Organometallics **2003,** *22,* 4739−4743

Highly Selective Nickel Ethylene Oligomerization Catalysts Based on Sterically Hindered Tris(pyrazolyl)borate Ligands

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Received July 11, 2003

The reaction of TlTp′ (Tp′ = HB(3-mesitylpyrazolyl)$_3^-$ (Tp$^{\mathrm{Ms}}$), HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$ (Tp$^{\mathrm{Ms*}}$)) with $\mathrm{NiCl_2 \cdot 6H_2O}$ affords Tp$^{\mathrm{Ms}}$NiCl (**1**) and Tp$^{\mathrm{Ms*}}$NiCl (**2**) in good yield. The compound **2** undergoes an isomerization process to form [{Tp$^{\mathrm{Ms**}}$}NiCl]$_2$ (**3**) (Tp$^{\mathrm{Ms**}}$= HB(5-mesitylpyrazolyl)$_2$(3-mesitylpyrazolyl)$^-$) in 68% yield. Treatment of the tris(pyrazolyl)borate nickel compounds **1** and **2** with alkylaluminum cocatalysts such as methylalumoxane (MAO) and trimethylaluminum (TMA) in toluene generates active catalysts for ethylene oligomerization. The compound **1** shows turnover frequencies in the range of (2.2−43.1) × 10^3 h^{-1}. Oligomerization reaction conditions can be adjusted that lead to selectivities as high as 81% for butene-1.

Introduction

Olefin oligomerization is a major industrial process,[1] and nickel complexes are the most frequently employed catalysts.[2] High-performance Ni catalysts that selectively produce oligomers have been obtained via tailoring of the surrounding ligands.[3] An embarrassingly large number of nickel complexes have been described as active in olefin oligomerization, and this is probably due to the fact that almost any of them can afford a nickel hydride that is active in carbon−carbon bond formation from alkenes; however, the number of systems that can selectively form 1-butene is rather limited.[4] This limitation comes from the fact that nickel hydrides are active in oligomerization as well as in the carbon−carbon double-bond migration (isomerization) reaction. The isomerization reaction proceeds through sequences of insertion/β-elimination steps, and only very specific systems can suppress (or limit) it. This is the case for the Ni(PO) ligands used in the SHOP (Shell higher olefins process), in which ethylene is oligomerized into $\mathrm{C_4}$−$\mathrm{C_{32}}$ α-olefins,[5] which are successively submitted to isomerization and metathesis in the same process. Currently, synthetic 1-butene is industrially produced by ethylene dimerization with titanium alkoxide catalysts in the Alfabutol process.[6] Although this process is used worldwide, it still has some drawbacks, such as the activity toward polymerization of the titanium which is eventually oxidized to Ti(IV) inside the reactor (or in any point of the industrial plant).

In this paper we are concerned with the chemistry of Ni(II) complexes bearing the monoanionic sterically hindered tris(pyrazolyl)borate ligands Tp′ (Tp′ = HB(3-mesitylpyrazolyl)$_3$ (Tp$^{\mathrm{Ms}}$)$^-$, HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl) (Tp$^{\mathrm{Ms*}}$)$^-$). Recently these ligands have been used in the preparation of highly active Ti(IV) and Zr(IV) catalysts for ethylene polymerization.[7] Moreover, these highly sterically demanding hydrotris(pyrazolyl)borate ligands can control coordination en-

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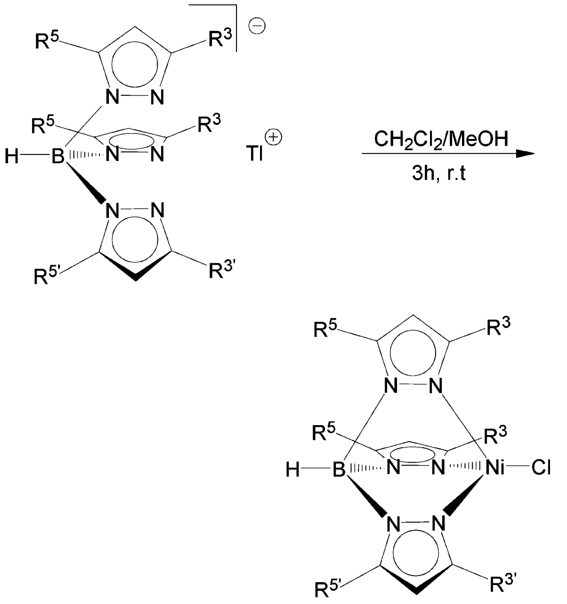
10.1021/om034035u CCC: $25.00 © 2003 American Chemical Society

vironments of the metal centers, preventing the formation of coordinatively saturated, less reactive complexes $\{Tp^R\}_2M$ and favoring the synthesis of tetrahedral Tp'MX complexes.[8] The coordination and organometallic chemistry of tris(pyrazolyl)borate nickel(II) compounds have been extensively studied,[9] but just a few examples have been employed as catalysts in the olefin polymerization.[10] Here, we describe the synthesis and characterization of Tp′NiX complexes that incorporate bulky substituents in the pyrazolyl 3- or 5-positions and their reactivity in ethylene oligomerization. Studies related to the influence of cocatalyst and oligomerization temperature on the activity and selectivity are also presented.

Results and Discussion

Synthesis and Structures of Tris(pyrazolyl)borate Nickel (II) Compounds. The reaction of TlTp′ (Tp′ = HB(3-mesitylpyrazolyl)$_3^-$ (Tp^{Ms}), HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$ (Tp^{Ms*})) with 1 equiv of $NiCl_2 \cdot 6H_2O$ in CH_2Cl_2/MeOH at room temperature affords the Ni(II) chloride compounds Tp^{Ms}NiCl (**1**) and Tp^{Ms*}NiCl (**2**). Recrystallization of the crude products from CH_2Cl_2/pentane yields **1** and **2** as pink solids in 82 and 64% yields respectively (eq 1). These compounds are air-stable and soluble in most polar solvents such as dichloromethane and methanol. The structures of **1** and **2** were assigned on the basis of elemental analysis and IR spectroscopy and by the X-ray structural determination carried out for **1**.



(1)

	R^3	R$^{3'}$	R^5	R$^{5'}$
1	Ms	Ms	H	H
2	Ms	H	H	Ms

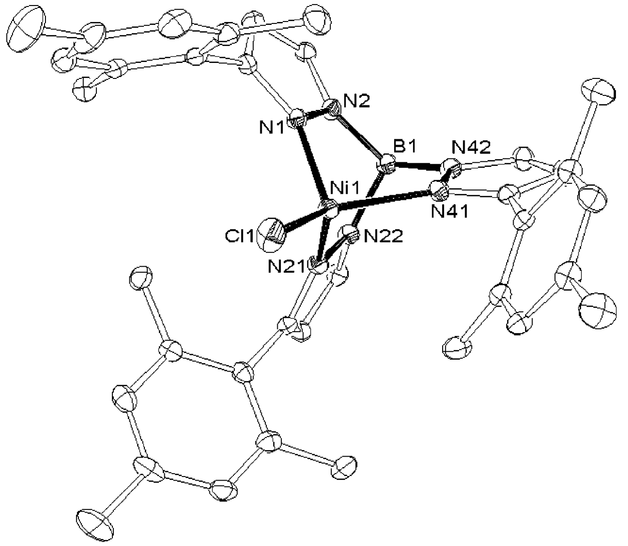


Figure 1. Molecular structure of compound **1** drawn at the 30% probability level (hydrogen atoms omitted for clarity). Only one of the two independent molecules is presented. Selected bond lengths (Å) and angles (deg): Ni(1)−N(41) = 1.990(3), Ni(1)−N(1) = 2.004(3), Ni(1)−N(21) = 1.993(3), Ni(1)−Cl(1) = 2.1473(10); N(41)−Ni(1)−N(21) = 91.58(12), N(21)−Ni(1)−N(1) = 90.26(12), N(41)−Ni(1)−N(1) = 92.86(12).

The elemental analyses of **1** and **2** are in agreement with the proposed formula Tp′NiCl. The IR spectra of **1** and **2** recorded in the solid state and solution showed only one ν(B−H) band at ∼2478 and ∼2517 cm^{-1}, respectively, indicating in both cases the coordination of the Tp ligands to the nickel center in a tridentate fashion.[11] The higher B−H stretching vibration found for the Tp^{Ms*} derivative is in agreement with the values observed for analogous compounds.[12]

Single crystals of compound **1** suitable for X-ray diffraction analysis were obtained from slow diffusion of hexane into the THF solution containing **1** at 25 °C. Two independent molecules were found in the asymmetric unit of **1**, but the two molecules are quite similar, so that only the distances and the angles for one of them are listed in Figure 1.

The crystal structure of **1** (Figure 1) confirms both the monomeric nature of the complex and κ^3 coordination of the Tp^{Ms} ligand, with the mesityl groups being all in the 3-position. The nickel center possesses a distorted tetrahedral geometry, as evidenced by the N−Ni−Cl (117.87−128.81°) and N−Ni−N bond angles (89.87−92.86°). The mesityl groups of the Tp^{Ms} ligand are away from the boron, thereby creating a pocket

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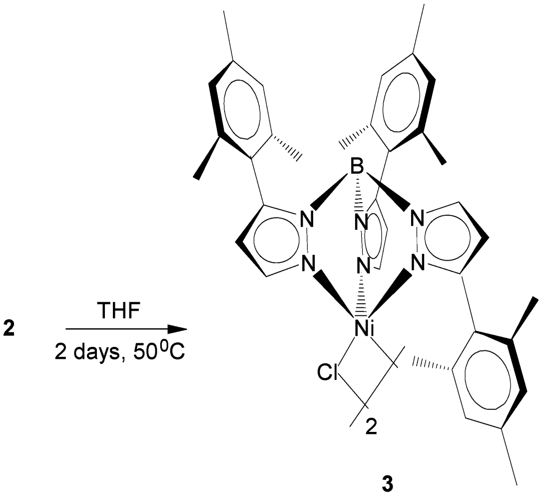
containing the chloride ligand. Furthermore, the chloro atom sits essentially on the 3-fold symmetry axis of the TpNi fragment defined by the B−Ni vector (B···Ni−Cl = 173.4°). The Ni−N (Ni−N_{av} = 1.996 Å, range 1.991(14)−2.004(13) Å) and Ni−Cl (2.1473(10) Å) bond distances are comparable to those found in similar nickel compounds having sterically hindered groups at the 3-position of the pyrazolyl ring, such as $Tp^{tBu}NiCl$[9a] (Ni−N_{av} = 2.021 Å; Ni−Cl = 2.172(2) Å), $Tp^{iPr}NiCl$[9c] (Ni−N_{av} = 1.973 Å; Ni−Cl = 2.172(2) Å), and $Tp^{Ph,Me}NiCl$[9d] (Ni−N_{av} = 1.988 Å; Ni−Cl = 2.153(2) Å).

In solution, the nickel compound **2** undergoes a dimerization process, affording chloro-bridged nickel(II) species. Thus, the THF solution containing **2** was stirred for 2 days at 50 °C to give the green compound $[\{Tp^{Ms**}\}NiCl]_2$ (**3**)[13] in 68% yield (eq 2). Characterization of this compound was difficult, due to its poor solubility in organic solvents and the fact that it is paramagnetic, precluding analysis by high-resolution NMR spectroscopy. Crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent from THF solution containing the mononuclear species **2** at room temperature.

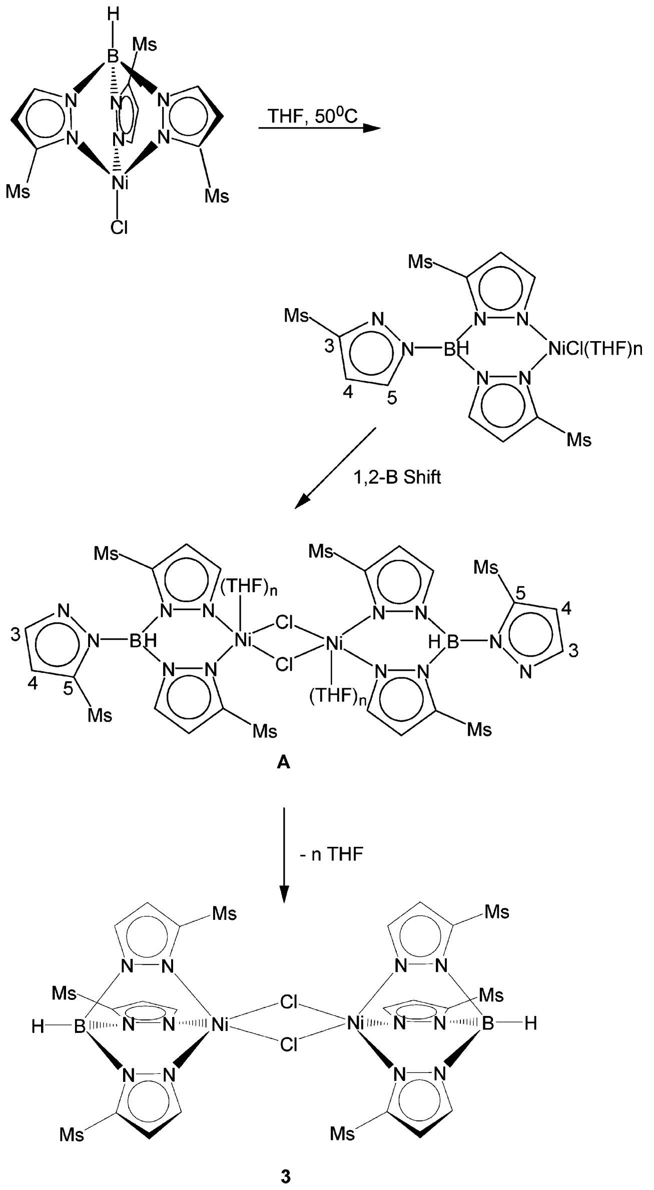


3

(2)

The main feature of **3** is the presence of two mesityl groups at the 5-position of the pyrazolyl ring and one at the 3-position of the pyrazolyl ring. To our knowledge, this compound represents the first structurally characterized example of a transition-metal complex bearing a Tp ligand that contains two bulky groups at the 5-position of the pyrazolyl ring.[8,14] We assume that this compound might be formed by an isomerization process, most likely a 1,2-borotropic shift, which is well-documented and can occur when bulky substituents are present at the pyrazolyl 3-positions.[7,15] In the present case the isomerization process involving **2** to produce **3** can be rationalized in terms of the sterically driven process to lead a more comfortable arrangement of the pyrazolyl groups in order to form a five-coordinated Ni(II) dimer. A plausible mechanism is shown in Scheme 1. The presence of a polar solvent such as THF facilitates the displacement of the 3-mesitylpyrazolyl group from the nickel center which undergoes the 1,2-borotropic shift. In this case, the migration of the mesityl group to the 5-position of the pyrazolyl ring allowed the formation of a less crowded nickel species that dimerizes, producing the intermediate dinuclear species **A**. Finally, the more nucleophilic 5-mesitylpyrazolyl groups provoke the displacement of the THF molecules from the coordination sphere of the nickel center, resulting in the formation of **3**.

Scheme 1



The molecular structure of **3** is depicted in Figure 2. The nickel compound **3** crystallizes as a centrosymmetric dimer with three nitrogen atoms (N1, N21, and N41) and two bridging chloride atoms (Cl1 and Cl1′) forming the coordination sphere around each five-coordinate nickel center. The bridge is planar, leading to a Ni−Ni separation of 3.503(2) Å. The coordination geometry of

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(13) The abbreviation Tp^{Ms**} was established on the basis of Trofimenko's rules[8] and indicates the presence of two mesityl groups at the 5-position of the pyrazolyl ring.

(14) NMR studies have demonstrated that the compound TpMe*Ir(COD) can rearrange in solution to $[HB(5\text{-}Mepz)_2(3\text{-}Mepz)]Ir(COD)$ after heating for 45 min at 70 °C. See: Albinati, A.; Bovens, M.; Rügger, H.; Venanzi, L. M. *Inorg. Chem.* **1997**, *36*, 5991.

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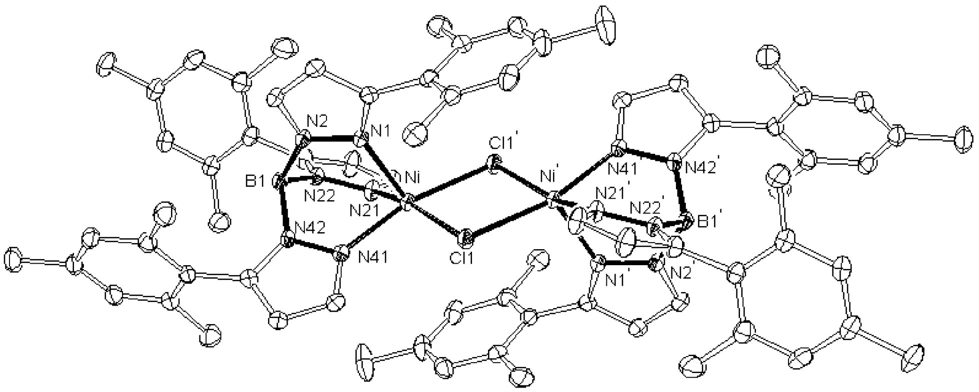

Figure 2. Molecular structure of compound **3** drawn at the 30% probability level (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−N(21) = 2.029(2), Ni(1)−N(1) = 2.0355(17), Ni(1)−N(41) = 2.0390(18), Ni(1)−Cl(1) = 2.3527(7), Ni(1)−Cl(1′) = 2.3804(8), Cl(1)−Ni(1′) = 2.3804(8); N(21)−Ni(1)−N(41) = 88.62(8), N(21)−Ni(1)−N(1) = 90.08(8), N(1)−Ni(1)−N(41) = 88.87(7), Cl(1)−Ni(1)−Cl(1′) = 84.52(3), Ni(1)−Cl(1)−Ni(1′) = 95.48(3).

each nickel atom ion is best described as square pyramidal with N_{basal}−Ni−Cl angles between 161.93 and 165.20°.

In contrast to the case found in dinuclear bis(μ-chloro) compounds of Cr(II)[16] and Pd(II)[17] bearing Tp ligands, the $Ni-N_{basal}$ (Ni−N41 = 2.036 Å; Ni−N21 = 2.029 Å) and $Ni-N_{axial}$ (2.036 Å) bond distances are equivalent, indicating the strong capacity of this ligand to coordinate to the Ni(II) center in the κ^3 mode. As expected, the Ni−Cl bond distances ($Ni-Cl_{av}$ = 2.365 Å) are longer than the Ni−Cl distances found in mononuclear compounds ($Tp^{tBu}NiCl$,[9a] Ni−Cl = 2.172(2) Å; $Tp^{iPr}NiCl$,[9c] Ni−Cl = 2.172(2) Å; $Tp^{Ph,Me}NiCl$,[9d] Ni−Cl = 2.153(2) Å).

Oligomerization of Ethylene. It is interesting to compare the performance of complexes **1**−**3** in the ethylene oligomerization in order to obtain insights concerning the effects of steric hindrance on the activity and on the selectivity of the system, with particular attention devoted to the relative importance of the oligomerization and isomerization reactions under different reaction conditions. The catalytic performance of tris(pyrazolyl)borate nickel compounds **1**−**3** has been evaluated in the oligomerization of ethylene using methylaminoxane (MAO) and trimethylaluminum (TMA) as cocatalysts. Table 1 shows the performance of the monomeric nickel complexes **1** and **2**, which are active for the ethylene oligomerization reactions carried out at 0 °C and 30 bar of ethylene, while the dimeric species **3** proved to be inactive under identical oligomerization conditions. A more detailed appreciation of the results from Table 1 shows that the more crowded nickel complex **1** is ca. 16 times more active than **2** (entries 3 and 4). However, for both cases the selectivity for 1-butene is very high, attaining 95−96% of the C_4 fraction (this means 81% of the total amount of olefins obtained in the oligomerization reaction).

Table 1. Results of Oligomerization of Ethylene with Complexes 1−3[a]

entry	precat.	cocat.	press (atm)	*T* (°C)	yield (g)	10^{-3} TOF[b] (h^{-1})	selectivity[c] (%) C_4	α-C_4	C_6	α-C_6
1	**1**	MAO	1.1	0	0.78	5.4	86	78	13	77
2	**1**	MAO	20	0	2.63	18.7	85	93	14	65
3	**1**	MAO	30	0	4.09	29.2	85	95	14	71
4	**2**	MAO	30	0	0.25	1.8	84	96	11	88
5[d]	**1**	MAO	30	0	14.4	20.5	76	93	23	37
6	**1**	MAO	1.1	30	0.31	2.2	86	70	13	64
7	**1**	MAO	30	30	4.83	34.6	87	90	13	83
8	**1**	TMA	1.1	0	2.61	18.7	68	61	32	24
9	**1**	TMA	30	0	6.16	43.1	81	94	18	67
10	**1**	TMA	1.1	30	0.92	6.5	45	80	55	10
11	**1**	TMA	30	30	2.94	20.9	73	89	26	37

[a] Reaction conditions: toluene 50 mL, [Ni] = 5 μmol, 1 h, Al/Ni = 200. [b] Mol of ethylene converted (mol of Ni)$^{-1}$ h^{-1} determined by GC. [c] Selectivity: C_n, amount of olefin with *n* carbon atoms in the oligomers; α-C_4, amount of terminal alkene in the C_4 fraction. [d] [Ni] = 25 μmol.

Considering the higher activity of **1**, some additional studies were performed aiming at evaluating the influence of the cocatalyst, oligomerization temperature, and ethylene pressure on the activity and selectivity of the system. Two sets of experiments were performed, one using MAO and the other using TMA as cocatalyst.

For the system **1**/MAO the enhancement of the ethylene pressure (from 1.1 to 30 atm) gives a proportional enhancement of the turnover frequency from 5.4 to 29.2 h^{-1} at 0 °C and from 2.2 to 34.6 h^{-1}at 30 °C. These results were expected as an effect of the increased ethylene concentration in the solvent. The enhancement of the ethylene pressure has roughly no effect on the selectivity in dimers (C_4, ca. 86%) and trimers (C_6, ca. 13%) but have a clear influence on the selectivity toward α-olefins, i.e., when the ethylene pressure is decreased, the α-olefin content decreases by ca. 20% (from 95 to 78% at 0 °C and from 90 to 70% at 30 °C, entries 3, 1, 7, and 6, respectively), due to the occurrence of a parallel isomerization reaction. At 0 °C and 30 bar very high selectivities for α-olefins have been observed. Under the appropriate conditions more than 96% of the total C_4 fraction is α-olefin (i.e, 1-butene), which is a technologically very attractive result.

The use of TMA instead of MAO gives interesting effects. The main tendencies, such as the effect of the ethylene pressure and temperature, have the same trends as for the system **1**/MAO, but the turnover frequencies of the system **1**/TMA are higher than for the system **1**/MAO and the selectivities in C_4 are lower, as can be seen by comparing entries 1 and 8, 3 and 9, and

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7 and 11. The dependence of the selectivity on the nature of the alkylaluminum cocatalyst suggests that these activators act as ligands attached to the nickel center, influencing the observed catalytic performance. The MAO molecule is much larger than TMA and has a more pronounced effect on the selectivity of the system.

It is worth noting that the lifetime of the nickel active species obtained with **1**/TMA is much lower than that for species issued from **1**/MAO. At 1.1 atm the system **1**/TMA is active until ca. 30 min and the system **1**/MAO is still active during the 60 min with no indication of deactivation. These results strongly suggest, as mentioned before, that the active species maintains the alkylaluminum species bonded to the nickel center, as observed in recent studies using XAS spectroscopy.[18]

In summary, we have introduced a new class of oligomerization catalysts based on nickel complexes containing sterically hindered tris(pyrazolyl)borate ligands which produce selectively 1-butene upon activation with alkylaluminum cocatalysts such as MAO and TMA. Higher turnover frequencies were obtained using $Tp^{Ms}NiCl$. Both turnover frequency and selectivity are dependent on the nature of the alkylaluminum cocatalyst employed in the oligomerization reactions, suggesting that these activators act as ligands attached to the nickel center. Further investigations into the reactivity of these nickel catalysts with propylene will be the subject of a future report.

Experimental Section

General Procedures. All manipulations were performed using standard vacuum line and Schlenk techniques under a purified argon atmosphere. Hexane, THF, and toluene were distilled from sodium benzophenone ketyl, and methanol was distilled from magnesium. Solvents were stored under argon or vacuum prior to use. $NiCl_2{\cdot}6H_2O$ was purchased from Aldrich and used as received. The compounds $Tl[Tp^{Ms}]$ and $Tl[Tp^{Ms*}]$ were prepared by literature procedures.[12] Ethylene, provided by Braskem Petrochemical Co., and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (13 Å) prior to use. MAO (Witco, 5.21 wt % Al solution in toluene) and TMA (Aldrich) were used as received. Elemental analyses were performed by the Analytical Central Service of the IQ-USP (Brazil). Infrared spectra were performed on a Bomem B-102 spectrometer. The gas chromatographic analysis of the reaction products has been 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) working at 36 °C for 15 min and then heating at 5 °C min^{-1} until 250 °C.

$Tp^{Ms}NiCl$ (1). To a methanol solution (10 mL) of $NiCl_2{\cdot}6H_2O$ (0.33 g, 1.40 mmol) was added a CH_2Cl_2 solution (40 mL) of $Tl[Tp^{Ms}]$ (1.07 g, 1.40 mmol), and the resulting cloudy mixture was stirred for 3 h at room temperature. The volatiles were removed under reduced pressure, and the resulting solid residue was extracted with toluene (3 × 20 mL). The toluene extract was filtered through Celite and concentrated to dryness, affording a pink solid with was washed with hexane (3 × 10 mL) and dried under vacuum. The product can be recrystallized in CH_2Cl_2/pentane (0.76 g, 82% based on $TlTp^{Ms}$). Anal. Calcd for $C_{36}H_{40}BClN_6Ni$: C, 65.37; H, 6.05; N, 12.70. Found: C, 65.18; H, 5.98; N, 12.57. IR (KBr): ν_{B-H} 2478 cm^{-1}.

$Tp^{Ms*}NiCl$ (2). This compound was prepared according to the method described for **1** using $NiCl_2{\cdot}6H_2O$ (0.15 g, 0.63 mmol) and (40 mL) of $Tl[Tp^{Ms}]$ (0.49 g, 0.63 mmol). **2** was obtained as a pink solid. The product can be recrystallized in CH_2Cl_2/pentane (0.27 g, 64% based on $TlTp^{Ms*}$). Anal. Calcd for $C_{36}H_{40}BClN_6Ni$: C, 65.37; H, 6.05; N, 12.70. Found: C, 65.22; H, 5.92; N, 12.48. IR (KBr): ν_{B-H} 2517 cm^{-1}.

$[Tp^{Ms**}NiCl]_2$ (3). The THF solution (50 mL) of **2** (0.15 g, 0.22 mmol) was stirred for 2 days at 50 °C. The color of the solution changed from brownish yellow to green. The volatiles were removed under reduced pressure, and the resulting solid was washed with hexane to yield **3** as a green solid (0.10 g, 68% yield). Anal. Calcd for $C_{36}H_{40}BClN_6Ni$: C, 65.37; H, 6.05; N, 12.70. Found: C, 65.21; H, 5.88; N, 12.45. IR (KBr): ν_{B-H} 2551 cm^{-1}.

Ethylene Oligomerizations. Ethylene oligomerization reactions were performed in (a) a 120 mL double-walled glass reactor equipped with a magnetic stirrer and thermocouple with continuous feed of ethylene at 1.1 atm and (b) a 250 mL double-walled stainless reactor equipped with mechanical stirring and continuous feed of ethylene (for reactions using ethylene pressure until 30 atm). For the two systems, the reaction temperature was controlled by a thermostated circulation bath. A typical reaction run was performed by introducing in the reactor, under argon, 5 μmol of the nickel(II) complex dissolved in 60 mL of toluene. The system was saturated with ethylene, and the oligomerization reaction was started by introduction of the proper amount of the alkylaluminum cocatalyst. Ethylene was continuously fed in order to maintain the ethylene pressure at the desired value. After 1 h the reaction was stopped by cooling the system to −20 °C, depressurizing, and introducing 1 mL of ethanol.

Acknowledgment. We are grateful to the CNPq for fellowships and CTPETRO-CNPq, CAPES, and FAPERGS (Brazil) for financial support of this research.

Supporting Information Available: Tables of X-ray crystallographic data and crystal data and structure refinement details, atomic coordinates, interatomic distances and angles, and hydrogen atom coordinates for compounds **1** and **3**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034035U

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