordinated Ni(II) precursors generating active oligomerization catalysts are described in the literature. For instance, Braunstein et al.[8] have recently reported a nickel phosphonite complex [$NiCl_2(NOPON^{Me2})$] [$NOPON^{Me2}$ = bis(4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydro-oxazole)phenylphosphonite] that is able to oligomerize ethylene upon activation with $AlEtCl_2$; however, this catalyst has shown low selectivity for 1-butene (<21%), favoring the thermodynamically more stable 2-butene. Herein, we report a new class of pentacoordinated Ni(II) complexes based on tridentate RN-, O-, or S-bridged bis(pyrazolyl) ligands, which, in combination

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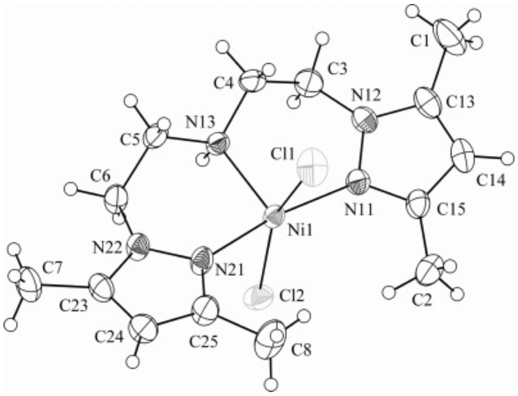
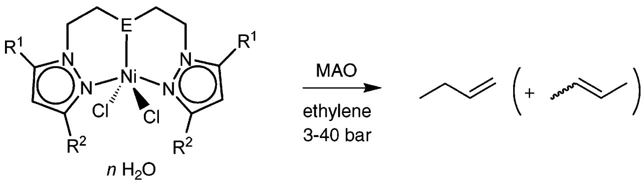


Figure 1. Molecular structure of $\mathbf{1}\cdot H_2O$. Thermal ellipsoids are drawn at the 50% probability level; the water molecule found in the unit cell is not shown. Selected bond distances (Å) and angles (deg): Ni(1) −N(11) = 2.069(2), Ni(1)−N(13) = 2.0317(19), Ni(1)−N(21) = 2.0334(19), Ni(1)−Cl(1) = 2.3647(9), Ni(1)−Cl(2) = 2.3628(8), N(13)−Ni(1)−N(21) = 95.55(8), N(13)−Ni(1)−N(11) = 94.12(8), N(21)−Ni(1)−N(11) = 170.13(8), N(13)−Ni(1)−Cl(2) = 100.46(6), N(21)−Ni(1)−Cl(2) = 87.05(7), N(11)−Ni(1)−Cl(2) = 93.14(7), N(13)−Ni(1)−Cl(1) = 100.67(6), N(21)−Ni(1)−Cl(1) = 90.20(7), N(11)−Ni(1)−Cl(1) = 86.07(7), Cl(2)−Ni(1)−Cl(1) = 158.86(3).

Scheme 1



1: E = NH; R^1, R^2 = Me; *n* = 0
2: E = O; R^1, R^2 = Me; *n* = 2
3: E = O; R^1 = H, R^2 = Ph; *n* = 2
4: E = O; R^1 = H, R^2 = *t*Bu; *n* = 2
5: E = S; R^1, R^2 = Me; *n* = 2

with MAO, give highly active catalysts for selective dimerization of ethylene to 1-butene.

Results and Discussion

The tridentate nitrogen-, oxygen-, or sulfur-bridged bis(pyrazolyl) ligands (NZN) used in this study, which include three new derivatives, were readily prepared in high yields via literature procedures[9] or through adaptation of these (see Experimental Section). Reaction of these NZN ligands with $NiCl_2\cdot 6H_2O$ in THF or MeOH at room temperature for 3 h afforded the corresponding complexes $NiCl_2(NZN)\cdot nH_2O$ (**1**−**5**), which were isolated in good to high yields (65−92%, Scheme 1). The identity of complexes **1**−**5** was established by elemental analysis and mass spectrometry. It was further confirmed by an X-ray diffraction study of suitable single crystals of **1** (Figure 1, Table 1), which represents a rare example of a five-coordinated nickel complex with a nitrogen-based tridentate ligand.

Table 1. Crystal Data and Structure Refinement for $\mathbf{1\cdot H_2O}$

empirical formula	$C_{14}H_{25}Cl_2N_5NiO$	
fw	409.00	
temperature	295(2) K	
wavelength	0.71073 Å	
cryst syst	orthorhombic	
space group	*Pna*2_1 (No. 33)	
unit cell dimens	a = 15.2841(4) Å	α = 90°
	b = 13.7542(4) Å	β = 90°
	c = 9.0503(2) Å	γ = 90°
volume	1902.56(9) $Å^3$	
Z	4	
density (calcd)	1.428 Mg/m^3	
abs coeff	1.310 mm^{-1}	
F(000)	856	
cryst size	0.35 × 0.22 × 0.18 mm^3	
θ range for data collection	1.99 to 25.50°	
index ranges	$-18 \leq h \leq 18$, $-16 \leq k \leq 16$, $-10 \leq l \leq 10$	
no. of reflns collected	38 947	
no. of indep reflns	3503 [R(int) = 0.0182]	
completeness to θ = 25.50°	99.8%	
max. and min. transmn	0.7983 and 0.6570	
refinement method	full-matrix least-squares on F^2	
no. of data/restraints/ params	3503/1/212	
goodness-of-fit on F^2	1.246	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0221, wR2 = 0.0673	
R indices (all data)	R1 = 0.0280, wR2 = 0.0883	
absolute struct param	0.005(13)	
largest diff peak and hole	0.558 and −0.595 $e\cdot Å^{-3}$	

Complex **1** is monomeric in the solid state with κ^3 coordination of the amino-bis(pyrazolyl) ligand onto the nickel center. The tridentate ligand coordinates to nickel meridionally as in the analogous complex $[Ni(pps)Cl_2]$ [pps = bis(3-(diphenylphosphino)propyl)sulfide],[10] resulting in a distorted square pyramidal coordination geometry, with unexceptional bond distances and angles. The Ni(1), N(13), N(11), and N(21) atoms are nearly coplanar, and the two six-membered chelate rings are almost identical, as indicated by the similar bite angles N(13)−Ni(1)−N(21) = 95.55(8)° and N(13)−Ni(1)−N(11) = 94.12(8)°.

The catalytic performances of nickel complexes **1**−**5** in the oligomerization of ethylene have been evaluated using methylaluminoxane (MAO) as cocatalyst (Scheme 1). Representative results are given in Table 2. Initial studies carried out at 30 °C under 20 bar of ethylene with MAO-to-Ni ratios of 250 showed that these catalyst systems are quite active. The activity of ethylene oligomerization is substantially affected by the ligand environment. High turnover frequencies (TOFs) in the range 7100−18 500 h^{-1} are obtained with N- and O-based ligands (entries 1−4), while the catalyst system derived from **5** that contains a sulfur-bridged ligand gives a very high TOF of 57 200 h^{-1} (entry 5). With the catalysts derived from N- and O-based ligands, the selectivity for butenes and especially 1-butene is very high, attaining 87.3−87.8% of the total amount of olefins formed in the oligomerization reactions under these conditions (i.e., ca. 88−89% of the C_4 fraction). We were, however, surprised to observe a minimal influence of the pyrazolyl substituents (R^2) on the product distribution in the homologous series of catalyst precursors **2**−**4**. Larger amounts of 2-butenes (ca. 27%) are produced from the sulfur-containing precursor **5**. In all cases, minimal amounts of hexenes[11] and no polymer were detected.

The selectivities and catalyst activity were monitored versus time in the ethylene oligomerization reaction promoted by the

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(11) Several isomers of hexenes were detected in GLC, of which 1-hexene is the most abundant one (ca. >90%). Because of the low total amount of C_6 formed, other hexene isomers could not be quantified accurately.

Table 2. Ethylene Oligomerization with 1−3/MAO Combinations[a]

						selectivity (%)[c]				
entry	complex	MAO/Ni	*T* (°C)	*P* (bar)	TOF[b] (10^3 h^{-1})	C_4	α-C_4	*cis*-C_4	*trans*-C_4	α-C_6
1	**1**	250	30	20	15.4	98.6	87.5	7.2	3.9	1.4
2	**2**	250	30	20	7.1	98.7	87.5	7.3	3.9	1.3
3	**3**	250	30	20	18.5	98.7	87.8	7.0	3.9	1.3
4	**4**	250	30	20	9.7	98.8	87.3	7.2	4.3	1.2
5	**5**	250	30	20	57.2	98.5	71.5	17.2	9.7	1.5
6	**1**	100	30	3	0.83	98.3	63.0	22.2	13.1	1.7
7	**1**	250	30	3	2.43	98.3	65.9	20.9	11.7	1.5
8	**1**	500	30	3	0.66	>99.9	68.3	19.9	11.8	<0.1
9	**1**	500	60	3	1.44	97.3	44.1	32.7	20.5	2.7
10	**1**	500	0	3	0.18	98.1	67.0	19.5	11.6	1.9
11	**1**	250	30	40	15.8	98.8	93.7	1.9	3.3	1.2
12	**3**	250	30	40	59.8	98.8	93.1	3.6	2.1	1.2
13	**4**	250	30	40	78.1	98.6	80.6	11.3	6.7	1.4
14	**5**	250	30	40	81.0	98.6	82.2	10.3	6.1	1.4

[a] Reaction conditions: toluene = 50 mL, [Ni] = 10.0 ± 0.5 μmol, oligomerization time = 20 min. 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] C_n, amount of olefin with *n* carbon atoms in the oligomers; α-C_n, amount of terminal alkene in the C_n fraction; as determined by quantitative GLC; see ref 11 for C_6.

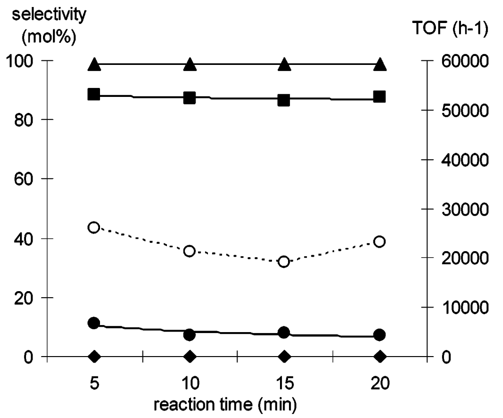

Figure 2. Monitoring of selectivities (solid lines) and activity (dash line) in the ethylene oligomerization reaction promoted by the **3**/MAO system ([MAO]/[Ni] = 250; *T* = 30 °C; 20 atm ethylene): ▲ C_4 products, ■ 1-butene, ● *cis*-2-butene, ◆ *trans*-2-butene (hexenes, mostly 1-hexene, were also produced in 1.1−1.6% selectivity and are not shown in this figure); ○ TOF.

3/MAO system (Figure 2). No significant decrease in the TOF values was determined over a 5−20 min period, indicating a rather long lifetime and good thermal stability of the catalytic species. The catalyst stability is also supported by the selectivities for butenes, which are virtually constant over the 20 min time period (Table 2, entry 3, ±1%). These results thus indicate that isomerization of butenes is a minor pathway in these reactions and that the observed selectivities directly reflect the dimerization abilities of the catalysts.

On the basis of these encouraging preliminary results, complex **1** was selected for further optimization, investigating the influence of the temperature, [Al]/[Ni] molar ratio, and ethylene pressure. Under 3 bar of ethylene, the oligomerization rate logically increased with temperature, with TOFs varying from 180 to 1440 h^{-1} from 0 to 60 °C (entries 8−10). However, increasing the oligomerization temperature caused a decrease of the selectivity for 1-butene, along with a more balanced 2-butene isomeric ratio (*cis* vs *trans*). A similar influence of temperature on the oligomer distribution produced with nickel-based systems has been reported by other groups.[8,12] When activated with 100 equiv of MAO, complex **1** gave a relatively low activity (TOF = 830 h^{-1}, entry 6), which was increased upon using 250 equiv of MAO (TOF = 2430 h^{-1}, entry 7). A greater loading of MAO (500 equiv) led to lower activity (TOF = 660 h^{-1}, entry 8), which is a fact with no straightforward explanation. At the same time, increasing the amount of MAO from 100 to 500 equiv led to slightly improved selectivities, for both the C_4 fraction (98.3 to >99.9%) and 1-butene (63.0 to 68.3%). A temperature of 30 °C and a MAO-to-Ni ratio of 250 appeared therefore as a good tradeoff between activity and selectivity.

Increasing the ethylene pressure resulted in much higher TOFs, probably as an effect of increased ethylene concentration in solution. Although an apparent limitation occurred with the **1**/MAO system above 20 bar (compare entries 1, 7, and 11), the activities of the **3**/MAO, **4**/MAO, and **5**/MAO systems are significantly enhanced at 40 bar, giving maximal TOFs of 78 000−81 000 h^{-1} (entries 13, 14). With the only exception of the **4**/MAO system, better selectivities for 1-butene were also observed at higher pressure (compare entries 1/11, 3/12, and 5/14). Increase of selectivity with monomer pressure is usually accounted for by increased dimerization activity, which in turn attenuates the effect of parallel isomerization of 1-butene into 2-butenes (i.e., chain transfer is favored relative to chain isomerization).[4d,m,13] Our monitoring results show, however, that the latter isomerization process plays no significant role with the current catalyst systems (Figure 2, vide supra).

In conclusion, under optimized conditions, the **3**/MAO catalyst system enables oligomerization of ethylene to produce up to ca. 92% of 1-butene with very high activity. This new simple class of nickel complexes based on readily available tridentate ligands compares favorably with the best dimerization nickel systems so far disclosed.[5c,14] Further studies are underway in our laboratories to investigate mechanistic aspects of these new dimerization systems.

Experimental Section

General Procedures. All manipulations were performed using standard vacuum line and Schlenk techniques under a purified argon atmosphere. Et_2O, THF, and toluene were distilled from sodium-benzophenone ketyl under argon and degassed by freeze−thaw−

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[14] During the reviewing process of the manuscript, new nickel complexes based on PNN ligands have been disclosed, which allow highly selective dimerization of ethylene to 1-butene (up to 97%), with good activities (TOF = 4 × 10^3 h^{-1} at 20 °C, 10 bar): Hou, J.; Sun, W.-H.; Zhang, S.; Ma, H.; Deng, Y.; Lu, X. *Organometallics* **2006**, *25*, 236.

vacuum cycles prior to use. $NiCl_2 \cdot 6H_2O$ (Aldrich) was used as received. The known ligands bis[2-(3,5-dimethylpyrazolyl)ethyl)]amine, bis[2-(3,5-dimethylpyrazolyl)ethyl)]ether, and bis[2-(3,5-dimethylpyrazolyl)ethyl)]sulfide were prepared by literature procedures.[9] The new ligands bis[2-(5-phenylpyrazolyl)ethyl)]ether and bis[2-(5-*tert*-butylpyrazolyl)ethyl)]ether were prepared following a similar procedure (see below). Ethylene (White Martins Co.) and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (3 Å) prior to use. MAO (Witco, 5.21 wt % Al solution in toluene) was used as received. Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry−UFRGS (Brazil) and by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations. ESI-HRMS of Ni complexes was performed on a Perkin-Elmer Sciex API-I single quadrupole spectrometer; the instrument was operated at atmospheric pressure in the positive-ion mode (5 kV). Quantitative gas chromatographic analysis of the reaction products was performed on a Varian 3400CX instrument with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d., and film thickness of 0.5 μm) operating at 36 °C for 15 min and then heating at 5 °C min^{-1} to 250 °C.

Bis[2-(5-phenylpyrazolyl)ethyl)]ether. Under an argon atmosphere, 3-phenylpyrazole (4.06 g, 0.028 mol) was slowly added to a suspension of NaH (1.02 g, 0.042 mol) in dry DMF (30 mL) and dry THF (20 mL). The mixture was stirred at 60 °C for 2 h. To the resulting solution was added dropwise under stirring a solution of bis(2-chloroethyl)ether (1.69 mL, 0.014 mol) in dry DMF (10 mL). The mixture was allowed to stir for 18 h at 60 °C, cooled, and treated cautiously with H_2O (15 mL) to decompose excess NaH. The solvents were then evaporated under reduced pressure. The residue was extracted with ethyl acetate (4 × 40 mL), washed with of 10% NaOH (2 × 30 mL) and H_2O (2 × 30 mL), and then dried over $MgSO_4$. The solvent was evaporated to give a tan solid (4.31 g, 86%), which was crystallized from ethyl acetate to give bis[2-(5-phenyl-l-pyrazolyl)ethyl]ether as white needles (3.91 g, 78%). ^1H NMR ($CDCl_3$, 298 K, 200 MHz): δ 3.79 (4H, t, $J = 4.90$ Hz), 4.26 (4H, t, $J = 4.90$ Hz), 6.45 (2H, s), 7.32 (8H, m), 7.75 (4H, m). Anal. Calcd for $C_{22}H_{22}N_4O$: C, 73.72; H, 6.19; N, 15.63. Found: C, 73.56; H, 6.25; N, 15.48.

Bis[2-(5-*tert*-butylpyrazolyl)ethyl)]ether. This product was prepared following a similar procedure as described above, starting from 3-*tert*-butylpyrazole (6.23 g, 0.050 mol), NaH (1.80 g, 0.075 mol), and bis(2-chloroethyl)ether (2.93 mL, 0.025 mol). After workup and purification by flash chromatography (SiO_2, EtOAc/hexane, 2:1), the ligand was recovered as a pale yellow oil (5.67 g, 71%). ^1H NMR ($CDCl_3$, 298 K, 300 MHz): δ 1.28 (18H, s, CH_3), 3.70 (4H, t, $J = 5.2$ Hz, OCH_2CH_2), 4.16 (4H, t, $J = 5.2$ Hz, OCH_2CH_2-pyr), 6.01 (2H, d, $J = 2.25$ Hz, CH pyr), 7.15 (2H, d, $J = 2.25$ Hz, C*H* pyr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, 75 MHz): δ 30.28 ($C(CH_3)_3$), 31.16 ($C(CH_3)_3$), 51.22 (OCH_2CH_2), 70.66 (OCH_2CH_2), 99.21 (CH pyr), 130.73 (CH pyr), 156.37 (C pyr). Anal. Calcd for $C_{18}H_{30}N_4O$: C, 67.92; H, 9.43; N, 17.61. Found: C, 67.71; H, 9.24; N, 17.40.

$NiCl_2$\{bis[2-(3,5-dimethylpyrazolyl)ethyl)]amine\} (1). To a solution of $NiCl_2 \cdot 6H_2O$ (109 mg, 0.46 mmol) in THF (10 mL) was added a solution of bis[2-(3,5-dimethylpyrazol)ethyl)]amine (120 mg, 0.46 mmol) in THF (10 mL), and the resulting solution was stirred for 3 h at room temperature. Volatiles were removed under reduced pressure, and the resulting green solid residue was washed with Et_2O (2 × 10 mL) to afford a bright green solid (165 mg, 92%). Anal. Calcd for $C_{14}H_{23}N_5Cl_2Ni$: C, 43.01; H, 5.93; N, 17.91. Found: C, 42.73; H, 6.17; N, 18.26. Single crystals of complex **1**·H_2O suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a toluene/wet acetonitrile (1:4) solution.

$NiCl_2$\{bis[2-(3,5-dimethylpyrazolyl)ethyl)]ether\} (2). This compound was prepared according to the method described for **1** using $NiCl_2 \cdot 6H_2O$ (116 mg, 0.49 mmol) and bis[2-(3,5-dimethylpyrazol)ethyl)]ether (128 mg, 0.49 mmol). Complex **2** was obtained as a turquoise blue solid (175 mg, 91%). Anal. Calcd for $C_{14}H_{22}N_4Cl_2NiO \cdot 2H_2O$: C, 39.29; H, 6.12; N, 13.09. Found: C, 39.98; H, 6.00; N, 12.83. HRMS (ESI, $CH_3OH/CHCl_3$ 1:1, *m/z*): $[M - 2Cl + Na + 2H_2O]^+$ ($C_{14}H_{26}N_4O_3NaNi$) calcd 379.1260; found 379.1257.

$NiCl_2$\{bis[2-(5-phenylpyrazolyl)ethyl)]ether\} (3). This compound was prepared according to the method described for **1** using $NiCl_2 \cdot 6H_2O$ (105 mg, 0.44 mmol) and bis[2-(5-phenylpyrazol)ethyl)]ether (158 mg, 0.44 mmol). Complex **3** was obtained as a yellow-green solid (140 mg, 65%). Anal. Calcd for $C_{22}H_{22}N_4OCl_2Ni \cdot 2H_2O$: C, 50.41; H, 5.59; N, 10.31. Found: C, 50.42; H, 5.00; N, 10.69. HRMS (ESI, $CH_3OH/CHCl_3$ 1:1, *m/z*): $[M - 2Cl + Na + 2H_2O]^+$ ($C_{22}H_{26}N_4O_3NaNi$) calcd 475.1258; found 475.1260.

$NiCl_2$\{bis[2-(5-*tert*-butylpyrazolyl)ethyl)]ether\} (4). This compound was prepared according to the method described for **1** using $NiCl_2 \cdot 6H_2O$ (60 mg, 0.25 mmol), bis[2-(5-*tert*-butylpyrazolyl)ethyl)]ether (80 mg, 0.25 mmol), and methanol in place of THF. Workup afforded **4** as a yellow solid (78 mg, 70%). Anal. Calcd for $C_{18}H_{30}Cl_2N_4NiO \cdot 2H_2O$: C, 44.66; H, 7.08; N, 11.57. Found: C, 44.87; H, 7.51; N, 11.74. HRMS (ESI, $CH_3OH/CHCl_3$ 1:1, *m/z*): $[M - Cl]^+$ ($C_{18}H_{30}N_4OClNi$) calcd 411.14616; found 411.1456, $[M - 2Cl + 2H_2O + Na]^+$ ($C_{18}H_{34}N_4O_3NaNi$) calcd 435.1882; found 435.1881.

$NiCl_2$\{bis[2-(3,5-dimethylpyrazolyl)ethyl)]sulfide\} (5). This compound was prepared according to the method described for **4** using $NiCl_2 \cdot 6H_2O$ (200 mg, 0.84 mmol) and bis[2-(3,5-dimethylpyrazolyl)ethyl)]sulfide (234 mg, 0.84 mmol). Complex **5** was obtained as a dark yellow solid (286 mg, 84%). Anal. Calcd for $C_{14}H_{22}Cl_2N_4NiS \cdot 2H_2O$: C, 37.87; H, 5.90; N, 12.62; S, 7.22. Found: C, 37.60; H, 5.77; N, 12.22; S, 7.10. HRMS (ESI, $CH_3OH/CHCl_3$ 1:1, *m/z*): $[M - Cl]^+$ ($C_{14}H_{22}N_4ClSNi$) calcd 371.0607; found 371.0603.

General Oligomerization Procedure. Ethylene oligomerization reactions were performed in two different reactors according to the pressure: (a) For reactions at 3 bar, a Fisher-Porter bottle (100 mL) equipped with a magnetic stirrer bar and a stainless steel pressure head fitted with inlet and outlet needle valves, a septum-capped ball valve for injections, and a pressure gauge was used. (b) For reactions conducted at higher pressure (20−40 bar), a 250 mL double-walled stainless Parr reactor equipped with mechanical stirring and continuous feed of ethylene was used. For the two systems, the reaction temperature was controlled by a thermostatic circulation bath. Both reactors were dried in an oven at 120 °C for 12 h prior to each run and then placed under vacuum for 30 min. A typical reaction was performed by introducing in the reactor, under argon, toluene (40 mL) and the proper amount of MAO cocatalyst. The system was saturated with ethylene and the oligomerization reaction was started by introduction of the nickel complex (10 μmol) dissolved in toluene (10 mL). The ethylene was continuously fed in order to maintain the ethylene pressure at the desired value. After 20 min, the reaction was stopped by cooling the system at −20 °C, depressurizing, and introducing 1 mL of ethanol. An exact amount of cyclohexane was introduced (as internal standard), and the mixture was analyzed by quantitative GLC.

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Supporting Information Available: Complete crystallographic data (CIF format) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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