New Nickel Ethylene Oligomerization Catalysts Bearing Bidentate *P,N*-Phosphinopyridine Ligands with Different Substituents α to Phosphorus†

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The new phosphinopyridine ligands *rac*-2-[(diphenylphosphanyl)benzyl]pyridine (**6**), *rac*-2-[1′-(diphenylphosphanyl)ethyl]pyridine (**7**), and 2-[1′-(diphenylphosphanyl)-1′-methyl]ethylpyridine (**8**) with variable substitution at the carbon α to P were used for the synthesis of the paramagnetic Ni(II) complexes [$NiCl_2$(P,N)] **9**−**11**, respectively. The complex **11**·0.5CH_2Cl_2 has been shown by X-ray diffraction to have an almost planar coordination geometry about the metal, although the coordination sphere of all complexes in solution was determined by the Evans method to be distorted tetrahedral. The Ni complexes provided activities for the catalytic oligomerization of ethylene up to 58 100 mol C_2H_4/mol Ni·h (**11**) in the presence of only 6 equiv of $AlEtCl_2$. The selectivity for C_4 olefins reached 81% for **9** in the presence of 2 equiv of $AlEtCl_2$, but the selectivity toward 1-butene was only 11−14%. In the presence of 400 or 800 equiv of methylalumoxane (MAO), complexes **9**−**11** yielded lower activities than with $AlEtCl_2$ as cocatalyst but higher selectivities for 1-butene. A turnover frequency of 22 800 mol C_2H_4/mol Ni·h was observed for **11** in the presence of 800 equiv of MAO. The selectivities were in the range 70−85% for the C_4 olefins and in the range 33−38% for 1-butene within the C_4 fraction. For these P,N ligands, increasing the degree of alkyl substitution at the carbon α to P leads to higher activities for ethylene oligomerization and more selective formation of α-olefins. The nature of the N-heterocycle influences the activity, as shown by the turnover frequencies of 58 100 mol C_2H_4/mol Ni·h for **11** in the presence of 6 equiv of $AlEtCl_2$ and 45 900 mol C_2H_4/mol Ni·h for the related phosphinooxazoline complex **16**. Under these conditions, the selectivity to 1-butene within the C_4 fraction was 11% for **11** and 20% for **16**. When MAO was used as a cocatalyst (800 equiv), a similar trend was observed for the activity, but the selectivity to 1-butene within the C_4 fraction increased to 38% for **11** and 37% for **16**.

Introduction

Phosphinopyridine ligands find widespread applications in the coordination chemistry[1−3] of transition metals and in homogeneous catalysis[1,4,5] owing to the simultaneous presence of the ubiquitous pyridine and phosphine donor groups. Their potential hemilabile character represents an additional advantage for the fine-tuning of catalytic processes, and such dynamic phenomena are usually readily monitored by variable-temperature ^{31}P NMR spectroscopy.[6] Phosphinopyridines, phosphinoquinolines, and phosphinonaphthyridines of type **1** are increasingly used in the synthesis of heterobimetallic or polymetallic compounds.[2,3,7,8] Introduction of chirality for asymmetric synthesis is achieved with ligands of type **2**.[1,9−12] Another family of phosphinopyridines with either C_2 symmetry (**3**)[13−16] or

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† Dedicated to Prof. M. I. Bruce on the occasion of his 65th birthday, with our warmest congratulations and best wishes.

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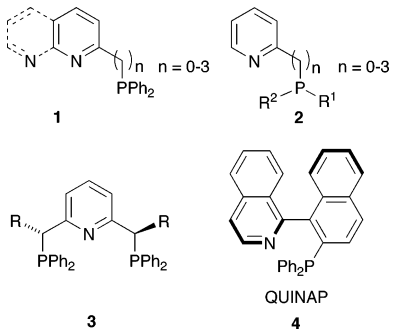
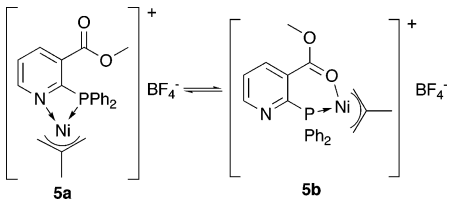
axial chirality (**4**)[17−20] has also been applied in asymmetric catalysis.

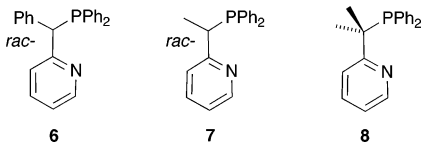


Despite the successful application of phosphinopyridines in asymmetric transfer hydrogenation,[13,16] asymmetric hydroboration,[19] allylic substitution,[20] and carbonylation reactions[21] including hydroformylation,[22] only a few complexes containing such ligands have been reported for their application in oligomerization or polymerization reactions of α-olefins,[23a,b] and these include **5a** and **5b** (Scheme 1).[24]

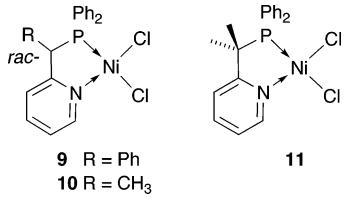
Scheme 1. Structural Ambivalence of the Complex [Ni(2-(diphenylphosphine)nicotinate)-methallyl]BF_4 (5a,b)



In view of the academic and industrial importance of olefin dimerization and oligomerization,[25] and as part of ongoing studies in our laboratories,[26] we sought to examine the influence of the ligand basicity in the new series of phosphinopyridines **6**−**8** on the catalytic activity and selectivity of Ni(II) complexes for ethylene oligomerization.

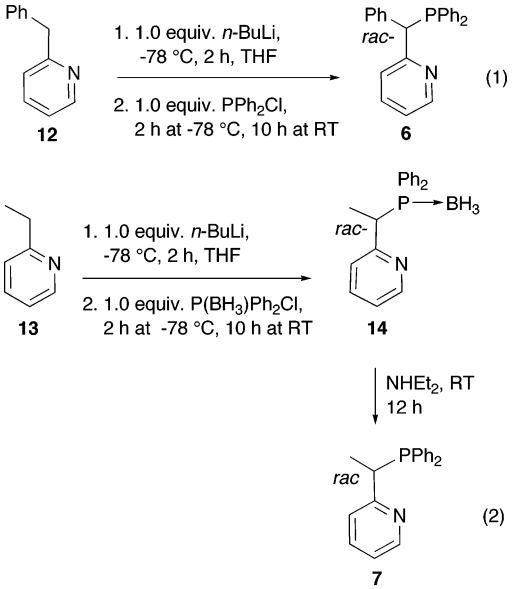


The synthesis and structure of the corresponding Ni(II) complexes **9**−**11** as well as their catalytic properties in the oligomerization of ethylene using $AlEtCl_2$ or methylalumoxane (MAO) as cocatalyst will be discussed here.



Results and Discussion

1. Synthesis of the Phosphinopyridine Ligands 6−8. The racemic phosphinopyridines **6** and **7** and ligand **8** were prepared in good yields by one- and two-step procedures (see Experimental Section). Ligand **6** was accessible by the reaction of 2-benzylpyridine **12** with *n*-BuLi at −78 °C and subsequent addition of PPh_2Cl (eq 1). The racemic ligand 2-ethyl-(1′-diphenylphosphino)pyridine **7** was synthesized similarly by using 2-ethylpyridine **13** and borane-protected PPh_2Cl as reagents (eq 2).



Phosphine **8** could not be prepared by simple metalation of 2-(isopropyl)pyridine and reaction of the meta-

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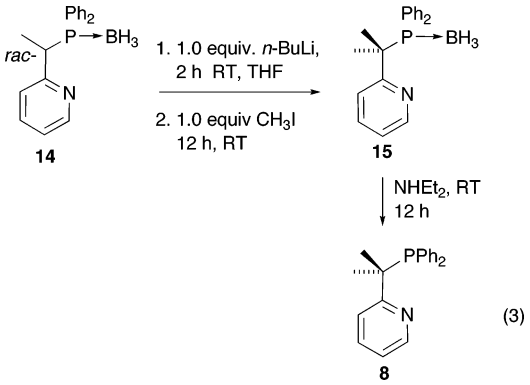
lated species with a chlorophosphine since only bases such as potassium diisopropylamine (KDA), Lochmann Schlosser base (*n*-BuLi/KO*t*-Bu),[27a] or $NaNH_2/NH_3$[27b] were able to deprotonate the isopropyl side chain. The remaining alcoholate or amine readily reacts with the chlorophosphine, and the desired phosphine **8** is obtained in only 10−30% yields.

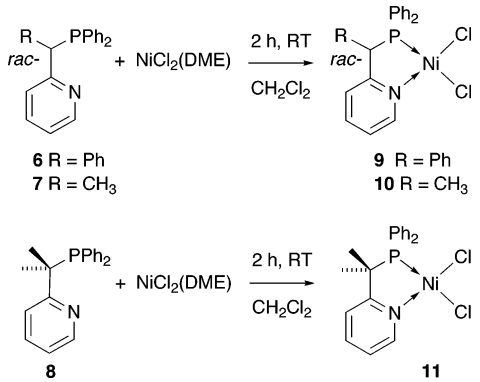
Another synthetic pathway was therefore explored, and phosphinopyridine **8** was prepared by adding first 1 equiv of *n*-BuLi at room temperature to the borane-protected phosphine **14** and, subsequently, 1 equiv of CH_3I. After quantitative deprotection and workup, the *gem*-disubstituted phosphinopyridine **8** was isolated in 74% yield (eq 3). The racemic ligands **6** and **7** and the achiral phosphinopyridine **8** show a resonance in the ^{31}P NMR spectrum at −1.0, 0.6, and 22.5 ppm, respectively.



(3)

2. Complexes [$NiCl_2$(phosphinopyridine)] 9−11. Complexes **9**−**11** were prepared by reaction between equimolar amounts of phosphine and [$NiCl_2$(DME)] for 2 h in CH_2Cl_2. After workup, the Ni complexes were isolated in 76−80% yields (Scheme 2).

Scheme 2. Synthesis of the Ni(II) Complexes 9−11



Coordination of the nitrogen heterocycle to the metal center can be easily verified by infrared spectroscopy with the characteristic shift of the ν_{C-C}, ν_{cycle}, $\nu_{\gamma(C-C)}$, $\nu_{R\ sens}$, and $\nu_{\beta(C-H)}$ vibrations.[28] All three complexes proved to be paramagnetic. Their magnetic moment was determined by means of the Evans method[29] and found to be 1.37, 1.35, and 1.20 μ_B, respectively. Therefore all three complexes should display in solution distorted square planar or tetrahedral geometry.[30,31] The solid-state structure of **11**·0.5CH_2Cl_2 was determined by X-ray diffraction, and a view of the structure is shown in Figure 1 and selected bond distances and angles are given in Table 1.

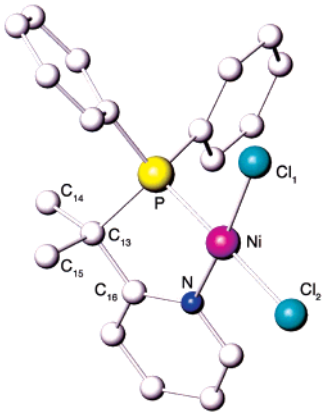


Figure 1. Molecular structure of [Ni(2-{1′-(diphenylphosphanyl)-1′-methyl}ethylpyridine)Cl_2] in **11**·0.5CH_2Cl_2.

Table 1. Selected Bond Distances (Å) and Angles (deg) in [Ni(2-{1′-(diphenylphosphanyl)-1′-methyl}ethylpyridine)Cl_2]·0.5CH_2Cl_2 (11·0.5CH_2Cl_2)

P−Ni	2.129(1)
N−Ni	1.950(3)
Ni−Cl(1)	2.167(1)
Ni−Cl(2)	2.221(1)
P−C(13)	1.866(3)
C(13)−C(16)	1.507(5)
C(16)−N	1.359(4)
Cl(1)−Ni−Cl(2)	91.98(4)
Cl(1)−Ni−P	88.03(4)
Cl(1)−Ni−N	170.01(9)
Cl(2)−Ni−P	178.47(4)
Cl(2)−Ni−N	96.61(9)
P−Ni−N	83.52(9)

The coordination sphere around the Ni(II) center is almost square planar since the maximum deviation out of the mean plane passing through Ni, N, P, Cl(1), and Cl(2) is 0.22(1) Å (for the N atom). This result is somewhat unexpected in view of the paramagnetic nature of this complex in solution, but of course solution and solid-state structures need not be identical.[30] According to the Cambridge Structure Database, [$NiCl_2$-(2-{1′-(diphenylphosphanyl)-1′-methyl}ethylpyridine)] (**11**) appears to be the first square planar [NiX_2(P,N)]-type complex characterized by X-ray crystallography. No comparative data are therefore available. Except for the ligand bite angle (P−Ni−N), the bond angles around the Ni atom, and the P−Ni distance, most structural parameters are similar to those observed for the recently described phosphinooxazoline complex **16**.[26b] The bite angle is increased to 83.59(2)° in comparison to 82.7-(1)° in **16** and 80.83(7)° in **17**.[26b]

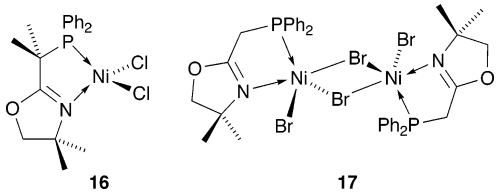


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Table 2. Comparative Catalytic Data for Complexes 9−11, 16,[26b] and $[NiCl_2(PCy_3)_2]$ in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	9	9	10	10	11	11	16	16	$[NiCl_2(PCy_3)_2]$	$[NiCl_2(PCy_3)_2]$
$AlEtCl_2$ [equiv]	6	2	6	2	6	2	6	2	6	2
selectivity C_4 [%]	72	81	66	75	65		54	67	86	88
selectivity C_6 [%]	26	18	30	23	32		40	28	14	12
selectivity C_8 [%]	2	1	3.5	2	2.5		1	3	0.5	
selectivity C_{10} [%]			0.3	0.1			2	2		
selectivity C_{12} [%]							3.5	1		
productivity (g C_2H_4/g Ni·h)	23 600	14 400	26 400	22 100	27 800	inactive	22 000	12 300	13 000	800
TOF (mol C_2H_4/mol Ni·h)	49 400	30 100	55 200	46 100	58 100	inactive	45 900	25 400	27 200	1600
α-olefin (C_4) [%]	11	14	11	14	11		20	25	9	12
k_α[b]	0.24	0.15	0.31	0.20	0.33		0.50	0.28	0.11	0.09

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

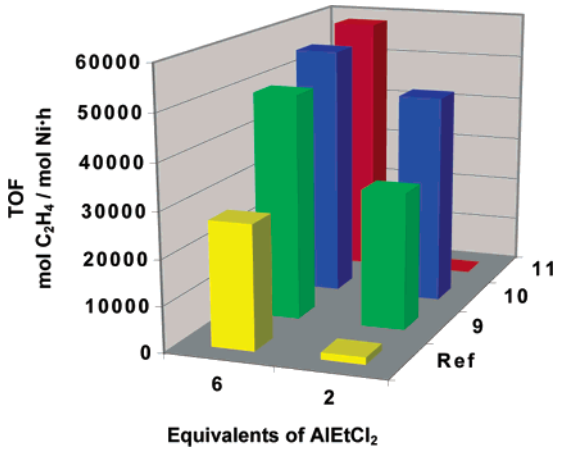

Figure 2. Activity of the complexes **9**−**11** for the oligomerization of ethylene using different quantities of $AlEtCl_2$. Conditions: T = 30 °C, 10 bar C_2H_4, 35 min, 4×10^{-2} mmol Ni, Ref: $[NiCl_2(PCy_3)_2]$.

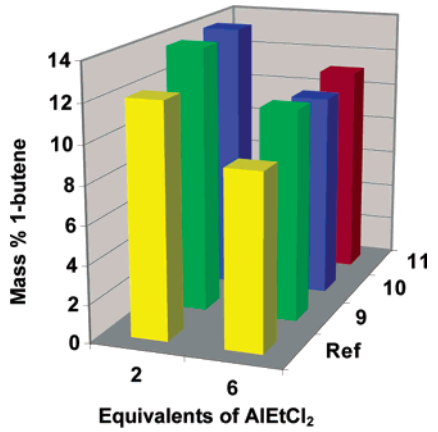

Figure 3. Selectivity to 1-butene within the C_4 fraction of the complexes **9**−**11** using different quantities of $AlEtCl_2$. Conditions: T = 30 °C, 10 bar C_2H_4, 35 min, 4×10^{-2} mmol Ni, Ref: $[NiCl_2(PCy_3)_2]$.

3. Catalytic Ethylene Oligomerization. The $[NiCl_2$(phosphinopyridine)] complexes **9**−**11** were tested for the oligomerization of ethylene in order to elucidate the influence of an increased substitution at the carbon atom α to P on the activity and selectivity of the catalysts. The cocatalysts used were methylalumoxane (MAO) or $AlEtCl_2$, and the complex $[NiCl_2(PCy_3)_2]$ was taken as a reference compound since it is a typical dimerization catalyst for α-olefins.[32] For comparison, we report in Table 2 the values found for this complex under our conditions, whereas no activity was observed for $[NiCl_2(PCy_3)_2]$ in the presence of either 400 or 800 equiv of MAO.

The catalytic properties of complexes **9**−**11** were evaluated in the presence of 2 and 6 equiv of $AlEtCl_2$. When 2 equiv of cocatalyst was used, complexes **9** and **10** showed turnover frequencies (TOF) of 30 100 mol C_2H_4/mol Ni·h (**9**) and 46 100 mol C_2H_4/mol Ni·h (**10**), whereas complex **11** was inactive (Table 2). The reference complex $[NiCl_2(PCy_3)_2]$ was hardly active in the presence of 2 equiv of cocatalyst but showed a TOF of 27 200 mol C_2H_4/mol Ni·h when 6 equiv of $AlEtCl_2$ was used (Figure 2). Under the latter conditions, complexes **9**−**11** were also more active than when only 2 equiv of $AlEtCl_2$ was used, with TOF values of 49 400, 55 200, and 58 100, respectively. The complexes remained active until the catalytic reactions were quenched by addition of 10 mL of ethanol, as indicated by monitoring the ethylene consumption. The selectivities for the ethylene dimerization products 1-butene and *cis*- and *trans*-2-butene varied between 65% and 81% depending on the amount of cocatalyst used. The moderate selectivity for 1-butene obtained with complexes **9**−**11** is comparable to that with $[NiCl_2(PCy_3)_2]$. This may be due to the strong exothermic character of the catalytic reactions, which favors isomerization of the α-olefins (Figure 3).[33] A larger amount of cocatalyst is generally responsible for a shift of the product distribution to longer chain oligomers, as observed experimentally with other cocatalysts.[33,34]

In general, a considerable excess of MAO is used as cocatalyst with Ni(II) or Pd(II) diimine complexes for the oligomerization and polymerization of ethylene.[34,35] When complexes **9**−**11** were tested in the presence of 400 or 800 equiv of MAO, the activities decreased compared to those observed with $AlEtCl_2$ as cocatalyst. In the presence of 400 equiv of MAO, turnover frequencies of 10 200, 10 000, and 7000 mol C_2H_4/mol Ni·h were observed for **9**, **10**, and **11**, respectively (Table 3). When 800 equiv of MAO was used, an increase of the TOF to 13 600, 12 200, and 22 800 mol C_2H_4/mol Ni·h, respectively, was observed (Figure 4).

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Table 3. Comparative Catalytic Data for Complexes 9−11 and 16[26b] in the Oligomerization of Ethylene with MAO as Cocatalyst[a,c]

	9	9	10	10	11	11	16
MAO [equiv]	400	800	400	800	400	800	800
selectivity C_4 [%]	81	77	85	83	73	69	72
selectivity C_6 [%]	16	18	14	15	22	22	23
selectivity C_8 [%]	2	3	2	3	4	8	5
selectivity C_{10} [%]		2			1	1	1
productivity (g C_2H_4/g Ni·h)	4850	6500	4800	5850	3300	10 900	3800
TOF (mol C_2H_4/mol Ni·h)	10 200	13 600	10 000	12 200	7000	22 800	7900
α-olefin (C_4) [%]	34	33	38	35	34	38	38
k_α[b]	0.14	0.16	0.11	0.12	0.20	0.22	0.21

[a] Conditions: T = 30 °C, 10 bar C_2H_4, 35 min, 4 × 10^{-2} mmol Ni complex, solvent: 20 mL of toluene. [b] k_α= hexenes [mol]/butenes [mol]. [c] No C_{12} oligomers were detected.

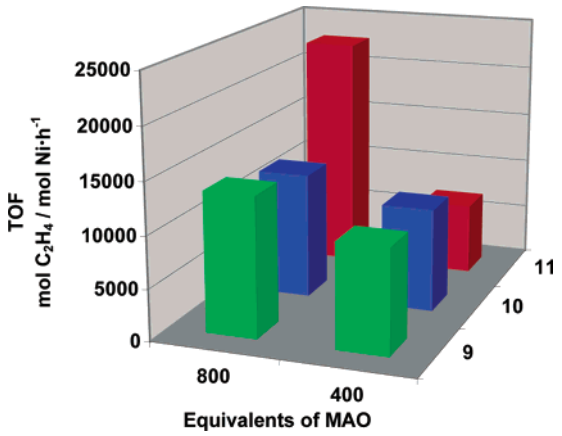

Figure 4. Activity of the complexes **9**−**11** for the oligomerization of ethylene using different quantities of MAO. Conditions: T = 30 °C, 10 bar C_2H_4, 35 min, 4 × 10^{-2} mmol Ni, Ref: [$NiCl_2(PCy_3)_2$].

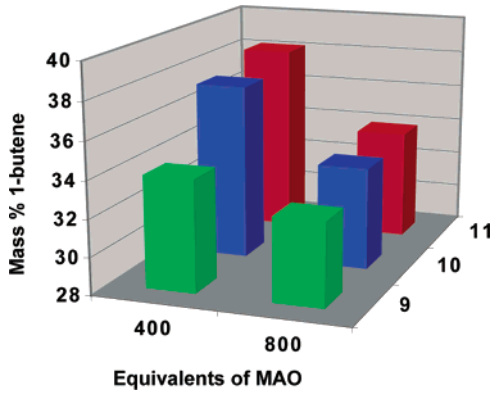

Figure 5. Selectivity to 1-butene within the C_4 fraction of the complexes **9**−**11** using different quantities of MAO. Conditions: T = 30 °C, 10 bar C_2H_4, 35 min, 4 × 10^{-2} mmol Ni.

The selectivities for α-olefins, which were low with $AlEtCl_2$ as cocatalyst, increased in the presence of either 400 or 800 equiv of MAO (Figure 5). Selectivities to 1-butene within the C_4 fraction of 33, 35, and 38% were observed in the presence of 800 equiv of MAO for **9**, **10**, and **11**, respectively, while the product distribution was shifted toward C_4 products, and up to 85% of ethylene dimerization products were formed. Increased substitution at the carbon α to phosphorus leads, in the presence of 800 equiv of MAO, to higher activities and better selectivities for 1-butene in the oligomerization of ethylene (Figures 2−5).

It is interesting to examine the influence of the nature of the N-heterocycle by comparing the catalytic properties of **11** with those of the related phosphinooxazoline nickel(II) complex **16**, of which the crystal structure shows a distorted tetrahedral metal cordination in the solid state.[26b] In the presence of 6 equiv of $AlEtCl_2$, the turnover frequency of 58 100 mol C_2H_4/mol Ni·h found for **11** is about 25% higher than that of 45 900 mol C_2H_4/mol Ni·h for **16** (Table 2).[26b] Both complexes show a significant selectivity for the C_4 olefins: 65% for **11** and 54% for **16**. However, the selectivity to 1-butene within the C_4 fraction increases from to 11% for **11** to 20% for **16**. Under these conditions, the phosphinopyridine complex **11** is therefore a more active but less selective catalyst for 1-butene than the phosphinooxazoline complex **16**. Note however that precatalyst **16** was already active in the presence of only 2 equiv of $AlEtCl_2$, in contrast to **11**.

When 800 equiv of MAO was used as cocatalyst, the turnover frequency of 22 800 mol C_2H_4/mol Ni·h provided by complex **11** was considerably higher than that of 7900 mol C_2H_4/mol Ni·h found for **16** (Table 3). Similar selectivities were obtained for the C_4 olefins, 69% with **11** and 72% for **16** and, for 1-butene, 38% of the C_4 fraction with **11** and **16**.[26b]

The k_α values given in Tables 2 and 3 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 fact that this value varies for a given catalyst as a function of the nature or quantity of cocatalysts used suggests that some of the C_6 production results from incorporation of 1-butene (consecutive reaction).

Conclusion

The new phosphinopyridine ligands **6**−**8** have allowed us to study the behavior of their corresponding paramagnetic Ni(II) complexes **9**−**11** as catalyst precursors for the oligomerization of ethylene using $AlEtCl_2$ or MAO as cocatalyst. The complex [$NiCl_2$(2-{1′-(diphenylphosphanyl)-1′-methyl}ethylpyridine)] (**11**) was shown by X-ray diffraction to have an almost planar coordination geometry about the metal, although the coordination sphere of all complexes in solution was determined by the Evans method to be distorted tetrahedral. The Ni(II) complexes provided catalytic activities up to 58 100 mol C_2H_4/mol Ni·h (**11**) in the presence of 6 equiv of $AlEtCl_2$. The selectivity for the C_4 olefins was as high as 81% (**9** in the presence of only 2 equiv of $AlEtCl_2$). Similar activities have been obtained by other groups in the dimerization of ethylene and propene, but they required the presence of 200−400 equiv of this cocata-

lyst.[36] In the presence of 400 or 800 equiv of MAO, complexes **9**−**11** yielded lower activities but higher selectivities for 1-butene. A turnover frequency of 22 800 mol C_2H_4/mol Ni·h was observed for **11** in the presence of 800 equiv of MAO. The selectivities for the C_4 olefins were in the range 70−85%, with a maximum selectivity to 1-butene within the C_4 fraction of 38% for **10** with 400 equiv of MAO or **11** with 800 equiv of MAO.

It thus appears for these P,N ligands that an increase in the degree of alkyl substitution at the carbon α to P tends to lead to higher activities and more selective formation of α-olefins. The influence of the nature of the N-heterocycle on the catalytic activity for ethylene oligomerization was shown by comparing the turnover frequencies of 58 100 mol C_2H_4/mol Ni·h for **11** and of 45 900 mol C_2H_4/mol Ni·h for the related phosphinooxazoline complex **16**[26b] in the presence of 6 equiv of $AlEtCl_2$. This indicates a beneficial effect of an increased basicity of the nitrogen donor atom. When MAO was used as cocatalyst (800 equiv), a similar trend was obtained, but the selectivities for 1-butene are similar for **11** and **16**. The limited selectivity for α-olefins may result from (i) reversible *β*-H elimination after ethylene insertion, followed by reinsertion with the opposite regiochemistry and chain transfer to give 2-butene, or (ii) a reuptake mechanism leading to isomerization of 1-butene.[37a] The known ability of Ni(II) complexes to isomerize α-olefins[37b] has been recently observed in the case of phosphino-pyridine chelates.[23b]

Experimental Section

All solvents were dried and distilled using common techniques unless otherwise stated. All manipulations were carried out using Schlenk techniques. Anhydrous $NiCl_2$ was obtained by heating $NiCl_2 \cdot 6H_2O$ for 6 h at 160 °C under vacuum. [NiX_2(DME)] (X = Cl, Br) was prepared according to the literature.[38] Other chemicals were commercially available and used without further purification unless otherwise stated. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ 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 a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness).

Synthesis of *rac*-2-[(Diphenylphosphanyl)benzyl]pyridine (6). To a solution of 2-benzylpyridine **12** (3.16 g, 18 mmol) in THF (40 mL) was added 1 equiv of *n*-BuLi (1.6 M solution in hexanes, 18 mmol, 11.7 mL), and the reaction mixture was stirred for 3 h at room temperature. The solution was then cooled to 0 °C, and 1 equiv of PPh_2Cl (4.12 g, 3.45 mL, 18 mmol) was added dropwise. The reaction mixture was stirred overnight and then hydrolyzed by addition of degassed water (40 mL). The organic phase was separated and the aqueous phase was extracted twice with diethyl ether (40 mL). The organic fractions were collected and dried over degassed $MgSO_4$, filtered, and taken to dryness, yielding the product as a white solid. Yield: 4.77 g, 13 mmol, 75%. ^1H NMR ($CDCl_3$) δ: 4.95 (d, 1H, PCH, ^2J(P,H) = 6.5 Hz), 7.01 (m, 1H, py-H^5, $^3J(H^5,H^4)$ = 6.2 Hz), 7.15−7.50 (m, 15H, Ph and PPh_2), 7.40 (m, 1H, py-H^3), 7.50 (m, 1H, py-H^4), 8.47 (dq, 1H, py-H^6, $^3J(H^6,H^5)$ = 6.2 Hz, $^4J(H^6,H^4)$ = 1.1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 55.4 (d, Ph*C*PPh_2, ^1J(P,C) = 12.3 Hz), 121.3 (s, py-C^5), 123.6 (s, py-C^4), 126.5 (s, py-C^3), 126.6 (s, Ph-C_p), 128.0−128.5 (m, PPh_2), 128.6 (s, Ph-C_m, and Ph-$C_{m'}$), 129.1 (s, Ph-C_o, ^2J(P,C) = 8.3 Hz), 129.2 (s, Ph-$C_{o'}$), 137.2 (s, Ph-C_{ipso}), 149.3 (s, py-C^6), 161.2 (s, py-C^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −1.0 (s). Anal. Calcd for $C_{24}H_{20}NP$: C, 81.57; H, 5.70; N, 3.96. Found: C, 81.23; H, 5.40; N, 3.76.

Synthesis of *rac*-2-[1′-(Diphenylphosphanyl)ethyl]pyridine (7). A solution of 2-ethylpyridine **13** (3.37 g, 31 mmol, 3.57 mL) in THF (150 mL) was cooled to −78 °C, and 1 equiv of *n*-BuLi (1.6 M solution in hexanes, 31 mmol, 19.38 mL) was added and the solution was stirred for 1 h at −78 °C, yielding a dark red solution. One equivalent of $P(BH_3)Ph_2Cl$ (7.26 g, 31 mmol, 5.8 mL) was then added at dry ice temperature. The solution was stirred for 1 h at −78 °C and warmed to room temperature overnight. The reaction mixture was hydrolyzed by addition of water (50 mL), and the organic layer was separated. The aqueous phase was extracted twice with dichloromethane (60 mL). The organic fractions were dried over $MgSO_4$, filtered, and taken to dryness, yielding the protected phosphine **14** as a white solid. Yield: 6.70 g, 23 mmol, 76%. NMR data of **14**: ^1H NMR ($CDCl_3$) δ: 0.5−2.0 (br, 3H, BH_3), 1.59 (dd, 3H, CH_3, ^3J(H,H) = 7.32 Hz, ^3J(P,H) = 3.6 Hz), 4.17 (dq, 1H, C*H*(PPh_2), ^3J(H,H) = 7.32 Hz, ^2J(P,H) = 7.8 Hz), 7.05 (m, 1H, py-H^5), 7.29 (m, 1H, py-H^3), 7.23−7.6 (m, 10H, PPh_2), 7.85 (m, 1H, py-H^4), 8.31 (m, 1H, py-H^6). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 25.4.

Quantitative deprotection of **14** (6.70 g, 0.023 mol) was performed by stirring it for 14 h at room temperature in $NHEt_2$ (50 mL). The volatiles were then evaporated, yielding phosphine **7** as a yellow oil. NMR data of **7**: ^1H NMR ($CDCl_3$) δ: 1.49 (dd, 3H, CH_3, ^3J(H,H) = 7.30 Hz, ^3J(P,H) = 15.9 Hz), 4.00 (dq, 1H, C*H*PPh_2), ^3J(H,H) = 7.32 Hz, ^2J(P,H) = 7.6 Hz), 7.10 (m, 1H, py-H^5), 7.30 (m, 1H, py-H^3), 7.23−7.6 (m, 10H, PPh_2), 7.85 (t, 1H py-H^4, ^3J(H,H) = 6.2 Hz), 8.31 (d, 1H, py-H^6, $^3J(H^6,H^5)$ = 5.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 27.4 (s, P*C*CH_3), 38.7 (d, ^1J(P,C) = 10.5 Hz, P*C*CH_3), 119.2 (s, py-C^5), 121.0 (s, py-C^3), 127.6 (m, PPh_2), 133.3 (s, py-C^4), 147.5 (s, py-C^6), 165.5 (s, py-C^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 0.6 (s). Anal. Calcd for $C_{19}H_{18}NP$: C, 78.33; H, 6.23; N, 4.81. Found: C, 77.90; H, 5.89; N, 4.55.

Synthesis of 2-[1′-(Diphenylphosphanyl)-1′-methyl]-ethylpyridine (8). To a solution of the protected racemic phosphine **14** (1.22 g, 4.18 mmol) in THF (50 mL) was added 1 equiv of *n*-BuLi (1.6 molar solution in hexanes, 2.6 mL, 4.18 mmol) at room temperature. The solution was stirred for 2 h, then 1 equiv of CH_3I (0.59 g, 0.25 mL, 4.18 mmol) was added at room temperature and the reaction mixture was stirred overnight, resulting in a color change from red to yellow. The solution was hydrolyzed by the addition of H_2O (30 mL). The organic phase was separated, and the aqueous phase was extracted twice with diethyl ether (40 mL). The organic fractions were dried over $MgSO_4$ and filtered with the help of a cannula, and the solvent was evaporated under reduced pressure, yielding the protected phosphine **15** as a white solid. Yield: 0.95 g, 3.11 mmol, 74%. NMR data of **15**: ^1H NMR ($CDCl_3$) δ: 0.5−2.0 (m, 3H, BH_3), 1.75 (d, 6H, $C(CH_3)_2$, ^3J(P,H) = 15 Hz), 7.0 (t, 1H, py-H^5, ^3J(H,H) = 7.1 Hz), 7.30 (d, 1H, py-H^3, ^3J(H,H) = 7.2 Hz), 7.1−7.6 (m, 10 H, PPh_2), 7.62 (t, 1H, py-H^4, ^3J(H,H) = 7.0 Hz), 8.45 (d, 1H, py-H^6, ^3J(H,H) = 7.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 35.2.

Quantitative deprotection of **15** (0.95 g, 3.11 mmol) was performed by stirring for 14 h at room temperature in $NHEt_2$. The volatiles were then evaporated, yielding the product **8** as a white solid. NMR data of **8**: ^1H NMR ($CDCl_3$) δ: 1.55 (d, 6H, $C(CH_3)_2$, ^3J(P,H) = 13.4 Hz), 7.0 (t, 1H, py-H^5, ^3J(H,H) = 7.1 Hz), 7.30 (d, 1H, py-H^3, ^3J(H,H) = 7.2 Hz), 7.1−7.6 (m, 10 H, PPh_2), 7.55 (t, 1H, py-H^4, ^3J(H,H) = 7.0 Hz), 8.60 (d, 1H, py-H^6, ^3J(H,H) = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 25.4 (d, $C(CH_3)_2$, ^2J(P,C) = 16.5 Hz), 40.7 (d, *C*$(CH_3)_2$, ^1J(P,C) = 18.2 Hz), 119.7 (s, py-C^5), 120.8 (s, py-C^3), 127.1 (m, PPh_2), 133.3

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(s, py-C^4), 147.3 (s, py-C^6), 165.0 (s, py-C^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 22.5. Anal. Calcd for $C_{20}H_{20}NP$: C, 78.67; H, 6.60; N, 4.59. Found: C, 78.70; H, 6.80; N, 4.75.

Synthesis of [Ni{*rac*-2-[(diphenylphosphanyl)benzyl]-pyridine}Cl_2] (9). To a suspension of [$NiCl_2$(DME)] (0.600 g, 2.83 mmol) in CH_2Cl_2 (60 mL) was added a solution of **6** (1.00 g, 2.83 mmol) in CH_2Cl_2 (40 mL) at room temperature, and the resulting solution was stirred for 2 h. The violet reaction mixture was filtered through Celite in order to separate unreacted [$NiCl_2$(DME)]. The filtrate was evaporated under reduced pressure, dissolved in CH_2Cl_2 (10 mL), and reprecipitated with hexane (30 mL). The supernatant liquid was removed with a cannula equipped with a filter cap. The solid was dissolved in toluene (15 mL) and reprecipitated by the addition of hexane. The olive green solid was filtered and dried under vacuum for 12 h. Yield: 1.07 g, 2.22 mmol, 78%. IR selected pyridine absorptions: 1601 s ($\nu_{C=C}$), 1158m ($\nu_{\beta(C-H)}$), 1027w and 998s (ν_{cycle}), 692vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{24}H_{20}\ Cl_2NNiP$: C, 59.68; H, 4.17; N, 2.90. Found: C, 61.10; H, 4.03; N, 2.75 (we have no explanation for the poor results of the carbon analysis).

Synthesis of [Ni{*rac*-2-[1′-(diphenylphosphanyl)ethyl]-pyridine}Cl_2] (10). To a suspension of [$NiCl_2$(DME)] (1.260 g, 5.96 mmol) in CH_2Cl_2 (60 mL) was added a solution of **7** (1.653 g, 5.96 mmol) in CH_2Cl_2 (40 mL) at room temperature, and the resulting solution was stirred for 2 h. The violet reaction mixture was filtered through Celite in order to separate unreacted [$NiCl_2$(DME)]. The filtrate was evaporated under reduced pressure, dissolved in CH_2Cl_2 (10 mL), and precipitated with hexane (30 mL). The supernatant liquid was removed with a cannula equipped with a filter cap. The solid was dissolved in the minimum volume of toluene (15 mL) and precipitated by the addition of hexane. The olive green solid was filtered and dried under vacuum for 12 h. Yield: 1.90 g, 4.53 mmol, 76%. IR selected pyridine absorptions: 1603s ($\nu_{C=C}$), 1160m ($\nu_{\beta(C-H)}$), 1038w and 997s (ν_{cycle}), 693vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{19}H_{18}Cl_2NNiP$: C, 54.21; H, 4.31; N, 3.33. Found: C, 55.00; H, 4.66; N, 3.30.

Synthesis of [Ni(2-{1′-(diphenylphosphanyl)-1′-methyl}-ethylpyridine)Cl_2] (11). To a suspension of [$NiCl_2$(DME)] (0.222 g, 1.05 mmol) in CH_2Cl_2 (20 mL) was added a solution of **8** (0.305 g, 1.05 mmol) in CH_2Cl_2 (10 mL) at room temperature, and the resulting solution was stirred for 2 h. The violet reaction mixture was filtered over Celite in order to separate unreacted [$NiCl_2$(DME)]. The filtrate was evaporated under reduced pressure, dissolved in CH_2Cl_2 (5 mL), and precipitated with hexane (20 mL). The supernatant liquid was removed with a cannula equipped with a filter cap. The solid was dissolved in toluene (10 mL) and precipitated by the addition of hexane. The red-violet solid was filtered and dried under vacuum for 12 h. Yield: 0.366 g, 0.842 mmol, 80%. IR (KBr) selected pyridine absorptions: 1605s ($\nu_{C=C}$), 1166m ($\nu_{\beta(C-H)}$), 1040w and 996s (ν_{cycle}), 694vs ($\nu_{R\ sens}$) cm^{-1}. Anal. Calcd for $C_{20}H_{20}Cl_2NNiP$: C, 55.23; H, 4.63; N, 3.22. Found: C, 55.00; H, 4.37; N, 3.08.

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 reaction. In all catalytic experiments with MAO and $AlEtCl_2$, 4.0×10^{-2} mmol of Ni complex were 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 following equation:

10 mL (Ni-solution) +
y mL (solvent) + z mL (cocatalyst solution) = 15 mL

Table 4. X-ray Experimental Data for [Ni(2-{1′-(diphenylphosphanyl)-1′-methyl}ethylpyridine)Cl_2]·0.5CH_2Cl_2 (11·0.5CH_2Cl_2)

formula	$C_{20}H_{20}Cl_2NNiP{\cdot}0.5CH_2Cl_2$
fw	477.41
cryst syst	tetragonal
space group	$P4_32_12$
$a = b$, Å	9.209(5)
c, Å	50.400(5)
V, Å^3	4274(3)
Z	8
color	red
cryst dimens, mm	0.15 × 0.12 × 0.10
D(calc), g cm^{-3}	1.484
F(000)	1960
μ, mm^{-1}	1.363
temp, K	173
wavelength, Å	0.71069
radiation	Mo Kα graphite monochromated
diffractometer	KappaCCD
θ limits, deg	2.25/33.13
no. of data measd	6872
no. of data with $I > 2\sigma(I)$	3980
no. of variables	240
R	0.0493
R_w	0.0951
GOF on F^2	0.98
largest peak in final diff map, e Å^{-3}	0.799

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 collected from the reactor only at the end of the catalytic experiment. At the end of each test, the reactor was cooled to 10 °C before transferring the gaseous phase 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 in 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.

Crystal Structure Determination of 11·0.5CH_2Cl_2. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The relevant data are summarized in Table 4. Data were collected using phi-scans, the structures were solved by direct methods using the SHELX 97 software,[39,40] and the refinement was done by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C-H} = 0.95$ Å, $U_{11} = 0.04$). Full data collection parameters and structural data are available as Supporting Information. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre, CCDC 227823. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of atomic coordinates, bond distances, angles, and anisotropic thermal parameters and ORTEP plot for **11**·0.5CH_2Cl_2; X-ray data in CIF format are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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