Nickel Complexes Bearing New *P,N*-Phosphinopyridine Ligands for the Catalytic Oligomerization of Ethylene

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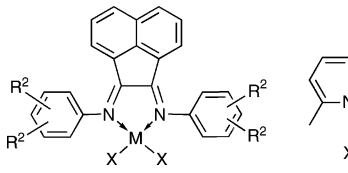
The new phosphinopyridine ligands 2-[(diphenylphosphanyl)methyl]-6-phenylpyridine (**5**), 2-(2,6-dimethylphenyl)-6-[(diphenylphosphanyl)methyl]pyridine (**6**), 2-(2,6-diisopropylphenyl)-6-[(diphenylphosphanyl)methyl]pyridine (**7**), and 2-[2-(diphenylphosphanyl)phenyl]-6-methylpyridine (**8**) have ben prepared in order to compare the influence of their stereoelectronic properties on the catalytic behavior of their respective mononuclear [$NiCl_2$(P,N)] complexes **9**−**12**. These Ni(II) complexes are paramagnetic in solution, as determined by the Evans method. Whereas they were inactive for the oligomerization of ethylene in the presence of methylalumoxane (MAO), they provided activities up to 61 000 mol of C_2H_4/((mol of Ni) h) (**11**) in the presence of only 6 equiv of $AlEtCl_2$. The selectivities for C_4 olefins were as high as 92% (**12** with 2 equiv of $AlEtCl_2$).

Introduction

Bidentate diimine ligands have played an increasing role in coordination chemistry as well as in the transition-metal-catalyzed oligomerization and polymerization of α-olefins.[1−7] Following the early works of Balch and Holm,[8] Walther,[9] and tom Dieck and co-workers,[10−12] Brookhart and co-workers[1b,13] discovered that [$NiCl_2$-(diimine)] complexes of type **1** provide excellent results



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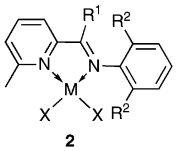

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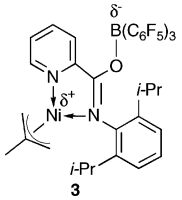
R^1 = H, CH_3
R^2 = H, CH_3, *i*-Pr, *t*-Bu
R^3 = *t*-Bu, H, Cl, OCH_3
M = Ni, Pd
X = Cl, Br



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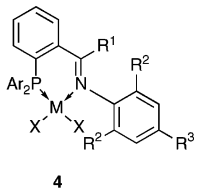

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for the conversion of α-olefins to oligomers and polymers in the presence of large quantities of methylalumoxane (MAO).[1] This triggered a renewed interest in this family of ligands and led to the synthesis of Ni(II) and Pd(II) complexes with, for example, unsymmetrical iminopyridine (**2**),[14−17] pyridinecarboxamido (**3**),[18] and iminophosphine ligands (**4**),[19,20] which have been used for the

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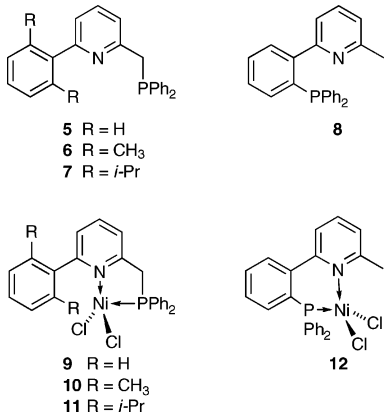
catalytic oligomerization or polymerization of ethylene and illustrate the versatility of these systems.

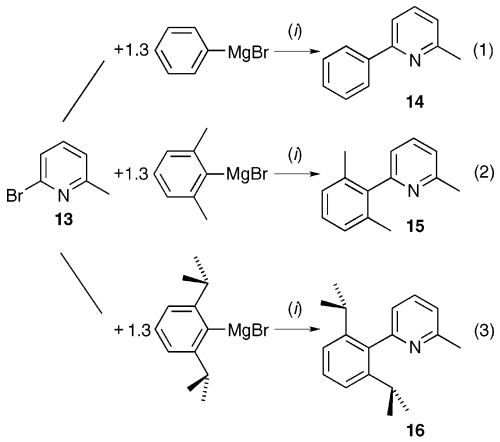
Only few complexes containing phosphinopyridines have been reported for their application in the oligomerization or polymerization of α-olefins,[1,21,22] despite the considerable academic and industrial importance of these reactions.[23] In view of the decisive influence of the ligands and, in particular, of the steric hindrance of their substituents in controlling oligomerization versus polymerization, we decided to prepare Ni(II) complexes bearing the new phosphinopyridines **5**−**8**, which possess



the characteristics of a pyridine heterocycle with its rigid and chemically inert structure and, at the same time, allow easy variation of the steric hindrance around the metal center. Modifying the ligand basicity also provides an excellent tool to influence the catalytic properties. Whereas in a previous study with other phosphinopyridine ligands we have focused on substituent effects in the one-carbon connection between the ortho pyridine carbon and the PPh_2 group,[22] we shall be dealing here, with **5**−**8**, with different substituents in the ortho position of the pyridine ring. The catalytic properties of the new Ni(II) halide complexes **9**−**12** have been investigated with the objective of favoring ethylene oligomerization vs polymerization while using the smallest possible amount of added cocatalyst.

Results and Discussion

Synthesis of the Ligands. To prepare the phosphinopyridines **5**−**8**, aryl substituents have to be introduced on the pyridine heterocycle **13**, and typical methods include Stille,[24] Suzuki,[25] and Kumada[26,27] coupling reactions. Stille and Suzuki reactions have found widespread use in the synthesis of annelated pyridine or bipyridine systems,[24,25,28] although they imply the use of Pd catalysts, aryltin compounds, or arylboronic acid esters which first have to be prepared from the corresponding aryl Grignard compounds or lithium reagents.[24,25] Therefore, the Kumada coupling reaction seemed to be the method of choice, since cheap Ni(II) salts are used as catalysts in the presence of phosphines. In contrast to the Stille or Suzuki couplings, Grignard reagents can be used directly. In some cases, the homocoupling reaction of the Grignard reagents dominates, which prevents a universal use of the Kumada reaction.[26] In our case, however, hardly any homocoupling products were observed (eqs 1−3).



(*i*) 1.3 mol% $Ni(acac)_2/P(t\text{-}Bu)_3$; Et_2O, reflux, 12 h

The Ni catalyst used for the Grignard coupling reactions was based on the $Ni(acac)_2/P(t\text{-}Bu)_3$ catalyst system,[29] although the experimental procedure had to be strongly modified for synthetic reasons (see Experimental Section). After the Grignard reagent was added at 0 °C to the catalyst/substrate mixture, the solution was refluxed overnight in diethyl ether, which afforded after workup the 2-aryl-6-methylpyridines **14**−**16** in good yields. The ^1H NMR spectrum of **16** contained two doublets for the isopropyl CH_3 protons. Assuming an orientation of the aryl group perpendicular to the pyridine ring, the isopropyl groups would be equivalent and carry two inequivalent methyl groups. Consistently, two singlets were observed in the ^{13}C NMR spectrum for these methyl groups. However, if the aryl and pyridine groups are oriented as shown in eq 3, in the mirror plane of the molecule, thus making the isopropyl groups inequivalent but the methyl protons of each isopropyl group equivalent, the spectral data would be consistent with the rotation of the 2,6-bis(isopropyl)-phenyl group around the aryl−pyridine bond being blocked at room temperature. Only one singlet was observed at room temperature for the *o*-CH_3 protons of the phenyl group in **15**, which could be consistent with a perpendicular orientation of the aryl and pyridine

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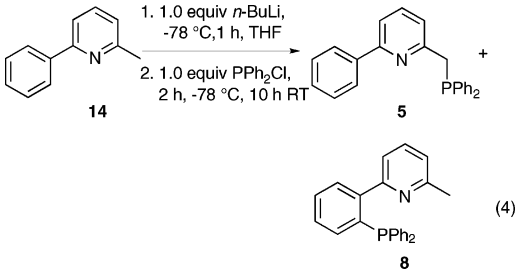
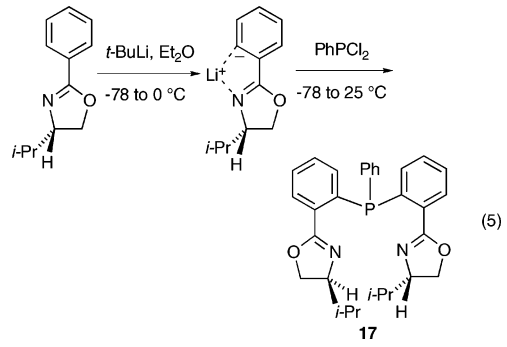
rings or with accidental equivalence of the *o*-Me groups in a structure where both aryl and pyridine rings are coplanar or there is easier rotation of the aryl group about the C−C axis. On the basis of steric arguments, the kinetic barrier for this rotation is anticipated to increase in the order **14** < **15** < **16**.

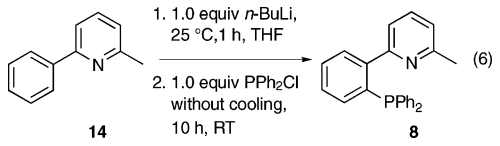
The first attempt to introduce the phosphine moiety was made by metalation of the pyridine-bound methyl group with an appropriate base and subsequent addition of 1 equiv of PPh_2Cl. This led to the formation of two



compounds, which could be identified as the desired 2-[(diphenylphosphanyl)methyl]-6-phenylpyridine (**5**) and the ortho-metalation product **8** (eq 4). A similar ortho-metalation reaction was observed by Zhang and co-workers[30] in the synthesis of the phosphine **17** (eq 5).

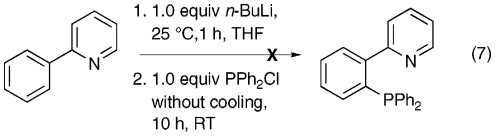


The mixture of the phosphinopyridines **5** and **8** proved difficult to separate by chromatographic methods or by distillation. Therefore, the synthetic pathway was modified: **14** was reacted at room temperature with 1 equiv of *n*-BuLi and the phosphine moiety was introduced by reaction of the ortho-metalated pyridine with PPh_2Cl without cooling of the exothermic reaction. The ligand **8** was isolated in 60% yield (eq 6). When a similar

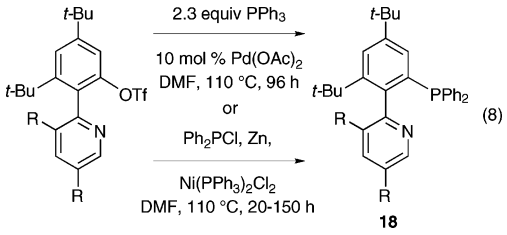


reaction was carried out using 2-phenylpyridine as substrate, no orthometalation was observed (eq 7). This suggests a directing ortho effect on the phenyl ring reasonably due to facilitated chelation of Li^+ by the more basic nitrogen atom of **14**.

Chan and co-workers[31,32] prepared atropisomeric phosphinopyridines **18** by refluxing the corresponding tri-

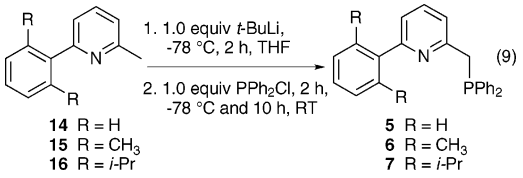


flate for 20−150 h in DMF in the presence of Pd(II) or Ni(II) catalysts. Their synthesis allows the presence of a large number of functional groups on the aromatic cycles (eq 8), except at the 6-position of the pyridine ring.



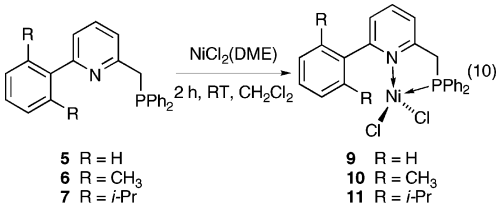
Yields of ca. 50−70% were observed with the Pd catalyst against 30−48% in the case of Ni. It remains to be verified whether our synthetic pathway can be extended to a large range of phosphinopyridines, but the ortho-metalation route appears rather elegant and cost-effective, since no palladium salts or aryl triflates are required.

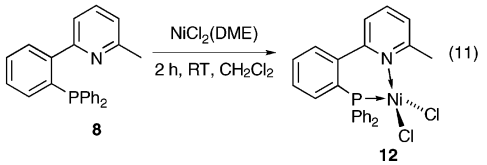
To introduce a diphenylphosphino substituent on the *o*-methyl group of the pyridine heterocycle, the arylpicolines **14**−**16** were lithiated at −78 °C with 1 equiv of *t*-BuLi. Slow addition of 1 equiv of PPh_2Cl at −78 °C afforded **5**−**7** in good yields (eq 9). These ligands display



a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −10.8, −9.7, and −9.4, respectively. This trend is consistent with a more electron donating R group increasing the electron density at the phosphorus atom.

Synthesis of the Ni(II) Complexes. The Ni(II) phosphinopyridine complexes **9**−**12** were prepared by stirring equimolar amounts of $[NiCl_2(DME)]$ with the corresponding ligand for 12 h in CH_2Cl_2 at 25 °C. After workup, the Ni complexes were isolated in 70−80% yields (eqs 10 and 11).





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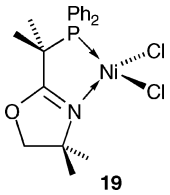
All four complexes are paramagnetic in solution, as determined by the Evans method,[33,34] with magnetic moments of 2.40 (**9**), 2.42 (**10**), 2.62 (**11**) and 1.82 μ_B (**12**), respectively. The magnetic moment of Ni(II) complexes depends strongly on the ligand field, and large variations can be observed.[35−39] Therefore, the magnetic moments of **9**−**12** should be compared to those of similar complexes whose molecular structures are known. The X-ray structure of [$NiCl_2${2-[1′-(diphenylphosphanyl)-1′-methylethyl]-4,4-dimethyl-4,5-dihydrooxazole}] (**19**) has



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been determined recently and showed a tetrahedral coordination sphere for the metal center, and a magnetic moment of 2.15 μ_B was experimentally determined in solution.[40]Therefore, a distorted-tetrahedral coordination geometry of the metal is assumed for complexes **9**−**12** in solution. A comparison of the infrared spectra of the phosphinopyridine ligands and their complexes clearly shows that the nitrogen heterocycle is coordinated to the metal center.[41]

Catalytic Properties of the Complexes [$NiCl_2$-(phosphinopyridine)] (9−12) for Ethylene Oligomerization. Compounds **9**−**12** were tested for the oligomerization of ethylene using the smallest possible quantities of the cocatalysts $AlEtCl_2$ and MAO. In the presence of either 2 or 6 equiv of $AlEtCl_2$ the complexes showed good activities (Figure 1). When 2 equiv of cocatalyst was used, turnover frequencies (TOF) were 47 300, 43 200, 44 400 and 22 100 mol of C_2H_4/((mol of Ni) h), respectively (Table 1). Increasing the amount of cocatalyst to 6 equiv raised the TOFs to 57 000, 57 200, 61 000 and 56 100 mol of C_2H_4/((mol of Ni) h), respectively.

In the presence of 400 or 800 equiv of MAO, only decomposition of complexes **9**−**12** was observed. This could be due to the presence of ca. 10% of $AlMe_3$ in commercial MAO.[42] Other groups have also reported that AlR_3 impurities in $AlClEt_2$ or pure trialkylaluminum compounds reduce Ni(II) catalysts to inactive Ni(0) species.[43] Consistently, complexes **9**−**12** decomposed in the presence of $AlEt_3$ under ethylene pressure.

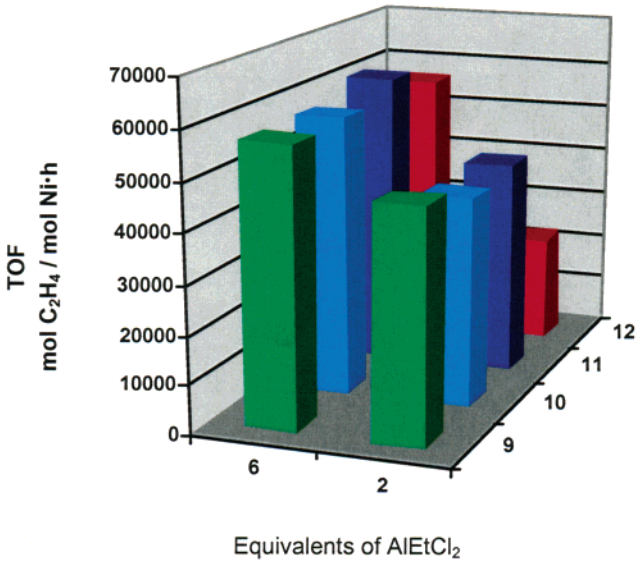
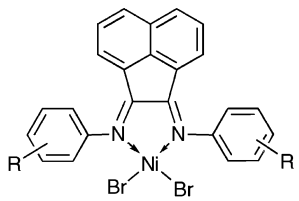


Figure 1. Activity of complexes **9**−**12** for the oligomerization of ethylene using different quantities of $AlEtCl_2$. Conditions: T = 30 °C, 10 bar of C_2H_4, 35 min, 4 × 10^{-2} mmol of Ni, 15 mL of toluene.

Only 2 equiv of $AlEtCl_2$ was sufficient to lead to a high selectivity for butenes: 82% (**9**), 83% (**10**), 73% (**11**) and 92% (**12**).

An increase in the amount of cocatalyst from 2 to 6 equiv tends, except for **11**, to reduce the selectivities for butenes to 71% (**9**), 78% (**10**), 77% (**11**), and 70% (**12**) (Figure 2). The remaining products were ethylene trimerization products (C_6) and very small quantities of C_8 oligomers. The selectivities to 1-butene within the C_4 fraction of only 9−14% could be due to the ability of complexes **9**−**12** to reversibly eliminate β-H after ethylene insertion and reinsert the olefin with the opposite regiochemistry and give 2-butene after chain transfer or to lead to isomerization of 1-butene by a re-uptake mechanism. The ability of Ni(II) complexes to isomerize α-olefins is well-known.[44] The k_α values given in Table 1 correspond to the ratio hexenes (mol)/butenes (mol) and not to the Schultz−Flory constant, since our catalysts are mainly dimerization and trimerization catalysts.

The considerable preference for ethylene dimerization stands in interesting contrast to observations by Brookhart and co-workers, who noted a wider distribution of oligomers in the oligomerization of ethylene and propylene catalyzed by the square-planar Ni−diimine complexes of type **20** with MAO, MMAO, MAO-IP, and $AlEtCl_2$ as cocatalysts. An increase of the steric hin-



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R = 4-CF_3, 4-H, 4-CH_3, 4-OCH_3, 2-CH_3

drance around the metal center caused by the ortho aryl substituents led to the formation of long-chain oligomers. The turnover frequencies were between 22 000

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Table 1. Comparative Catalytic Data for Complexes 9−12, 19, 23, and [$NiCl_2(PCy_3)_2$] in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	9		10		11		12		19	23	[$NiCl_2(PCy_3)_2$]	
amt of $AlEtCl_2$ (equiv)	6	2	6	2	6	2	6	2	6	6	6	2
selectivity C_4 (%)	71	82	78	83	77	73	70	92	54	65	86	88
selectivity C_6 (%)	29	18	21	18	22	26	28	8	40	32	14	12
selectivity C_8 (%)	1	1	1		1	1.5	2		1	2.5	0.5	
selectivity C_{10} (%)												
selectivity C_{12} (%)									3.5			
productivity (g of C_2H_4/((g of Ni) h))	27 200	22 600	27 300	20 600	29 100	21 200	26 800	10 500	22 000	27 800	13 000	800
TOF (mol of C_2H_4/((mol of Ni) h))	57 000	47 300	57 200	43 200	61 000	44 400	56 100	22 100	45 900	58 100	27 200	1600
α-olefin (C_4) (%)	9	9	9	14	10	9	9	13	20	11	9	12
k_α[b]	0.27	0.14	0.18	0.14	0.19	0.23	0.27	0.06	0.50	0.33	0.11	0.09

[a] Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-2} mmol of Ni complex, solvent 15 mL of toluene. [b] k_α= hexenes (mol)/butenes (mol).

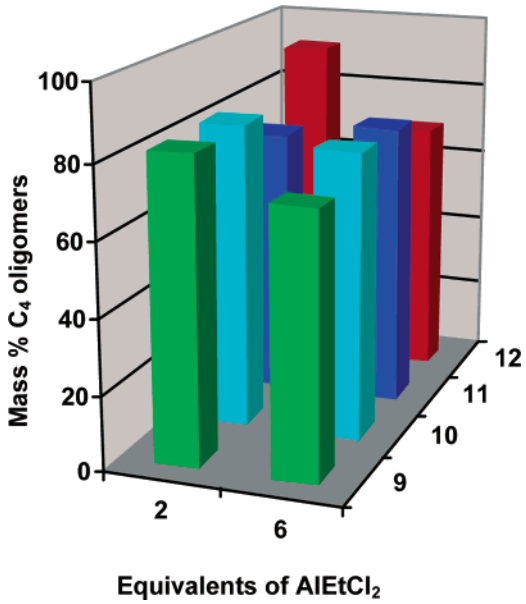
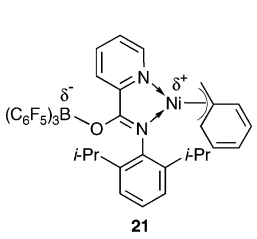


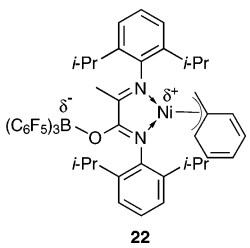
Figure 2. Selectivity of complexes **9**−**12** for C_4 oligomers in mass percent. Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-2} mmol of Ni, 15 mL of toluene.

and 140 000 mol of C_2H_4/((mol of Ni) h) in the presence of 200−400 equiv of cocatalyst, and a maximum selectivity of 91% for α-olefin was observed.[45]

Recently Bazan et al. reported that ethylene oligomerization is favored over polymerization with pyridinecarboxamidato ligands that do not fully shield the nickel center, as shown in **21**. This was contrasted with the situation in complex **22**, where the ligand has almost similar electronic but different steric properties.[18]

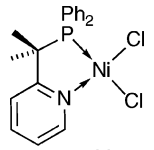


21



22

No significant effect of the R group was noticed for the catalysts **9**−**12**. This is at variance with other systems, where steric blocking of the axial positions of the metal is crucial for chain length control,[1,13,18b] and could indicate that our R groups were not bulky enough to induce significant variations. The product distribution observed with our catalysts may also be related to the different metal coordination geometries, since our Ni(II) complexes have a tetrahedral environment. This seems to lead to catalysts that favor formation of internal olefins, although this should not be generalized. Selectivities to 1-butene within the C_4 fraction similar to those of our complexes were also observed with the square-planar complex [$NiCl_2(PCy_3)_2$], a typical α-olefin dimerization catalyst, at variance with the results of Bazan and co-workers.[18] Our ligand system leads, however, to a catalyst ca. 2.5 times more active than that with PCy_3. Table 1 contains comparative data, including the five-membered-ring complex **19**, which has a tetrahedral geometry and contains a dimethyl-substituted phosphinooxazoline ligand,[40] and **23**, which



23

is almost planar in the solid state.[22] Greater similarities appear between the complexes with pyridine-containing ligands than with the phosphinooxazoline. However, a complete understanding and fine tuning of the parameters that lead to highly active and selective catalysts for 1-butene are not yet available.

Conclusion

The mononuclear Ni(II) complexes **9**−**12** have been prepared from the new phosphinopyridine ligands **5**−**8** for their evaluation as catalyst precursors in ethylene oligomerization. They are paramagnetic in solution, as determined by the Evans method. Whereas in the presence of MAO as a cocatalyst complexes **9**−**12** were inactive, they provided activities up to 61 000 mol of C_2H_4/((mol of Ni) h) (**11**) in the presence of only 6 equiv of $AlEtCl_2$. The selectivities for C_4 oligomers were as high as 92% (**12** in the presence of 2 equiv of $AlEtCl_2$). Similar activities were obtained by other groups in the

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dimerization of ethylene and propene, but only when using between 200 and 400 equiv of cocatalyst.[45] That the k_α value varies for a given catalyst as a function of the nature or quantity of the cocatalyst suggests that the C_6 products are formed by both ethylene oligomerization and incorporation of some of the 1-butene formed ($C_4 + C_2$, consecutive reaction).

In general, the ligand basicity and the geometry of the coordination sphere of the metal center have an important influence on the catalytic properties. Nevertheless, a complete picture of the parameters that lead to highly active and selective dimerization catalysts is not yet available.

Experimental Section

All solvents were dried and distilled using common techniques, unless otherwise stated. All experiments were carried out under an inert-gas atmosphere using standard Schlenk techniques. $NiCl_2 \cdot 6H_2O$ was dried by heating for 6 h at 160 °C under vacuum to give $NiCl_2$. [NiX_2(DME)] (X = Cl, Br),[46] 2-bromo-6-methylpyridine,[47] 2,6-dimethyl-1-bromobenzene,[48] and 2,6-diisopropyl-1-bromobenzene[48] were prepared according to the literature. All Grignard reagents were prepared by slow addition of the corresponding aryl bromides to a suspension of magnesium in diethyl ether (100 mL). The magnesium was activated by adding some iodine crystals. Finally, the reaction mixture was refluxed overnight and titrated against phenolphthalein before use. Other chemicals were commercially available and used without further purification, unless otherwise described. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded at 500.13 or 300.13, 121.5, and 76.0 MHz, respectively, on FT Bruker AC300, Avance 300, and Avance 500 instruments. IR spectra in the range 4000−400 cm^{-1} were recorded on a Bruker IFS66FT and a Perkin-Elmer 1600 Series FTIR. Gas chromatographic analyses were performed on an Thermoquest GC8000 Top Series gas chromatograph using an HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness).

Synthesis of the Ligands. We first describe the synthesis of **14**−**16**, which are needed for the preparation of ligands **5**−**8**.

(2-Methyl-6-phenyl)pyridine (14). To a mixture of 2-bromo-6-methylpyridine[47] (**13**; 14.66 g, 9.77 mL, 85 mmol), [Ni(acac)$_2$] (0.400 g, 1.56 mmol), and P(*t*-Bu)$_3$ (0.316 g, 0.388 mL, 1.56 mmol) in 250 mL of diethyl ether in an ice bath was added phenylmagnesium bromide (110 mmol of PhMgBr in 100 mL of diethyl ether) over a period of 10 min. After the solution was refluxed overnight, the reaction mixture was hydrolyzed by pouring it into 200 mL of diluted hydrochloric acid. The solution was stirred for 15 min before the organic phase was separated. The aqueous phase was extracted twice (50 mL) with diethyl ether, and the ether was again discarded. The aqueous phase was neutralized by slow addition of K_2CO_3 until no further CO_2 evolution was observed and a pale yellow precipitate was formed. The basic solution was extracted three times with CH_2Cl_2 (150 mL), and the organic phase was dried over Na_2SO_4. Then the CH_2Cl_2 fraction was evaporated under reduced pressure, yielding an NMR-pure brown oil, which was used directly. If needed, the product can be distilled under reduced pressure (5 mbar, 120 °C) to afford a pale yellow liquid (9.141 g, 54 mmol, 64%). ^{1}H NMR ($CDCl_3$): δ 2.65 (s, 3H, py−C*H*$_3$), 7.09 (d, 1H, py H^5, ^3J(H^5,H^4) = 7.6 Hz), 7.41 (dd, 1H, Ph H$_p$, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.7 Hz), 7.46 (d, 1H, py H^3, ^3J(H^3,H^4) = 7.8 Hz), 7.50 (d, 2H, Ph H$_m$, ^3J(H,H) = 8.6 Hz, ^4J(H,H) not observed), 7.62 (d, 1H, py H^4, ^3J(H,^{4}H^3) = 7.8 Hz, ^4J(H,H) not observed), 7.7 (dd, 2H, Ph H$_o$, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.0 (s, py−CH_3), 103.7 (s, py C^3), 107.9 (s, py C^5), 113.3 (s, Ph C$_o$), 115.0 (s, Ph C$_m$), 122.7 (s, Ph C$_p$), 126.0 (s, py C^4), 143.1 (s, py C^6), 144.7 (s, py C^2), 158.0 (s, Ph C$_{ipso}$). Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.94; H, 6.23; N, 8.10.

2-(2,6-Dimethylphenyl)-6-methylpyridine (15). To a mixture of **13**[47] (6.25 g, 4.10 mL, 36 mmol), [Ni(acac)$_2$] (0.131 g, 0.51 mmol), and P(*t*-Bu)$_3$ (0.103 g, 0.130 mL, 0.51 mmol) in diethyl ether (100 mL) in an ice bath was added (2,6-dimethylphenyl)magnesium bromide (45 mmol of (2,6-dimethylphenyl)magnesium bromide in 100 mL of diethyl ether) over a period of 10 min. After workup, as described for **14**, an NMR-pure brown oil was obtained, which was used without further purification. If needed, the product may be distilled under reduced pressure (5 mbar, 160 °C), affording a pale yellow liquid (5.15 g, 26 mmol, 73%). ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 6H, Ph *o*-(C*H*$_3$)$_2$), 2.61 (s, 3H, py−C*H*$_3$), 7.02 (d, 1H, py H^5, ^3J(H,^{5}H^4) = 7.8 Hz), 7.08 (d, 1H, py H^3, ^3J(H,H) = 7.8 Hz), 7.14 (t, 1H, Ph H$_p$, ^3J(H,H) = 8.6 Hz), 7.17 (d, 2H, Ph H$_m$, ^3J(H,H) = 8.6 Hz), 7.63 (t, 1H, py H^4, ^3J(H^4,H^{3,5}) = 7.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.5 (s, Ph *o*-(CH_3)$_2$), 24.3 (s, py−CH_3), 120.9 (s, py C^3), 121.2 (s, py C^5), 127.3 (s, Ph C$_m$), 127.7 (s, Ph C$_p$), 135.4 (s, Ph C$_o$), 136.2 (s, py C^4), 140.4 (s, Ph C$_{ipso}$), 158.2 (s, py C^2), 159.1 (s, py C$_6$). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.52; H, 7.82; N, 6.98.

2-(2,6-Diisopropylphenyl)-6-methylpyridine (16). To a mixture of **13**[47] (7.35 g, 4.90 mL, 43 mmol), [Ni(acac)$_2$] (0.201 g, 0.784 mmol), and P(*t*-Bu)$_3$ (0.157 g, 0.195 mL, 0.784 mmol) in diethyl ether (100 mL) in an ice bath was added (2,6-diisopropylphenyl)magnesium bromide (0.055 mol in 100 mL of diethyl ether) over a period of 10 min. After workup, as described for **14**, a yellow-brown solid was obtained, which was further purified by sublimation under reduced pressure (5 mbar, 190 °C), yielding a yellow solid (4.96 g, 19 mmol, 45%). ^{1}H NMR ($CDCl_3$): δ 1.15 (d, 6H, Ph(CH(CH_3)(C*H*$_3$))$_2$, ^3J(H,H) = 6.9 Hz), 1.22 (d, 6H, Ph(CH(C*H*$_3$)(CH_3))$_2$, ^3J(H,H) = 6.9 Hz), 2.52 (sept, 2H, Ph(C*H*(CH_3)$_2$)$_2$, ^3J(H,H) = 6.9 Hz), 2.60 (s, 3H, py−CH_3), 7.06 (d, 1H, py H^3, ^3J(H,H) = 7.8 Hz), 7.15 (d, 1H, Ph H$_p$, ^3J(H,H) = 8.6 Hz), 7.46 (d, 1H, py H^4, ^3J(H,H) = 7.8 Hz), 7.6 (dd, 2H, Ph H$_m$, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.8 (s, Ph(CH(CH_3)(CH_3))$_2$), 24.1 (s, Ph(CH(C*H*$_3$)(CH_3))$_2$), 24.4 (s, py−CH_3), 30.0 (s, Ph(*C*H-(CH_3)$_2$)$_2$), 120.8 (s, py C^3), 121.7 (s, py C^5), 122.3 (s, Ph C$_m$), 128.2 (s, Ph C$_p$), 135.7 (s, py C^4), 138.3 (s, Ph C$_{ipso}$), 146.2 (s, Ph C$_o$), 157.8 (s, py C^2), 159.0 (s, py C^6). Anal. Calcd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.25; H, 9.10; N, 5.42.

2-[(Diphenylphosphanyl)methyl]-6-phenylpyridine (5). A solution of **14** (3.18 g, 19 mmol) in THF (50 mL) was cooled to −78 °C, and 1 equiv of *t*-BuLi (1.7 M solution in pentane, 11.18 mL, 19 mmol) was added. The reaction mixture was stirred for 2 h at −78 °C before 1 equiv of PPh_2Cl (3.40 g, 2.6 mL, 19 mmol) was added dropwise. The solution was further stirred at −78 °C for 2 h before it was warmed to room temperature overnight. The reaction mixture was hydrolyzed with degassed water (20 mL), and the organic phase was separated and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, yielding the product as a yellow oil (5.04 g, 14 mmol, 75%). ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 2H, PC*H*$_2$), 7.25 (m, 1H, py H^4), 7.30 (m, 1H, Ph H$_p$), 7.30−7.60 (m, 10H, PPh_2), 7.40 (m, 2H, Ph H$_m$), 7.60 (s, 1H, py H^3), 8.06 (d, 2H, Ph H$_o$, ^3J(H,H) = 6.9 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 37.9 (d, PCH_2, ^1J(P,C) = 16.5 Hz), 117.6 (s, py C^3), 127.0 (s, py C^5), 127.2 (s, Ph C$_o$), 127.6 (s, Ph C$_p$), 132.9 (s, Ph C$_m$), 128.1−128.7 (m, PPh_2), 136.9 (s, py C^4), 139.5 (s, Ph C$_{ipso}$), 156.7 (s, py C^2), 158.0 (s, py C^6). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −10.8 (s). Anal. Calcd for $C_{24}H_{20}NP$: C, 81.57; H, 5.70; N, 3.96. Found: C, 81.30; H, 5.55; N, 3.85.

2-(2,6-Dimethylphenyl)-6-[(diphenylphosphanyl)methyl]pyridine (6). A solution of **15** (2.61 g, 13 mmol) in THF

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(50 mL) was cooled to −78 °C, and 1 equiv of *t*-BuLi (1.7 M solution in pentane, 7.6 mL, 13 mmol) was added. The reaction mixture was stirred for 2 h at −78 °C before 1 equiv of PPh_2Cl (2.32 g, 1.76 mL, 13 mmol) was added dropwise. The solution was further stirred at −78 °C for 2 h before it was warmed to room temperature overnight. The reaction mixture was hydrolyzed with degassed water (20 mL), and the organic phase was separated and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, yielding the product as a yellow oil (3.77 g, 9.88 mmol, 76%). ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 6H, $Ph(CH_3)_2$), 3.72 (s, 2H, PCH_2), 7.05 (m, 1H, py H^5), 7.10−7.15 (m, 3H, Ph H_m, Ph H_p), 7.30−7.50 (m, 10H, PPh_2), 7.45 (m, 1H, py H^3) 7.60 (t, 1H, py H^4, $^3J(H^4,H^{3,5}) = 7.71$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.9 (s, $Ph(CH_3)_2$), 39.4 (d, PCH_2, $^1J(P,C) = 16.5$ Hz), 121.7 (s, py C^3), 121.9 (s, py C^5), 127.9 (s, Ph C_o), 128.1 (s, Ph C_p), 128.7−129.0 (m, PPh_2), 133.2 (s, Ph C_m), 136.8 (s, py C_4) 141.0 (s, Ph C_{ipso}), 158.3 (s, py C^2), 159.8 (s, py C^6). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.7 (s). Anal. Calcd for $C_{26}H_{24}NP$: C, 81.87, H, 6.34; N, 3.67. Found: C, 81.50; H, 6.22; N, 3.45.

2-(2,6-Diisopropylphenyl)-6-[(diphenylphosphanyl)-methyl]pyridine (7). A solution of **16** (1.61 g, 6.35 mmol) in THF (40 mL) was cooled to −78 °C, and 1 equiv of *t*-BuLi (1.7 M solution in pentane, 3.73 mL, 6.35 mmol) was added. The reaction mixture was stirred for 2 h at −78 °C before 1 equiv of PPh_2Cl (1.40 g, 1.10 mL, 6.35 mol) was added dropwise. The solution was further stirred at −78 °C for 2 h before it was warmed to room temperature overnight. The reaction mixture was hydrolyzed with degassed water (20 mL), and the organic phase was separated and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, yielding the product as a yellow oil (1.99 g, 4.57 mmol, 72%). ^{1}H NMR ($CDCl_3$): δ 1.17 (d, 6H, $Ph(CH(CH_3)(CH_3))_2$, $^3J(H,H) = 6.8$ Hz), 1.22 (d, 6H, $Ph(CH(CH_3)(CH_3))_2$, $^3J(H,H) = 6.8$ Hz), 2.49 (sept. 2H, $CH(CH_3)_2$, $^3J(H,H) = 6.8$ Hz), 3.70 (s, 2H, PCH_2), 7.0 (d, 1H, py H^5, $^3J(H^5,H^4) = 7.65$ Hz), 7.20 (d, 2H, Ph H_m, $^3J(H,H) = 8.55$ Hz), 7.30 (m, 1H, Ph H_p), 7.30−7.40 (m, 10H, PPh_2), 7.42 (m, 1H, py H^3), 7.72 (t, 1H, py H,^{4} $^3J(H^4,H^5) = 7.65$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.5 (s, $Ph(CH(CH_3)(CH_3))_2$), 24.2 (s, $Ph(CH(CH_3)(CH_3))_2$), 30.6 (s, $Ph(CH(CH_3)_2)_2$), 39.4 (d, PCH_2, $^1J(P,C) = 16.1$ Hz), 121.4 (s, py C^3), 122.7 (s, py C^5), 123.0 (s, Ph C_m), 128.7−129.0 (m, PPh_2, Ph C_o, Ph C_p), 133.0 (s, py C^4), 136.0 (s, Ph C_{ipso}), 152.3 (s, py C^2), 156.8 (s, py C^6). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.4 (s). Anal. Calcd for $C_{30}H_{32}NP$: C, 82.35; H, 7.37; N, 3.20. Found: C, 82.30; H, 7.32; N, 3.20.

2-[2-(Diphenylphosphanyl)phenyl]-6-methylpyridine (8). To a solution of **14** (2.439 g, 14 mmol) in THF (50 mL) was added 1 equiv of *n*-BuLi (1.6 M solution in hexanes, 9.0 mL, 14 mmol) at room temperature, and the reaction mixture was stirred for 2 h. One equivalent of PPh_2Cl (3.18 g, 2.6 mL, 14 mmol) was then added dropwise over 5 min. This exothermic reaction brought the temperature to about 60 °C. The solution was stirred at room temperature overnight before it was hydrolyzed with degassed water (30 mL). The organic phase was separated with a cannula, and the aqueous phase was extracted twice with Et_2O (40 mL). The organic phases were collected and dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure, yielding the reaction product as a white powder (2.95 g, 8.3 mmol, 60%). ^{1}H NMR ($CDCl_3$): δ 2.67 (s, 3H, py−CH_3), 7.10 (d, 1H, py H^5, $^3J(H^5,H^4) = 7.0$ Hz), 7.24−7.6 (m, 10 H, PPh_2), 7.43 (d, 1H, py H^3, $^3J(H^3,H^4) = 7.0$ Hz), 7.41 (dd, 1H, py H^4, $^3J(H^4,H^{3,5}) = 7.0$ Hz), 7.46−7.70 (m, 3H, Ph $H_{m,o}$), 8.01 (dd, 1H, Ph H_o, $^3J(H,H) = 6.75$ Hz, $^4J(P,H) = 1.74$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.7 (s, py−CH_3), 118.7 (s, py $C^{3,5}$), 125.9 (s, Ph $C_{o,p}$), 127.5−128.6 (m, Ph C_m, PPh_2 $C_{m,p}$), 130.2 (d, PPh_2 C_o), 131.1 (d, PPh_2 C, $^1J(P,C) = 16.6$ Hz), 131.3 (s, py C^4), 151.6 (s, Ph C_{ipso}), 156.9 (s, py $C^{2,6}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.2 (s). Anal. Calcd for $C_{24}H_{20}NP$: C, 81.57; H, 5.70; N, 3.96. Found: C, 81.85; H, 6.00; N, 4.00.

Synthesis of {2-[(Diphenylphosphanyl)methyl]-6-phenylpyridine}nickel Dichloride (9). Using a procedure similar to that detailed below for **11**, a suspension of $[NiCl_2(DME)]$ (0.506 g, 2.38 mmol) in CH_2Cl_2 (30 mL) was added to a solution of the phosphinopyridine **5** (0.846 g, 2.38 mmol) in CH_2Cl_2 (15 mL) at room temperature, and the mixture was stirred for 12 h. After workup, the red-brown solid product was dried under vacuum for 12 h (0.867 g, 1.79 mmol, 78%). IR (KBr; selected pyridine vibrations): 1595 m ($\nu_{C=C}$), 1160 m ($\nu_{\beta(C-H)}$), 998 s and 1022 w (ν_{cycle}), 692 vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{24}H_{20}Cl_2NNiP$: C, 59.68; H, 4.17; N, 2.90. Found: C, 60.05, H, 4.27; N, 2.48.

Synthesis of {2-(2,6-Dimethylphenyl)-6-[(diphenylphosphanyl)methyl]pyridine}nickel Dichloride (10). Using a procedure similar to that detailed below for **11**, a suspension of $[NiCl_2(DME)]$ (0.287 g, 1.35 mmol) in CH_2Cl_2 (30 mL) was added to a solution of the phosphinopyridine **6** (1.35 mmol, 0.515 g) in CH_2Cl_2 (10 mL) at room temperature, and the mixture was stirred for 12 h. After workup, the green-brown solid product was dried under vacuum for 12 h (1.26 g, 1.04 mmol, 77%). IR (KBr; selected pyridine vibrations): 1596 m ($\nu_{C=C}$), 1161 m ($\nu_{\beta(C-H)}$), 997 s and 1024 w (ν_{cycle}), 692 vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{26}H_{24}Cl_2NNiP$: C, 61.11; H, 4.73; N, 2.74. Found: C, 61.13, H, 4.51; N, 2.70.

Synthesis of {2-(2,6-Diisopropylphenyl)-6-[(diphenylphosphanyl)methyl]pyridine}nickel Dichloride (11). To a suspension of $[NiCl_2(DME)]$ (0.592 g, 2.78 mmol) in CH_2Cl_2 (30 mL) was added a solution of the phosphinopyridine **7** (1.218 g, 2.78 mmol) in CH_2Cl_2 (20 mL) at room temperature, and the reaction mixture was stirred for 12 h and then filtered through Celite in order to separate unreacted $[NiCl_2(DME)]$. The brown filtrate was evaporated under reduced pressure, dissolved in CH_2Cl_2 (10 mL), and reprecipitated with hexane (20 mL). The supernatant liquid was filtered with a cannula equipped with a filter cap. The solid was partially dissolved in toluene (15 mL) and precipitated by addition of hexane. The green-brown solid was dried under vacuum for 12 h (1.26 g, 2.22 mmol, 80%). IR (KBr; selected pyridine vibrations): 1599 m ($\nu_{C=C}$), 1166 m ($\nu_{\beta(C-H)}$), 996 vs and 1026 w (ν_{cycle}), 695 vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{30}H_{32}Cl_2NNiP$: C, 63.53; H, 5.69; N, 2.47. Found: C, 63.10; H, 5.71; N, 2.79.

Synthesis of {2-[2-(Diphenylphosphanyl)phenyl]-6-methylpyridine}nickel Dichloride (12). To a suspension of $[NiCl_2(DME)]$ (1.77 g, 8.30 mmol) in CH_2Cl_2 (100 mL) was added a solution of the phosphinopyridine **8** (2.945 g, 8.30 mmol) in CH_2Cl_2 (60 mL) at room temperature, and the reaction mixture was stirred for 2 h. The red solution was filtered through Celite in order to separate unreacted $[NiCl_2(DME)]$. The filtrate was evaporated under reduced pressure, and the solid was dissolved in CH_2Cl_2 (50 mL) and reprecipitated with hexane (150 mL). The supernatant solution was filtered with a cannula equipped with a filter cap. The solid was partially dissolved in toluene (70 mL) and precipitated by the addition of hexane. The brick red solid was dried under vacuum for 12 h (2.72 g, 5.79 mmol, 70%). IR (KBr; selected pyridine vibrations): 1565 m ($\nu_{C=C}$), 1188 m ($\nu_{\beta(C-H)}$), 998 vs and 1026 w (ν_{cycle}), 688 vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{24}H_{20}Cl_2NNiP$: C, 59.68; H, 4.17; N, 2.90. Found: C, 59.48; H, 4.18; N, 2.67.

Oligomerization of Ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 100 mL stainless steel autoclave. The interior of the autoclave was protected from corrosion by a protective coating. All catalytic tests were started at 30 °C, and no cooling of the reactor was done during the reaction. In all catalytic experiments with MAO and $AlEtCl_2$, 4.0×10^{-2} mmol of the Ni complex was used. The necessary amount of complex for six catalytic runs was dissolved in 60 mL of toluene. For each catalysis, 10 mL of this solution was injected into the reactor. Depending on the amount of cocatalyst added, between 0 and 5 mL of solvent was added so that the total volume of all solutions was 15 mL. This can be summarized by the equation

10 mL (Ni solution) +

y mL (solvent) + *z* mL (cocatalyst solution) = 15 mL

When MAO was used as cocatalyst, the total volume was increased to 20 mL. After injection of the catalyst solution under a constant low flow of ethylene, the reactor was brought to working pressure and continuously fed with ethylene, using a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. The temperature increase observed resulted solely from the exothermicity of the reaction. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test, the reactor was cooled to 10 °C before the gaseous phase was transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by addition of ethanol (10 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap distillation (120 °C, 20 Torr). All volatiles were evaporated (120 °C, 20 Torr static pressure) and recovered in a second flask previously immersed in liquid nitrogen in order to avoid any loss of product. For gas chromatographic analyses, 1-heptene was used as internal reference.

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