Mono- and Dinuclear Nickel Complexes with Phosphino-, Phosphinito-, and Phosphonitopyridine Ligands: Synthesis, Structures, and Catalytic Oligomerization of Ethylene

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The P,N-type ligands 2-[(diphenylphosphino)methyl]pyridine (**12**), 2-[2-(diphenylphosphino)ethyl]pyridine (**13**), 2-methyloxy(diphenylphosphino)pyridine (**14**), 2-methyloxy(dibenzyl-1,2-oxaphosphorino)pyridine (**15**), and 2-methyloxy(di-*tert*-butylphosphino)pyridine (**16**) have been prepared in good yields, and **12** and **13** have been used to synthesize Ni(II) complexes of formula $[Ni(P,N)Cl_2]$, **17** (P,N = **12**) and **18** (P,N = **13**), by reaction with $NiCl_2$ in methanol. The crystal structure of **18** has been determined by X-ray diffraction to be dinuclear with a distorted square-base pyramidal geometry around the Ni(II) centers. To examine the possible influence of the nature of the spacer link between the P and N donor atoms, we compared ligand **13**, with a CH_2CH_2 spacer, with **14** and **16**, which have a isosteric CH_2-O spacer. Reactions of the phosphinitopyridine ligands **14** and **16** and of the phosphonitopyridine **15** with $[NiX_2(DME)]$ (X = Cl or Br) afforded the complexes $[Ni(P,N)Cl_2]$ **20** (X = Cl; P,N = **14**), **21** (X = Br; P,N = **14**), **22** (X = Cl; P,N = **16**), and **23** (X = Cl; P,N = **15**), respectively. The mononuclear structure of complex **22** has been established by X-ray diffraction and showed a distorted tetrahedral geometry around the metal center. Complexes **17**, **18**, and **20**−**22** have been tested as precatalysts in the oligomerization of ethylene, with $AlEtCl_2$ or MAO as cocatalyst, in order to evaluate the influence of the stereoelectronic properties of the phosphorus substituents. With only 6 equiv of $AlEtCl_2$ as cocatalyst and 4×10^{-5} mol precatalyst, complex **18** was the most active, with turnover frequencies (TOF) up to 91 200 C_2H_4/(mol Ni·h), and **20** with 2 equiv of $AlEtCl_2$ showed the highest selectivities for ethylene dimers (up to 97%) and in 1-butene (up to 72%). When only 10^{-5} mol precatalyst was used, the TOF values went up to 207 600 for **18** and 150 100 for **20**. With only 25 equiv of MAO as cocatalyst, complex **18** was again the most active, with TOF values up to 20 600 C_2H_4/(mol Ni·h). Despite the high selectivity for C_4 olefins of **17**, **18**, **20**, and **21** (up to 93% for **20**), **22** presented the best selectivities for 1-butene (up to 73%) with MAO as cocatalyst, and its high reactivity for the reinsertion of 1-butene resulted in 2-ethyl-1-butene being the main product of the catalytic reaction (up to 91%).

Introduction

The catalytic production of linear α-olefins (LAO) has enjoyed major industrial developments since the seminal works of Ziegler and Natta on the oligomerization and polymerization of ethylene with metal catalysts activated by alkylaluminiums.[1–4] By favoring chain transfer over propagation during the catalytic cycle, late transition metals such as Ni, Pd, Co, and Fe are good candidates for the formation of oligomerization catalysts.[5–9] The discovery of the "nickel effect" by Ziegler in 1953 proved the preference of this metal for the oligomerization of ethylene,[10] and many systems based on nickel complexes with P,O,[11–18] N,N,[19–21] N,O,[22–27] P,P,[28] and P,N[8] chelating ligands have

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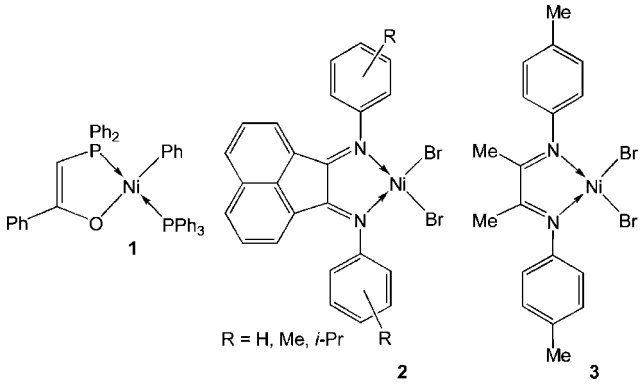
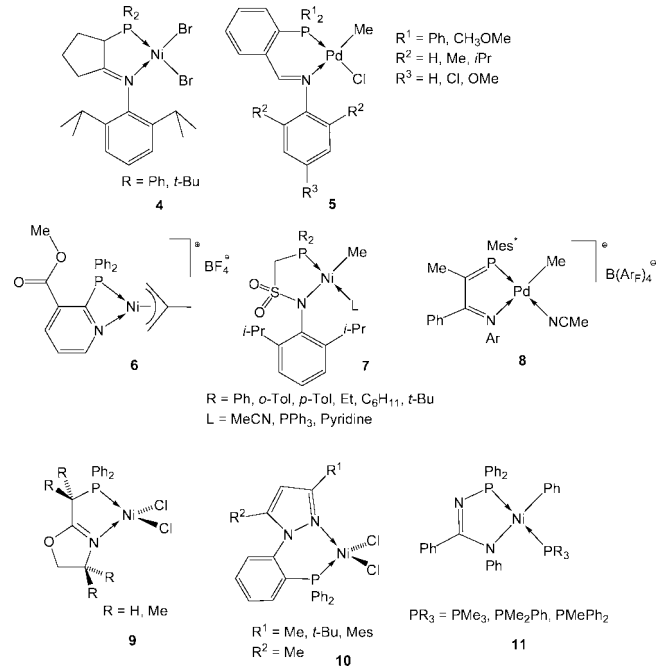
provided very interesting catalytic results. The SHOP process, which is based on neutral phenyl nickel complexes of type **1** and does not require any cocatalyst, remains a reference in oligomerization of ethylene with its remarkable selectivity for LAO and Schulz−Flory distribution.[11,12] The α-diimine Ni(II) complexes **2** and **3** also form very active and selective catalysts for LAO when activated by a cocatalyst such as methylalumoxane (MAO).[20,21]



In combination with divalent nickel or palladium, P,N-type ligands, such as phosphinoimines in **4** and **5**,[29,30] phosphinonicotine methyl esters in **6**,[31] phosphinosulfonamides in **7**,[32] phosphinidine-imines in **8**,[33] phosphinooxazolines in **9**,[34,35] and phosphinopyrazole in **10**,[36] or derived from α-iminoazatriphenylphosphoranes in **11**,[37] result in active catalysts for ethylene oligomerization or polymerization (Scheme 1).

The properties and applications of transition metal complexes with phosphinopyridine ligands have been reviewed,[38–41] and some of their Ni(II) complexes catalyze the oligomerization of ethylene in the presence of MAO[42–45] or $AlEtCl_2$[46] as cocatalyst.

Scheme 1. Complexes with P,N-Type Ligands for the Catalytic Oligomerization or Polymerization of Ethylene (references given in the text)



We have recently reported Ni(II) complexes with phosphinopyridine ligands that led to high selectivities for the dimerization of ethylene but modest selectivities for α-olefins, and some ethylene trimerization was also noted.[47–50] We were therefore interested in the synthesis of new Ni(II) catalyst precursors based on phosphinopyridine ligands with different substituents on phosphorus to modify its electronic and steric effects and examine the consequences for this catalytic reaction. Introducing *tert*-butyl substituents on phosphorus will result in ligands with a larger cone angle,[51] and their influence on the stability of the complexes and their catalytic properties has now been investigated.

Results and Discussion

Synthesis of the Ligands. The ligand 2-[(diphenylphosphino)methyl]pyridine (**12**) was prepared by deprotonation of 2-methylpyridine with *n*-BuLi, followed by reaction with excess chlorotrimethylsilane at −78 °C and reaction with 1 equiv of chlorodiphenylphosphine at −78 °C.[52] This procedure is crucial for a high-yield synthesis of the corresponding ligand because the direct reaction of the carbanion with PPh_2Cl gives rise to byproducts. The ligand 2-[2-(diphenylphosphino)ethyl]pyridine (**13**) was synthesized by reaction of 2-(pyridine)ethanol with $SOCl_2$ to give 2-chloroethylpyridine, which was then reacted

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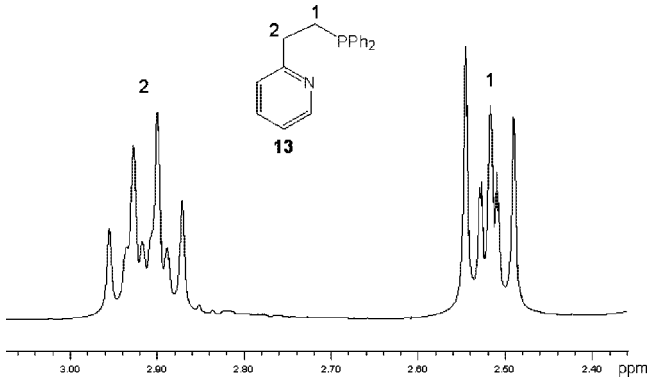
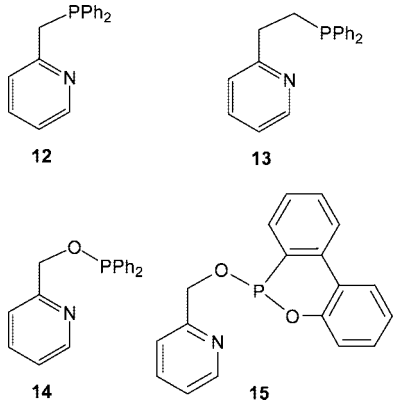
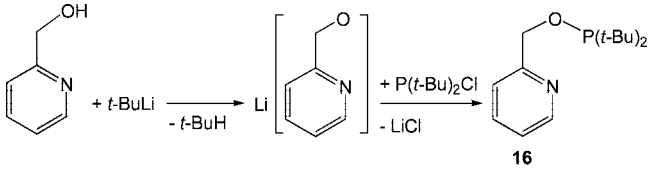


Figure 1. ^{1}H NMR spectrum (300 MHz) of **13** showing the P-CH_2 and the Py-CH_2 protons.

with $NaPPh_2$.[53,54] The ^{1}H NMR spectrum of **13** was analyzed using the MestRec software[55] by considering an AA′BB′X spin system for the P-CH_2 and Py-CH_2 protons (Figure 1). The reaction of (pyridin-2-yl)methanol with 1 equiv of PPh_2Cl or chloro(dibenzyl-1,2-oxa)phosphorine in the presence of excess triethylamine (to neutralize the HCl liberated) afforded the new ligands 2-methyloxy(diphenylphosphino)pyridine (**14**)[56] and 2-methyloxy(dibenzyl-1,2-oxaphosphorino)pyridine (**15**), respectively. Their properties are similar to those of their methyl derivatives containing a $POCMe_2$ instead of a $POCH_2$ moiety.[50]



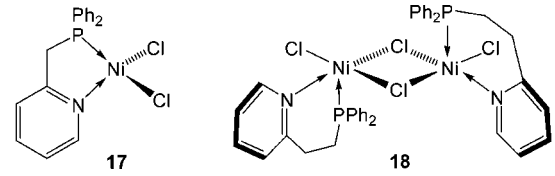
For the synthesis of 2-methyloxy(di-*tert*-butylphosphino)pyridine (**16**), 2-(pyridine)ethanol had to first be deprotonated and reacted with di-*tert*-butyl(chloro)phosphine (eq 1), because the phosphine is not electrophilic enough to react directly with a pyridine-alcohol owing to the electron donor effect of the two *tert*-butyl substituents.



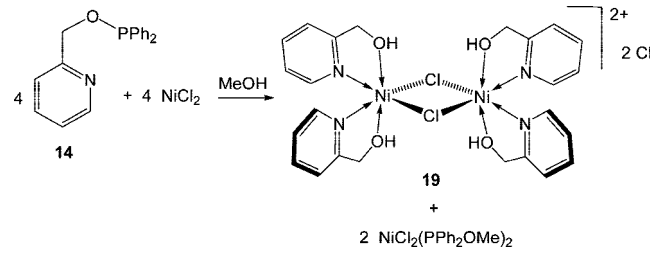
(1)

All the ligands have been characterized by ^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, COSY, HMBC, and HMQC NMR spectroscopy. We note the high $^{31}P\{^1H\}$ chemical shifts of **16** (δ 166.3 ppm) compared to that of the phosphinite **14** (δ 117.7 ppm), which results from the steric effect of the *tert*-butyl substituents.

Synthesis of the Ni(II) Complexes. To examine the possible influence of the nature of the spacer link between the P and N donor atoms, we compared ligand **13**, which contains a CH_2-CH_2 spacer, with **14** and **16**, which have a isosteric CH_2-O spacer. The Ni(II) phosphinopyridine complexes **17** and **18** were prepared by reaction of 1 equiv of the corresponding phosphine with $NiCl_2$ in methanol. The immediate color change, from green to red, indicated a fast reaction. After workup, gray and green powders of **17** and **18** were obtained in 83% and 80% yields, respectively. Slow diffusion of pentane into a CH_2Cl_2 solution of **18** afforded single crystals suitable for X-ray diffraction, which established its dinuclear structure (see below). A red-violet complex has been reported from the reaction of **13** with $NiCl_2$ in refluxing *n*-butanol.[57]



The complexation of $NiCl_2$ by ligand **14** in methanol led to cleavage of the phosphinite P−O bond and substituent exchange at the phosphorus to form $[Ni(\mu\text{-}Cl)_2(2\text{-pyridine ethanol})_2]Cl_2$ (**19**) and $[NiCl_2(PPh_2OMe)_2]$ (eq 2). The very low solubility of **19** in CH_2Cl_2 facilitated separation of the Ni(II) complexes. This reaction is consistent with the sensitivity of phosphonites to the presence of alcohols,[58] and the breaking of the P−O bond does not necessarily require the presence of a metal cation. Complex **19** has been obtained directly from (pyridin-2-yl)methanol and $NiCl_2$ and was shown by X-ray diffraction to have a dinuclear structure.[59]



(2)

The use of methanol for metal complexation with phosphinite **14** or **16** and phosphonite **15** should therefore be avoided, but other solvents (MeCN, THF, or CH_2Cl_2) led to poor yields owing to the very low solubility of $NiCl_2$. However, reaction of $[NiCl_2(DME)]$ or $[NiBr_2(DME)]$ in CH_2Cl_2 with **14**−**16** led to the high-yield formation of the Ni(II) complexes **20**–**23**, respectively (up to 92%). Their colors in the solid state are respectively gray, green, red, or maroon, but all complexes afforded red CH_2Cl_2 solutions. Red single crystals of **22** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of the complex in chlorobenzene, and **22** presented a mononuclear structure (see below).

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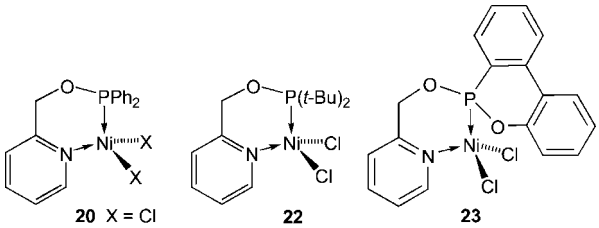
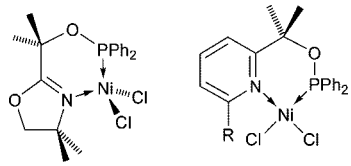


20 X = Cl
21 X = Br
22 **23**

Although some nickel complexes with P,N- or P,N,P-type ligands are diamagnetic in solution,[60] complexes **17**, **18**, **20**, **22**, and **23** proved to be paramagnetic in $CDCl_3$, CD_2Cl_2, CD_3CN, CD_3CD_2OD, or CD_3OD solution. Their magnetic moments per Ni atom, determined by the Evans method in CD_2Cl_2,[61–64] were 2.2 (**17**), 2.7 (**18**), 2.8 (**20**), 3.0 (**22**), and 1.9 (**23**) μ_B, respectively.[65,66] These values are similar to those recently reported for other Ni(II) complexes with P,N-type ligands.[34,47–50] Relatively low magnetic moments, such as those for **17** and **23**, may also be due to equilibria with their square-planar, diamagnetic isomer.[67]

These complexes have also been characterized by IR, elemental analysis, and mass spectrometry, but no NMR spectra could be recorded. High-resolution mass spectrometry (HRMS) with the electrospray ionization method afforded spectra where the main peak corresponds to $[Ni(P,N)Cl]^+$. The structures of **18** and **22** are shown in Figures 2 and 3, and selected bond distances and angles are given in Tables 1 and 2.



26 **27** R = H
28 R = Me

Complex **18** has a dinuclear structure with pentacoordinated metal centers and six-membered-ring chelates. The *cisoid* coordination of the two pyridine functions with respect to the Ni−Ni axis makes the structure non-centrosymmetric, but it possesses a C_2 symmetry axis passing through Cl2 and Cl3. The coordination geometry around the metals is distorted square-pyramidal, with the square base being formed by N and the three chlorides (Scheme 2). The Ni atom is out of this plane by 0.3777(1) Å.

It is interesting to compare the structure of **18** with those of the distorted square-pyramidal dinuclear Ni(II) complexes **24** and **25**, which contain five- and seven-membered-ring P,N chelates.[42,50]

In contrast to **18**, complexes **24** and **25** have centrosymmetric structures and their square bases contained the atoms P, N, and the two bridging chlorides Cl(1) and Cl(1a) (Scheme 2). The larger N−Ni−P coordination angle (96.18(9)°, Table 1) of **18** compared to **24** (84.48(9)°) or **25** (85.37(5)°) leads to the apical position being occupied by the phosphorus donor atom instead of a chloride ligand. The Ni−P and Ni−N distances in **18**, of

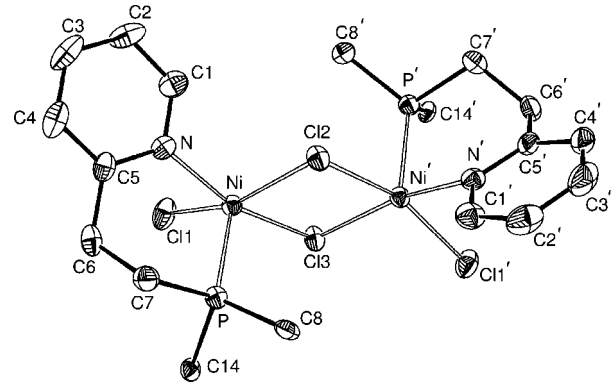


Figure 2. ORTEP view of the molecular structure of **18** (ellipsoids enclose of 50% electronic density; only the phenyl *ipso* carbons are shown and the H atoms are omitted for clarity).

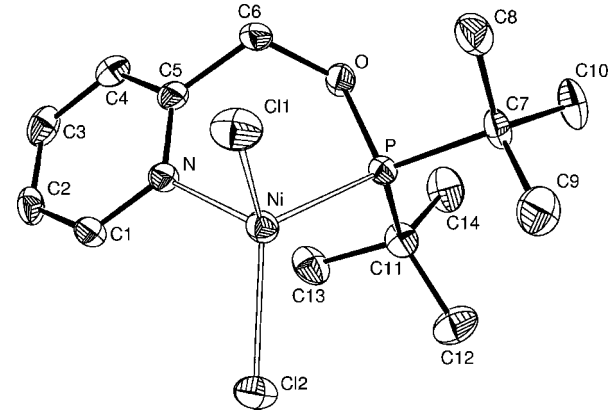
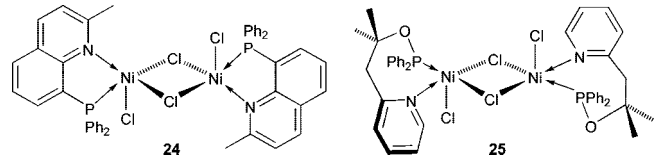


Figure 3. ORTEP view of the molecular structure of **22** (ellipsoids enclose 50% electronic density; H atoms are omitted for clarity).



2.305(1) and 2.061(3) Å, respectively, are similar to those in the dinuclear complexes **24** and **25** but are longer than in related mononuclear Ni(II) complexes.[50]

Complex **22** has a mononuclear structure with a distorted tetrahedral geometry similar to that of complex **26**, in contrast to the square-planar geometry of complexes **27** and **28** (Figure 3).[50] The Ni−P and Ni−N distances of **22**, 2.304(1) and 2.006(3) Å (Table 2), are significantly longer than in complexes **26**–**28**. The large Cl−Ni−Cl angle (123.47(5)°) and the small N−Ni−P angle (92.1(1)°, Table 2) result in complex **22** adopting a distorted tetrahedral geometry instead of a square-planar geometry. The steric properties of the *tert*-butyl substituents on phosphorus probably explain the tetrahedral coordination in **22**. Tetrahedral Ni(II) complexes coordinated by phosphinopyridine[43,44] or phosphinoimine ligands[30] have been used previously in ethylene oligomerization, and we shall now examine the catalytic properties of complexes **17**, **18**, and **20**–**22** in this reaction.

This structural study emphasizes the influence of sometimes seemingly minor variations in the stereoelectronic properties of the ligands on the structure of their corresponding Ni(II) complexes. With related phosphino-oxazoline and -thiazoline ligands, it was recently found that tetranuclear Ni(II) complexes

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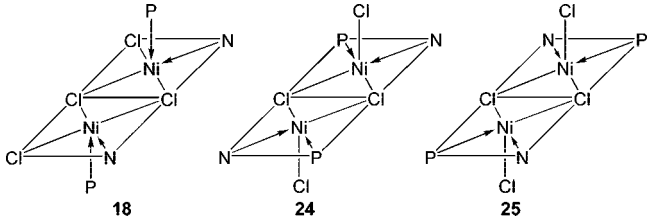
Table 1. Selected Bond Lengths (Å) and Angles (deg) in 18

Ni−P	2.305(1)	C6−C7	1.543(5)
Ni−N	2.061(3)	C5−C6	1.500(5)
Ni−Cl1	2.291(1)	C5−N	1.357(4)
Ni−Cl2	2.4227(9)	P−C8	1.821(4)
Ni−Cl3	2.3508(9)	P−C14	1.818(4)
P−C7	1.822(4)		
Cl1−Ni−Nl2	158.69(4)	Cl3−Ni−N	162.92(9)
Cl1−Ni−Cl3	92.09(4)	Cl3−Ni−P	100.18(3)
Cl1−Ni−N	87.97(8)	N−Ni−P	96.18(9)
Cl1−Ni−P	106.28(4)	Ni−P−C7	105.5(1)
Cl2−Ni−Cl3	84.53(3)	C7−C6−C5	113.4(3)
Cl2−Ni−N	89.23(8)	C6−C5−N	118.5(3)
Cl2−Ni−P	95.03(3)	C5−N−Ni	126.8(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complex 22

Ni−P	2.304(1)	P−0	1.626(3)
Ni−N	2.005(3)	O−C6	1.454(6)
Ni−Cl1	2.217(2)	C5−C6	1.505(6)
Ni−Cl2	2.227(1)	C5−N	1.350(5)
P−C7	1.865(5)	P−C11	1.860(5)
N−Ni−P	92.2(1)	N−Ni−Cl1	102.9(1)
Ni−P−O	105.9(1)	N−Ni−Cl2	108.3(1)
P−O−Cl	118.8(2)	Cl1−Ni−Cl2	123.47(5)
O−C1−C2	112.1(3)	Cl1−Ni−P	112.74(5)
C1−C2−N	116.8(4)	C12−Ni−P	111.77(5)
C2−N−Ni	122.5(3)		

Scheme 2. Representation of the Square-Pyramidal Coordination Geometries around the Metals in 18, 24, and 25



are formed and a dramatic effect of pressure was evidenced, which results in its breaking into four mononuclear complexes.[67]

Catalytic Oligomerization of Ethylene. Complexes **17**, **18**, and **20–22** have been tested as precatalysts in the oligomerization of ethylene with variable amounts of $AlEtCl_2$ or MAO as cocatalyst. In previous studies, $[NiCl_2(PCy_3)_2]$, which is a typical α-olefin dimerization catalyst,[68] was used to compare the catalytic results, but considering the sensitivity of this complex, we choose another reference compound, $[NiCl_2\{P(n\text{-}Bu_3)\}_2]$, which is diamagnetic and thus readily amenable to purity check by NMR spectroscopy and is also highly active in oligomerization with $AlEtCl_2$.[69] The analysis of the different C_6 oligomers was performed in order to differentiate between a chain growth mechanism and the reinsertion of butenes. The formation of 2-hexene, 3-hexene, and 2-ethyl-1-butene by reinsertion of 1-butene and the formation of 3-methyl-2-pentene and 3-methyl-1-pentene by reinsertion of 2-butene depending on the insertion mode (2,1- or 1,2-insertion) have been discussed previously.[27] Isomerization of 1-hexene leads to the formation of 2-hexene and 3-hexene.

Use of $AlEtCl_2$ as Cocatalyst. Complexes **17**, **18**, and **20–22** have been tested in the presence of 2, 4, or 6 equiv of $AlEtCl_2$ in toluene (Al/Ni ratios of 2, 4, or 6, respectively), and the catalytic results are presented in Table 3 and shown in Figures 4−6.

The highest activities when 4×10^{-5} mol precatalyst was used were obtained for complex **18** with turnover frequencies (TOF) of 78 200 and 91 200 mol C_2H_4/(mol Ni·h), with either 4 or 6 equiv of $AlEtCl_2$, respectively. Complexes **17**, **20**, **21**, and **22** had similar activities (Figure 4), which increased with the amount of cocatalyst, between 17 000 and 20 400 mol C_2H_4/(mol Ni·h) with 2 equiv of $AlEtCl_2$, 43 500 and 46700 mol C_2H_4/(mol Ni·h) with 4 equiv, and 56600 and 63 600 mol C_2H_4/(mol Ni·h) with 6 equiv. However, **20** showed very low activity with 2 equiv of $AlEtCl_2$ (1100 mol C_2H_4/(mol Ni·h)).

The selectivity for 1-butene was modest and less than 17% for all the complexes except for **20** with 2 equiv of $AlEtCl_2$ (72%, Figure 6). The high concentration of 2-butene indicates that isomerization of 1-butene is largely favored. The exothermicity of the catalytic reaction (temperatures up to 115 °C) with very active systems is most likely responsible for the lower selectivity in 1-butene.[70] The selectivities for C_4 olefins were between 97% and 50% for complexes **17**, **18**, and **20–22** (Figure 5), and this showed that dimerization is much favored over chain growth. The second largest is constituted by the hexenes (Table 3), with the reinsertion of 1-butene and 2-butene being very significant on the basis of the branched olefins formed (Table 4).

Increasing the amount of $AlEtCl_2$ had a significant influence on the catalytic results by forming a more active but less selective system. Higher activities were associated with an increasing isomerization of 1-butene to 2-butene. With **18**, for example, the fraction of 1-butene decreased from 13% to 2%. The higher concentration of 2-butene favored its reinsertion to give C_6 oligomers (Table 4).

To study the influence of the concentration of the complexes on the oligomerization of ethylene, precatalysts **18** and **20** have been tested with only 1×10^{-5} mol of complex in 15 mL of solution instead of 4×10^{-5} mol for the standard procedure. The catalytic results with 6 equiv of $AlEtCl_2$ showed that the complexes are more active and selective for C_4 oligomers under these conditions (Table 3). Under these conditions, the TOF values went up to 207 600 for **18** and 150 100 for **20**.

To determine the robustness of the P−O bond of complex **20** and the lifetime of the catalyst, we increased the reaction time to 120 min and compared the catalytic results with those for complex **18** (Table 3). The high and constant activities during the catalytic run (the ethylene consumption was constant, no plateau of activity was observed, and the final activities were 104 100 and 83 100 mol C_2H_4/(mol Ni·h) for **18** and **20**, respectively) suggested a reasonable lifetime for the catalysts. The lower TOF values calculated for these experiments compared with those where the reaction time was 35 min are due to the nonlinearity of the ethylene consumption as a function of time.

Use of MAO as Cocatalyst. Complexes **17**, **18**, and **20–22** have also been evaluated in the presence of 12.5, 25, 50, 100, and 200 equiv of MAO in toluene as cocatalyst, and the catalytic results are given in Tables 5 and 6 and shown in Figures 7−10.

In contrast to analogous Ni(II) complexes with pyridine−phosphine and pyridine−phosphinite ligands tested under similar conditions,[8] the precatalysts **17**, **18**, and **20–22** presented high activities with very small amounts of MAO (Figures 7−9). In particular, **18** showed activities up to

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Table 3. Comparative Catalytic Data for Complexes 17, 18, and 20−22 in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	quantity of complex (10^{-5} mol)	$AlEtCl_2$ (equiv)	time (min)	selectivity[b] (%) C4	C6	C8	productivity (g C_2H_4/(g Ni·h))	TOF (mol C_2H_4/(mol Ni·h))	1-butene[c] (%)	k_α[d]
17	4	2	35	87	12	<1	9700	20 400	17	<0.10
17	4	4	35	71	28	<1	22 300	46 700	14	0.26
17	4	6	35	55	43	2	30 300	63 600	7	0.53
18	4	2	35	76	21	3	8400	17 600	13	0.19
18	4	4	35	52	44	4	37 300	78 200	3	0.57
18	4	6	35	50	43	7	43 500	91 200	2	0.59
18	1	6	35	69	30	1	99 000	207 600	1	0.31
18	1	6	120	70	28	2	49 700	104 100	9	0.27
20	4	2	35	97	2	<1	500	1100	72	<0.10
20	4	4	35	75	24	1	20 700	43 500	5	0.21
20	4	6	35	63	35	2	27 900	58 500	3	0.38
20	1	6	35	71	27	2	71 600	150 100	11	0.24
20	1	6	120	72	27	1	39 700	83 100	14	0.25
21	4	4	35	74	24	2	21 100	44 100	6	0.21
21	4	6	35	59	38	3	24 800	56 600	4	0.43
22	4	2	35	85	14	1	8200	17 000	16	0.11
22	4	4	35	68	28	4	21 500	45 100	6	0.27
22	4	6	35	66	31	3	27 200	57 000	6	0.31
ref[e]	4	2	35	83	15	2	4000	8400	13	0.12
ref[e]	4	4	35	60	35	5	35 300	74 100	3	0.39
ref[e]	4	6	35	61	34	5	35 000	73 600	3	0.37

[a] Conditions: T = 25–30 °C, 10 bar C_2H_4, solvent 14 mL of chlorobenzene and 1 mL of cocatalyst solution in toluene, 13 mL of chlorobenzene and 2 mL of cocatalyst solution, and 12 mL of chlorobenzene and 3 mL of cocatalyst solution for 2, 4, or 6 equiv of $AlEtCl_2$, respectively. [b] No C_{10} oligomers were detected. [c] Within the C_4 fraction. [d] k_α = hexenes [mol]/butenes [mol]. [e] reference: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

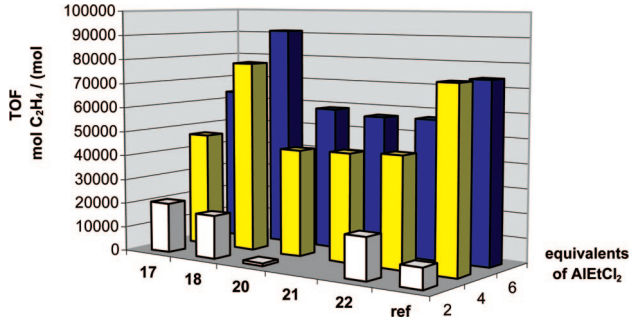

Figure 4. Catalytic activities of the complexes **17**, **18**, and **20–22** in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst, ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

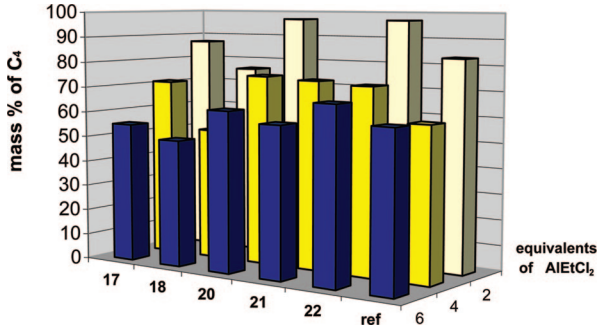

Figure 5. Selectivity of the complexes **17**, **18**, and **20–22** for C_4 compounds using $AlEtCl_2$ as cocatalyst (1-butene and 2-butene), ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

18 400 and 20 600 mol C_2H_4/(mol Ni·h) with only 12.5 and 25 equiv of MAO, respectively. The use of fresh MAO under strict conditions could explain these high activities of **17**, **18**, and **20–22**, respectively, since MAO is known to be very sensitive to air and moisture and can rapidly evolve to a poor cocatalyst.[71] Increasing the amount of cocatalyst did not have a major impact on the catalytic results. Precatalysts **17**, **18**,

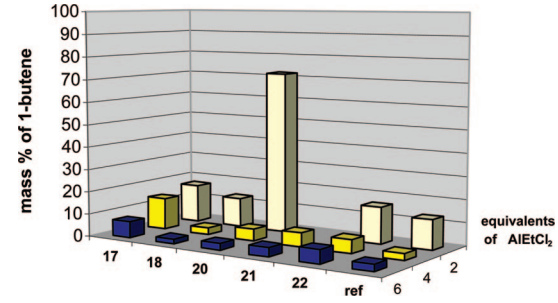

Figure 6. Selectivity of the complexes **17**, **18**, and **20–22** for 1-butene using $AlEtCl_2$ as cocatalyst, ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

and **20–22** had similar activities, between 14 100 and 19 600 mol C_2H_4/(mol Ni·h). The precatalyst **17**, with a smaller bite angle ligand than **18–22**, presented slightly lower activities but better selectivities for 1-butene.

In contrast to complex **20**, which has phenyl substituents on the phosphorus atom, complex **22** has *tert*-butyl groups and their steric and electronic donor effects significantly affected the catalytic results. Under standard conditions, precatalyst **20** led to a low selectivity for 1-butene (less than 11% of the C_4 fraction), which is characteristic of an isomerizing catalyst, and to a high concentration of C_6 oligomers formed by reinsertion of 2-butene (up to 68%, Table 6). In contrast, **22** did not favor the isomerization of 1-butene and had a selectivity up to 42% for 1-butene within the C_4 fraction. However **22** led overall to a low selectivity in C_4 products (less than 23%) owing to the reinsertion of 1-butene to form 2-ethyl-1-butene (up to 77%, Table 6) and presented a very different mass distribution of oligomers compared to **20** (Figure 10). Heinicke et al. have observed similar effects with cationic methallylnickel phosphinophenol complexes where cyclohexyl substituents on the phosphorus donor function favored the formation of 2-ethyl-1-butene, in contrast to the phenyl substituents, which favored the formation of *cis*-3-methyl-2-pentene.[72]

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Table 4. Catalytic Data and Distribution of the C_6 Oligomers for Complexes 17, 18, and 20−22 in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

		selectivity (mass %)			
	$AlEtCl_2$ (equiv)	1-hexene	linear C_6[b]	C_6[c] from 1-butene	C_6[d] from 2-butene
17	2	3	37	17	43
17	4	1	37	20	42
17	6	1	30	14	55
18	2	1	27	15	57
18	4	<1	19	13	67
18	6	<1	19	13	67
18[e]	6	<1	18	14	67
18[e, f]	6	1	22	15	62
20	2	67	15	15	3
20	4	1	29	14	56
20	6	<1	25	11	63
20[e]	6	1	40	6	53
20[e,f]	6	3	45	6	46
21	4	2	22	13	63
21	6	3	26	9	62
22	2	18	49	11	22
22	4	1	32	7	60
22	6	1	31	7	61

[a] Conditions: T = 25–30 °C, 10 bar C_2H_4, 35 min, 4×10^{-5} mol of complex, solvent 14 mL of chlorobenzene and 1 mL of cocatalyst solution in toluene, 13 mL of chlorobenzene and 2 mL of cocatalyst solution, and 12 mL of chlorobenzene and 3 mL of cocatalyst solution for 2, 4, or 6 equiv of $AlEtCl_2$, respectively. [b] Sum of 2-*cis*-hexene, 2-*trans*-hexene, 3-*cis*-hexene, and 3-*trans*-hexene. [c] Corresponding to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene, and 3-methyl-2-*trans*-pentene. [e] 1×10^{-5} mol of complex. [f] Reaction time: 120 min.

When the quantity of precatalyst **20** and **22** was decreased to 10^{-5} mol, very high activities were still observed. Under these conditions, **20** showed a slightly better selectivity for C_4 products and **22** a slightly higher selectivity for 1-butene.

Increasing the pressure to 30 bar resulted in increased catalytic activities with **20** and **22**, from 30 100 to 36 800 mol C_2H_4/(mol Ni·h) with **20** and from 24 200 to 45 500 mol C_2H_4/(mol Ni·h) with **22**. It has been shown with related systems that TOF can be independent or not of ethylene pressure.[20,70] In the former case, the alkyl olefin species is the catalyst resting state.[73] According to the literature,[20] a higher ethylene concentration favors the formation of α-olefins, and the selectivities for 1-butene with **20** (34%) and **22** (73%) were indeed higher. The selectivity for C_4 products with **20** increased to 93% (Table 5), but the mass distribution of the oligomers produced by **22** did not change. The high concentration of 1-butene resulted in a marked increase of the concentration in 2-ethyl-1-butene (up to 91%). These rather surprising results with **22** suggest that the *tert*-butyl substituents on the P donor atom favor the formation of 1-butene and that its isomerization to 2-butene is disfavored with respect to formation of the C_6 product 2-ethyl-1-butene. One could envisage that the latter originates from unselective insertion of 1-butene into the Ni−ethyl bond of a primarily formed intermediate[72] (Scheme 3, route A) or by β-elimination of a metallacyclic intermediate resulting from the coupling of 1-butene with ethylene (Scheme 3, route B). Although this remains speculative in the absence of, for example, H/D labeling experiments, Ni(II) metallacyclic compounds have been previously considered in olefin chemistry.[74]

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Conclusion

New P,N ligands with a pyridine function have been synthesized in good yields and characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. These ligands present various bite angles and phosphorus functions (phosphine, phosphinite, or phosphonite functions) with different substituents on the phosphorus atom (phenyl or *tert*-butyl groups). The Ni(II) complexes **17**, **18**, and **20–22**, prepared in 70–92% yields from ligands **12–16**, respectively, were characterized by IR, elemental analysis, and high-resolution mass spectroscopy. Whereas complex **18** was shown by X-ray diffraction to have a dinuclear structure with a distorted square-base pyramidal geometry, **22**, in which a CH_2 group of the spacer between the pyridine and the phosphorus has been replaced with an oxygen and the phenyls on phosphorus by *t*-Bu substituents, has a mononuclear structure with a distorted tetrahedral geometry. One should of course keep in mind that the nuclearity of a complex may be different in the solid state and in solution. Related Ni(II) complexes with phosphino-oxazoline and -thiazoline ligands have been recently found to form unprecedented tetranuclear structures, which illustrates the considerable diversity of this chemistry. A dramatic effect of pressure on the solid was evidenced that resulted in breaking of the complex into four mononuclear entities.[67]

The precatalysts **17**, **18**, and **20–22** have been evaluated in the catalytic oligomerization of ethylene with $AlEtCl_2$ or MAO as cocatalyst. All the complexes presented high activities with $AlEtCl_2$ as cocatalyst, and the most active was **18** (91 200 mol C_2H_4/(mol Ni·h)) with 6 equiv of $AlEtCl_2$. **20** with 2 equiv of $AlEtCl_2$ showed the best selectivities in butenes (97%) and in 1-butene (72%). The high activities of **18** and **20** when the reaction time was increased to 120 min suggested a good stability of the catalysts. Precatalysts **17**, **18**, and **20–22** favored the dimerization and trimerization of ethylene, but the high proportions of branched oligomers suggested a significant contribution of 1-butene and 2-butene reinsertion. The generally modest selectivity for 1-butene is consistent with the isomerizing character of **17**, **18**, and **20–22**.

The precatalysts **17**, **18**, and **20–22** presented high activities already with small amounts of MAO as cocatalyst. Complex **18** was the most active under 10 bar of ethylene with 25 equiv (20 600 C_2H_4/(mol Ni·h)) and **17** the most selective in C_4 oligomers (89%) and in 1-butene (35%) in the presence of 50 equiv of MAO. In contrast to **17**, **18**, **20**, and **21**, complex **22**, with *tert*-butyl substituents on phosphorus, largely favored 1-butene reinsertion over isomerization and afforded 2-ethyl-1-butene as the main product. Increasing the pressure to 30 bar made the precatalysts **20** and **22** more active and increased their selectivity for C_4 products and for 1-butene.

Experimental Section

General Considerations. All solvents were dried and freshly distilled under nitrogen prior to use using common techniques. All manipulations were carried out using Schlenk techniques. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13, 121.5, and 76 MHz, respectively, on a Bruker AC300 instrument. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". IR spectra in the range 4000–400 cm^{-1} were recorded on a Bruker IFS28FT. Mass spectra were recorded with a Bruker Daltonics microTOF (ESI; positive mode; capillary voltage: 4.8 kV; nebulizer pressure: 0.2 bar; desolvation temperature: 180 °C; desolvation gas flow rate: 4.5 L/min). Magnetic moments were determined by the Evans method in CD_2Cl_2 using a solution

Table 5. Comparative Catalytic Data for Complexes 17, 18, and 20−22 in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

	amount of complex (10^{-5} mol)	amt of MAO (equiv)	selectivity (%) C4	C6	C8	>C8	productivity (g C_2H_4/(g Ni·h))	TOF (mol C_2H_4/(mol Ni·h))	1-butene[b] (%)	k_α[c]
17	4	50	89	10	1	0	1300	2800	35	<0.10
17	4	100	61	32	6	<1	5700	12 000	19	0.36
17	4	200	64	29	6	0	6800	14 300	19	0.31
17	4	400	72	23	5	0	5700	12 000	25	0.21
18	4	12.5	70	28	2	0	8800	18 400	10	0.27
18	4	25	69	30	1	0	9800	20 600	8	0.29
18	4	50	72	23	4	<1	8300	17 300	11	0.21
18	4	100	65	28	6	<1	8400	17 600	14	0.29
18	4	200	64	28	7	<1	8200	17 300	16	0.30
20	4	25	79	17	4	0	8400	17 00	11	0.14
20	4	50	72	22	5	<1	7000	14 800	10	0.21
20	4	100	75	20	5	0	6700	14 100	11	0.18
20	4	200	72	21	6	1	9400	19 600	9	0.19
20	1	100	84	13	2	<1	14 300	30 100	13	0.10
20[e]	1	100	93	6	1	0	17 500	36 800	34	<0.10
21	4	200	65	30	4	1	9000	18 900	11	0.49
22	4	25	17	52	20	11	7000	14 800	38	2.00
22	4	50	20	49	22	9	7900	16 600	42	1.60
22	4	100	23	52	20	5	6500	13 600	42	1.50
22	1	100	26	47	17	10	11 500	24 200	56	1.18
22[e]	1	100	27	50	15	8	21 700	45 500	73	1.22
ref[d]	4	50	43	46	8	3	18 600	40 000	3	0.72
ref	4	100	25	54	14	7	19 200	41 300	3	1.47
ref	4	200	26	52	16	6	17 600	36 900	3	1.31
ref	4	400	41	45	10	4	18 900	39 600	4	0.72

[a] Conditions: T = 25–30 °C, 10 bar C_2H_4, solvent 10 mL of chlorobenzene and 0.5, 1, 2, 4, or 8 mL of cocatalyst solution in toluene for 12.5, 25, 50, 100, or 200 equiv of MAO, respectively. [b] Within the C_4 fraction. [c] k_α = hexenes [mol]/butenes [mol]. [d] Reference: [$NiCl_2${P(*n*-Bu)$_3$}$_2$]. [e] Pressure: 30 bar.

Table 6. Catalytic Data and Distribution of the C_6 Oligomers for Complexes 17, 18, and 20−22 in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

	MAO (equiv)	selectivity (mass %) 1-hexene	linear C_6[b]	C_6[c] from 1-butene	C_6[d] from 2-butene
17	50	14	37	17	43
17	100	3	43	10	44
17	200	4	46	10	40
17	400	5	47	11	37
18	12.5	<1	38	15	47
18	25	<1	46	14	39
18	50	2	40	10	38
18	100	3	42	9	36
18	200	3	45	10	42
20	25	1	17	15	67
20	50	1	29	14	56
20	100	1	20	11	68
20	200	2	29	10	60
20[e]	100	2	25	12	61
20[e,f]	100	8	27	12	53
21	200	1	14	10	76
22	25	2	5	77	16
22	50	1	3	75	21
22	100	1	3	75	21
22[e]	100	3	5	83	9
22[e,f]	100	5	2	91	2

[a] Conditions: T = 25–30 °C, 10 bar C_2H_4, 35 min, 4 × 10^{-5} mol of complex, solvent 10 mL of chlorobenzene and 0.5, 1, 2, 4, and 8 mL of cocatalyst solution in toluene for 12.5, 25, 50, 100, or 200 equiv of MAO, respectively. [b] Sum of 2-*cis*-hexene, 2-*trans*-hexene, 3-*cis*-hexene, and 3-*trans*-hexene. [c] Corresponding to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene, and 3-methyl-2-*trans*-pentene. [e] 1 × 10^{-5} mol of complex. [f] Pressure: 30 bar.

of CH_3NO_2 in CD_2Cl_2 (20:80, v/v) as reference.[61–64] Corrections for diamagnetic susceptibility were done for the solvent but not for the ligands. The complexes $NiCl_2 \cdot 6H_2O$ and $NiBr_2 \cdot 6H_2O$ were dried by heating at 160 °C overnight under vacuum to give anhydrous $NiCl_2$ and $NiBr_2$. The commercial compounds 2-picoline and (pyridin-2-yl)methanol were distilled at 130 and 115

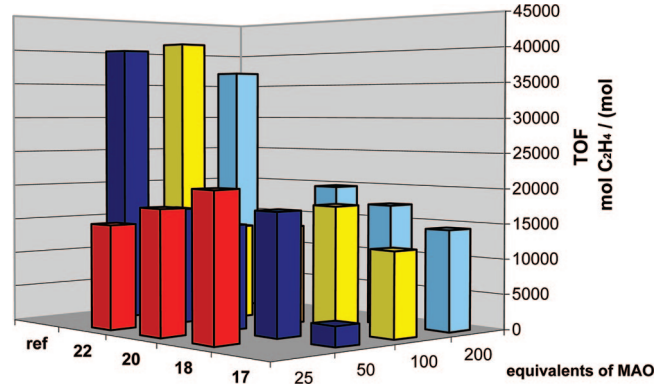

Figure 7. Catalytic activities with **17**, **18**, **20**, and **22** in the oligomerization of ethylene using MAO as cocatalyst, ref: [$NiCl_2${P(*n*-Bu)$_3$}$_2$].

°C, respectively, and degassed with nitrogen before use. A solution of $NaPPh_2$ was prepared according to the literature,[75] by addition of PPh_2Cl (7.40 g, 6 mL, 33.4 mmol) to a suspension of Na (4.00 g, 174.0 mmol) in THF (100 mL). After the mixture was stirred at reflux for 4 h, the solution became red and a gray precipitate of NaCl appeared. The salt and unreacted Na were eliminated by filtration through a canula, and the compound was kept in THF. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness). Details of the synthesis and analytical data for known compounds are given below because of slight modifications or new data introduced.

2-[(Trimethylsilyl)methyl]pyridine...[76] A solution of *n*-BuLi (96.0 mmol, 1.6 M in hexane) was added dropwise over 15 min to a solution of 2-picoline (8.94 g, 96.0 mmol) in 100 mL of THF at

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(76) van den Ancker, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* **2000**, *19*, 4437–4444.

−78 °C. After complete deprotonation, the red anion precipitated, and after further stirring for 1 h at −78 °C, degassed chlorotrimethylsilane (TMSCl, 14.00 g, 112.0 mmol) was added dropwise to the solution. The brown mixture was allowed to reach room temperature overnight, and the solvents and unreacted TMSCl were evaporated under reduced pressure. The residue was distilled (120 °C, 12 mbar) to afford pure, liquid 2-[(trimethylsilyl)methyl]pyridine. Yield: 6.61 g, 42%. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9H, $Si(CH_3)$], 2.32 (s, 2H, $SiCH_2$), 6.93 (m, 2H, Py), 7.45 (m, 1H, Py), 8.39 (d, 1H, $^3J_{H\text{-}H}$ = 4.2 Hz, HCN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −1.7 (s, $SiCH_3$), 30.25 (s, $SiCH_2$), 119.04 (s, Py), 122.06 (s, Py), 135.72 (s, Py), 148.94 (s, Py), 161.28 (s, HCN).

2-[(Diphenylphosphino)methyl]pyridine, 12..[52] To a solution of 2-[(trimethylsilyl)methyl]pyridine (4.21 g, 25.5 mmol) in 50 mL of THF was added 4.70 mL of PPh_2Cl (5.62 g, 25.5 mmol) at −78 °C, and the mixture was stirred overnight at room temperature. After filtration and solvent removal under reduced pressure, **12** was isolated as a colorless oil. Yield: 5.60 g, 79%. Spectroscopic data are consistent with the literature values.

2-(2-Chloroethyl)pyridine.[53,54] Pure $SOCl_2$ (4.10 g, 2.5 mL, 34.2 mmol) was added to a solution of 2-pyridine-ethanol (2.50 g, 20.3 mmol) in THF and stirred at reflux for 2 h. After reaction, the THF was removed under reduced pressure and 2-(2-chloroethyl)pyridine was extracted with 50 mL of CH_2Cl_2 and washed with water saturated with $NaHCO_3$ (3 × 20 mL). After elimination of CH_2Cl_2 under reduced pressure, 2-(2-chloroethyl)pyridine was isolated as a dark oil. Yield: 2.40 g, 84%. ^{1}H NMR ($CDCl_3$): δ 3.24 (t, 2H, $^3J_{HH}$ = 6.8 Hz, $ClCH_2$), 3.92 (t, 2H, $^3J_{HH}$ = 6.8 Hz, Py-CH_2), 6.97 (d, 1H, $^3J_{HH}$ = 7.8 Hz, Py), 7.22 (m, 2H, Py), 7.65 (t, 1H, $^3J_{HH}$ = 5.8 Hz, Py), 8.55 (d, 1H, $^3J_{HH}$ = 5.4 Hz, NCH).

2-[2-(Diphenylphosphino)ethyl]pyridine, 13.[53,54] A solution of 2-(2-chloroethyl)pyridine (2.40 g, 17.0 mmol) in 30 mL of THF was added to a solution of $NaPPh_2$ in THF (100 mL, 33.4 mmol) and stirred overnight. After reaction, NaCl was eliminated by filtration and THF was removed under reduced pressure. Compound **13** was purified by column chromatography (length of the stationary phase 50 cm, column diameter 2.5 cm) over silica gel using a mixture of pentane/ethylacetate (3:1 and 5% diethylamine) and was isolated as a white powder. Yield: 2.17 g, 45%. ^{1}H NMR ($CDCl_3$): δ AA′BB′X spin system (A = A′ = B = B′ = H, X = P) 2.51 (m, 2H, $^2J_{AA'}$ = 13.5 Hz, $^2J_{AB}$ = 5.2 Hz, $^2J_{AB'}$ = 11 Hz, $^2J_{A'B}$ = 11 Hz, $^2J_{AB'}$ = 5.2 Hz, $^2J_{AP}$ = 0.7 Hz, $^2J_{A'P}$ = 0.7 Hz, PCH_2), 2.90 (m, 2H, $^2J_{BB'}$ = 13.5 Hz, $^2J_{AB}$ = 5.2 Hz, $^2J_{AB'}$ = 11 Hz, $^2J_{A'B}$ = 11 Hz, $^2J_{AB'}$ = 5.2 Hz, $^2J_{BP}$ = 8.5 Hz, $^2J_{A'P}$ = 8.5 Hz, CH_2Py), 7.10 (d, 2H, $^3J_{HH}$ = 7.0 Hz, Py) 7.26 (m, 6H, Ph), 7.33 (m, 4H, Ph), 7.45 (dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.0 Hz, Py), 8.52 (d, 1H, $^3J_{HH}$ = 4.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.0 (d, $^1J_{PC}$ = 12.5 Hz, PCH_2), 28.0 (d, $^2J_{PC}$ = 18.0 Hz, $PyCH_2$),121.2 (s, Py), 122.8 (s, Py), 128.5 (d, $^3J_{PC}$ = 14.1 Hz, *m*-Ph), 128.5 (s, *p*-Ph), 132.8 (d, $^2J_{PC}$ = 18.5 Hz, *o*-Ph), 136.4 (s, Py), 138.4 (d, $^1J_{PC}$ = 13.0 Hz, *ipso*-Ph), 149.4 (s, Py), 161.8 (d, $^3J_{PC}$ = 13.4 Hz, N*C*CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −14.2 (s).

Synthesis of 2-Methyloxy(diphenylphosphino)pyridine, 14...[56] To a solution of (pyridin-2-yl)methanol (3.04 g, 27.9 mmol) in THF containing 3 equiv of triethylamine (12 mL, 85.0 mmol) was added 5 mL of PPh_2Cl (6.15 g, 27.9 mmol) at −78 °C. The solution was stirred for 2 h from −78 °C to room temperature, and all volatiles were removed under reduced pressure. The residue was dissolved in diethyl ether to precipitate triethylammonium chloride. After filtration, the solvents were removed under reduced pressure and **14** was isolated as a pale yellow oil. Yield: 7.52 g, 92%. ^{1}H NMR ($CDCl_3$): δ 2.50 (t, 2H, $^3J_{HH}$ = 8.7 Hz, PCH_2), 7.17 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.8 Hz, C*H*CHN), 7.36(m, 6H, Ph), 7.47 (d, 1H, $^3J_{HH}$ = 7.6 Hz CCH), 7.55(m, 4H, Ph), 7.67(dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, CHC*H*CH), 8.53 (d, 1H, $^3J_{HH}$ = 4.8 Hz, CHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 72.2 (d, $^2J_{PC}$ = 16.2 Hz, $POCH_2$), 121.2 (s, Py), 122.4 (s, Py), 128.4 (d, $^3J_{PC}$ = 6.9 Hz, *m*-Ph), 129.6 (s, *p*-Ph), 130.6 (d, $^2J_{PC}$ = 21.9 Hz, *o*-Ph), 136.7 (s, Py), 141.4 (d, $^1J_{PC}$ = 18.3 Hz, *ipso*-Ph), 149.1 (s, Py), 158.7 (d, $^2J_{PC}$ = 8.8 Hz, N*C*CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 117.7 (s); IR (KBr) 1592 (s), 1477 (m), 1435 (s), 1096 (s), 1050 (s), 751 (s), 697 (s) cm^{-1}.

2-Methyloxy(dibenzyl-1,2-oxaphosphorino)pyridine, 15. To a solution of (pyridin-2-yl)methanol (1.08 g, 10.0 mmol) in THF containing 3 equiv of triethylamine (4.2 mL, 30.0 mmol) was added chloro(dibenzyl-1,2-oxa)phosphorine (2.34 g, 10.0 mmol) at −78 °C. The solution was stirred for 2 h from −78 °C to room temperature, and then the volatiles were removed under reduced pressure. The residue was dissolved in diethyl ether to precipitate triethylammonium chloride. After filtration, the solvents were removed under reduced pressure and **15** was isolated as a pale yellow oil. Yield: 2.70 g, 88%. ^{1}H NMR ($CDCl_3$): δ ABX spin system (A, B, X = P) 4.86 (1H, dd, J_{AB} = 13.8 Hz, $^2J_{XB}$ = 8.7

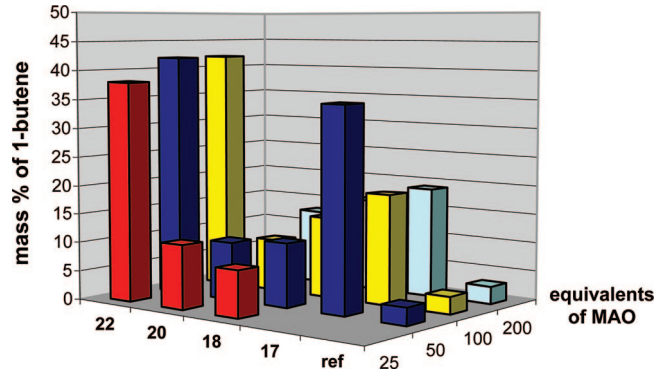


Figure 8. Selectivity of **17**, **18**, **20**, and **22** for 1-butene using MAO as cocatalyst (1-butene and 2-butene), ref: [$NiCl_2\{P(n\text{-}Bu)_3\}_2$].

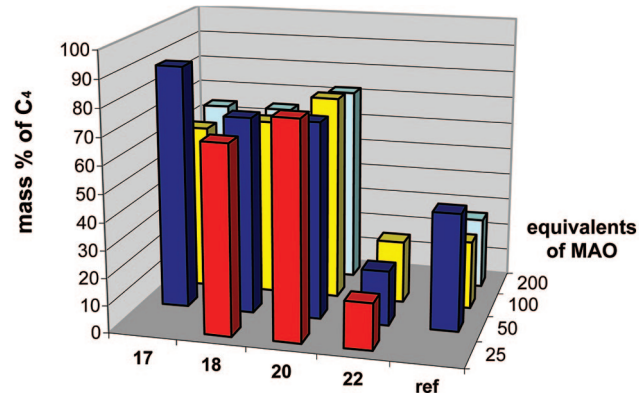


Figure 9. Selectivity of **17**, **18**, **20**, and **22** for C_4 compounds using MAO as cocatalyst (1-butene and 2-butene), ref: [$NiCl_2\{P(n\text{-}Bu)_3\}_2$].

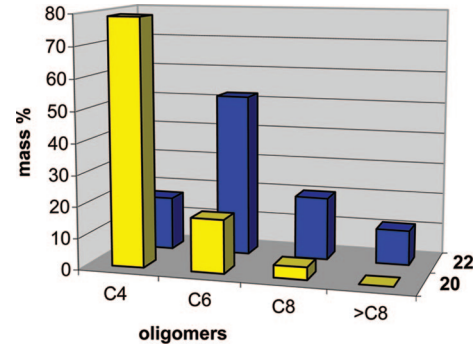
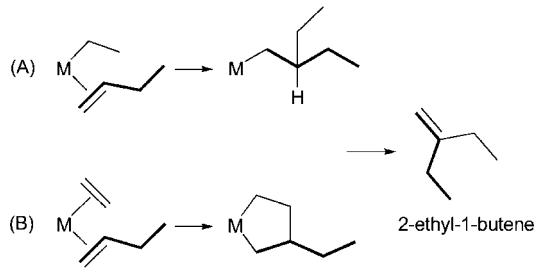


Figure 10. Mass distribution of the oligomers produced by **20** and **22** (4 × 10^{-5} mol of complex, 25 equiv of MAO, 10 bar, 35 min).

Scheme 3. Proposed Pathways to Explain the Formation of 2-Ethyl-1-butene



Hz, $POCH_2$) and 4.93 (1H, dd, J_{AB} = 13.8 Hz, $^2J_{XA}$ = 10.2 Hz, $POCH_2$), 7.04 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 7.10 (t, 2H, $^3J_{HH}$ = 5.1 Hz), 7.19 (dt, 1H, $^3J_{HH}$ = 7.5 Hz, J_{PH} = 1.5 Hz), 7.30 (m, 1H,), 7.50 (m, 2H), 7.64 (m, 1H), 7.98 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, J_{PH} = 1.8 Hz), 8.02 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.46 (dq, 1H, $^3J_{HH}$ = 3.9 Hz, J_{PH} = 0.9 Hz, Py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 70.6 (d, $^2J_{PC}$ = 10.8 Hz, $POCH_2$), 120.6 (s, Ph), 120.8 (s, Py), 122.3 (s, Py), 122.5 (d, $^2J_{PC}$ = 6.2 Hz, PC*C*C), 123.4 (s, Ph), 123.5 (s, Ph), 124.9 (s, Ph), 127.7 (d, $^3J_{PC}$ = 13.4 Hz, PCCH*C*H), 129.6 (s, Ph), 131.5 (d, $^2J_{PC}$ = 48.2 Hz, PC*C*H), 131.7 (s, Ph), 131.9 (s, Ph), 132.2 (d, $^3J_{PC}$ = 2.8 Hz, POC*C*), 136.5 (s, Py), 141.9 (s, Py), 149.7 (d, $^2J_{PC}$ = 9.3 Hz, POC Ph), 158.1 (d, $^2J_{PC}$ = 4.7 Hz, N*C*CH$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 130.5 (s).

Chloro-di-*tert*-butylphosphine...[77] It was synthesized according to the literature[77] by dropwise addition of a solution of *t*-BuLi (60.0 mL, 102.0 mmol, 1.7 M in pentane) to a solution of PCl_3 (7.00 g, 51.0 mmol) in 100 mL of pentane at −78 °C. The mixture was stirred overnight from −78 °C to room temperature. LiCl was removed by filtration, and pentane was slowly removed under reduced pressure. The residue was distilled under reduced pressure (70 °C, 10 mbar), and chloro-di-*tert*-butylphosphine was isolated as a colorless liquid. Yield: 2.90 g, 32%. ^1H NMR ($CDCl_3$): δ 1.24 (d, 18H, $^3J_{PH}$ = 12.1 Hz, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 148.0 (s).

2-Methyloxy(di-*tert*-butylphosphino)pyridine, 16. A solution of *t*-BuLi (4.00 mL, 6.7 mmol, 1.7 M in pentane) was added to a solution of (pyridin-2-yl)methanol (0.725 g, 6.7 mmol) in 30 mL of THF at −78 °C. The solution became red and was stirred for 30 min. Di-*tert*-butylchlorophosphine (1.20 g, 6.7 mmol) in 20 mL of THF was added to the mixture to afford a pale yellow solution, which was stirred overnight from −78 °C to room temperature. THF was removed under reduced pressure, and diethyl ether was added to precipitate LiCl. After filtration and removal of the solvents under reduced pressure, **16** was isolated as a pale yellow oil. Yield: 1.52 g, 89%. ^1H NMR ($CDCl_3$): δ 1.13 (d, 18H, $^3J_{PH}$ = 11.7 Hz, CH_3), 4.93 (d, 2H, $^3J_{PH}$ = 5.7 Hz, CH_2), 7.18 (m, 1H, Py), 7.55 (d, 1H, $^3J_{HH}$ = 7.8 Hz, Py), 7.70 (dt, 1H, $^3J_{HH}$ = 7.5 Hz $^4J_{HH}$ = 1.8 Hz, Py), 8.53 (d, 1H, $^3J_{HH}$ = 4.8 Hz, Py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.4 (d, $^2J_{PC}$ = 15.1 Hz, CH_3), 35.4 (d, $^2J_{PC}$ = 24.3 Hz, PC), 76.1 (d, $^2J_{PC}$ = 21.7 Hz, OCH_2), 120.9 (s, Py), 122.1 (s, Py), 136.6 (s, Py), 149.0 (s, Py), 159.5 (d, $^3J_{PC}$ = 10.6 Hz, N*C*CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 166.3 (s).

[$NiCl_2$(DME)]...[78] $NiCl_2$ (100 g, 771.6 mmol) was dissolved in a mixture of 300 mL of methanol and 50 mL of trimethylorthoformate and stirred at reflux overnight. After reaction, unreacted $NiCl_2$ was eliminated by filtration and 80% of the solution was removed under reduced pressure to obtain a green gel. It was dissolved in a minimum of methanol, and 300 mL of DME was added. The solution was stirred at reflux overnight. A yellow powder of [$NiCl_2$(DME)] precipitated and was isolated by filtration through a canula. The powder was washed with pentane and dried under a nitrogen flux. Yield: 135.0 g, 80%. Anal. Calcd for $C_4H_{10}Cl_2NiO_2$: C, 21.87; H, 4.59. Found: C, 21.26; H, 4.68.

[$NiBr_2$(DME)]..[78] This compound was prepared using a method similar to that described for [$NiCl_2$(DME)] starting from $NiBr_2$ (10.0 g, 45.8 mmol). It was isolated as an orange powder. Yield: 12.3 g, 87%. Anal. Calcd for $C_4H_{10}Br_2NiO_2$: C, 15.57; H, 3.27. Found: C, 15.72; H, 3.73.

[Ni{2-{(diphenylphosphino)methyl}pyridine}Cl_2], 17. A solution of **12** (1.36 g, 4.9 mmol) in methanol was added to a solution of $NiCl_2$ (0.63 g, 4.9 mmol) at room temperature. The solution became red and was stirred for 1 h. Methanol was removed under reduced pressure, and the residue was dissolved in 30 mL of CH_2Cl_2. Unreacted $NiCl_2$ was eliminated by filtration. The solution was concentrated to 10, and 40 mL of pentane was added to precipitate **17**. After filtration, **17** was washed with 20 mL of diethyl ether, dried under vacuum, and isolated as a gray powder. Yield: 1.66 g, 84%. Anal. Calcd for $C_{18}H_{16}Cl_2NNiP$: C, 53.13; H, 3.96; N, 3.44. Found: C, 53.39; H, 4.11; N, 3.45. HRMS: Mass Calcd for $C_{18}H_{16}ClNNiP$: 362.0006. Found: 361.9984 $[Ni(P,N)Cl]^+$. IR (KBr): 1604 (vs), 1566 (w), 1476 (vs), 1435 (vs), 1310 (m), 1158 (s), 1101 (vs), 1021 (m), 998 (m), 843 (s), 743 (vs), 692 (vs), 603 (w), 522 (m), 487 (m) cm^{-1}.

[Ni(μ-Cl)$_2${2-{2-(diphenylphosphino)ethyl}pyridine}$_2$]$_2Cl_2$, 18. This compound was prepared using a method similar to that described for **17** by reaction of ligand **13** (2.17 g, 6.0 mmol) with $NiCl_2$ (0.78 g, 6.0 mmol). **18** was isolated as a green powder. Yield: 2.19 g, 80%. Anal. Calcd for $C_{38}H_{36}Cl_4N_2Ni_2P_2$: C, 54.21; H, 4.31; N, 3.33. Found: C, 53.92; H, 4.39; N, 3.10. HRMS: Mass Calcd for $C_{19}H_{18}ClNNiP$: 384.0213. Found: 384.0227 $[Ni(P,N)Cl]^+$. IR (KBr): 1605 (vs), 1484 (vs), 1437 (vs), 1377 (m), 1158 (m), 1101 (s), 1025 (m), 998 (m), 869 (m), 757 (s sh), 743 (s), 718 (m), 698 (vs), 526 (s), 500 (m), 475 (m) cm^{-1}.

[Ni(μ-Cl)$_2${(pyridin-2-yl)methanol}$_2$]$_2Cl_2$, 19, and [Ni{P(OMe)-Ph$_2$}$_2Cl_2$]. A MeOH solution of ligand **14** (0.89 g, 3.0 mmol) was added to a MeOH solution of $NiCl_2$ (0.39 g, 3.0 mmol). The resulting red solution was stirred at reflux for 1 h. After reaction, the solvent was removed under vacuum, and 20 mL of CH_2Cl_2 was added. A green precipitate was isolated from the red solution by filtration and was identified as [Ni(μ-Cl)$_2${(pyridin-2-yl)methanol}$_2$]$_2Cl_2$, **19**. Yield: 0.52 g, 98%. Anal. Calcd for $C_{24}H_{28}Cl_4N_4Ni_2O_4$: C, 41.43; H, 4.06; N, 8.05. Found: C, 41.82; H, 4.37; N, 7.86. HRMS: Mass Calcd for $C_{12}H_{14}ClN_2O_2Ni$: 311.0092. Found: 311.0099 $[Ni(N,O)_2Cl]^+$. IR (KBr): 1608 (s), 1571 (m), 1483 (m), 1444 (s), 1286 (m), 1237 (m), 1156 (m), 1033 (s), 765 (s), 727 (m) cm^{-1}.

All the volatiles of the red solution were removed under reduced pressure, and the residue was dissolved in 20 mL of diethyl ether. Then 80 mL of pentane was added to the solution, and a red powder precipitated, which was characterized as [Ni{P(OMe)Ph_2}$_2Cl_2$]. Yield: 0.71 g, 84%. Anal. Calcd for $C_{26}H_{26}Cl_2NiO_2P_2$: C, 55.56; H, 4.66. Found: C, 55.40; H, 4.69.

[Ni{2-methyloxy(diphenylphosphino)pyridine}Cl_2], 20. Solid [$NiCl_2$(DME)] (2.51 g, 11.5 mmol) was added to a solution of **14** (3.21 g, 11.0 mmol) in 30 mL of CH_2Cl_2. The solution became red and was stirred for 2 h. After reaction, unreacted [$NiCl_2$(DME)] was eliminated by filtration. The solution was concentrated to 10 mL, and 40 mL of pentane was added to precipitate **20**. After filtration, **20** was washed with diethyl ether, dried under vacuum, and isolated as a green powder. Yield: 4.28 g, 92%. Anal. Calcd for $C_{18}H_{16}Cl_2NNiOP$: C, 51.12; H, 3.81; N, 3.31. Found: C, 50.81; H, 4.04; N, 3.00. HRMS: Mass Calcd for $C_{18}H_{16}ClNNiOP$: 386.0006. Found: 386.0007 $[Ni(P,N)Cl]^+$. IR (KBr): 1606 (s), 1571 (m), 1484 (s), 1438 (vs), 1380 (w), 1313 (m), 1232 (w), 1185 (w), 1158 (m), 1130 (m), 1010 (vs), 833 (w), 741 (vs), 696 (vs) 618 (m), 539 (s), 486 (s) cm^{-1}.

[Ni{2-methyloxy(diphenylphosphino)pyridine}Br_2], 21. This compound was prepared using a method similar to that described

(77) Naiini, A. A.; Han, Y.; Akinc, M.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 5394–5395.

(78) Ward, L. G. L. *Inorg. Synth.* **1971**, *13*, 154–164.

Table 7. Crystallographic Data for Complexes 18 and 22

	18	**22**
chemical formula	$C_{38}H_{36}Cl_4N_2Ni_2P_2$	$C_{14}H_{24}Cl_2NNiOP$
M_r	841.85	382.92
cell setting, space group	monoclinic, *C*2/*c*	monoclinic, $P2_1/n$
temperature (K)	173(2)	173(2)
a (Å)	20.4250(8)	8.8770(3)
b (Å)	15.5080(7)	17.1160(6)
c (Å)	11.9040(6)	12.0180(5)
β (deg)	103.913(2)	102.7270(12)
V (Å^3)	3660.0(3)	1781.14(11)
Z	4	4
D_x (Mg m^{-3})	1.528	1.428
radiation	Mo Kα	Mo Kα
F(000)	1728	800
μ (mm^{-1})	1.44	1.47
cryst size (mm)	0.12 × 0.03 × 0.02	0.12 × 0.10 × 0.08
no. of measd, indept, and obsd reflns	9382, 5331, 3826	7317, 4076, 3133
criterion for obsd reflns	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.078	0.064
θ_{max} (deg)	30.0	27.5
data set (*h*; *k*; *l*)	−28/28; −19/21; −16/16	−11/11; −22/20; −15/15
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.096, 0.116, 1.21	0.083, 0.117, 1.19
no. of reflns	5331	4076
no. of params	218	181

for **20** by reaction of [$NiBr_2$(DME)] (0.77 g, 2.6 mmol) with ligand **14** (0.65 g, 2.6 mmol). **21** was isolated as a green powder. Yield: 0.92 g, 72%. Anal. Calcd for $C_{14}H_{24}Br_2NNiOP$: C, 42.24; H, 3.15; N, 2.74. Found: C, 42.05; H, 3.33; N, 2.68. IR (KBr): 1605 (s), 1484 (s), 1438 (s), 1157 (m), 1131 (m), 1102 (s), 758 (s), 696 (s) cm^{-1}.

[Ni{2-methyloxy(di-*tert*-butylphosphino)pyridine}Cl_2], 22. This compound was prepared using a method similar to that described for **20** by reaction of [$NiCl_2$(DME)] (0.57 g, 2.6 mmol) with ligand **17** (0.65 g, 2.6 mmol). **22** was isolated as a red powder. Yield: 0.70 g, 70%. Anal. Calcd for $C_{14}H_{24}Cl_2NNiOP$: C, 43.91; H, 6.32; N, 3.66. Found: C, 43.25; H, 6.37; N, 3.62. HRMS: Mass Calcd for $C_{14}H_{24}ClNNiOP$: 346.0632. Found: 346.0677 [Ni(P,N)Cl]$^+$. IR (KBr): 1607 (s), 1479 (s), 1438 (m sh), 1370 (m), 1315 (m), 1060 (w), 1026 (vs), 999 (vs), 808 (m), 780 (s), 764 (s), 743 (m), 622 (s) cm^{-1}.

[Ni{2-methyloxy(dibenzyl-1,2-oxa-phosphorino)pyridine}Cl_2], 23. This compound was prepared using a method similar to that described for **20** by reaction of [$NiCl_2$(DME)] (1.93 g, 8.8 mmol) with ligand **15** (2.70 g, 8.8 mmol). **23** was isolated as a maroon powder (2.88 g, 6.6 mmol). Yield: 2.88 g, 75%. Anal. Calcd for $C_{14}H_{24}Cl_2NNiOP$: C, 49.49; H, 3.23; N, 3.21. Found: C, 47.64; H, 4.27; N, 2.90 (despite several attempts, better analysis were not obtained). HRMS: Mass Calcd for $C_{14}H_{24}ClNNiOP$: 399.9804. Found: 399.9815 [Ni(P,N)Cl]$^+$. IR (KBr): 1675 (s sh), 1638 (s), 1608 (vs), 1583 (m sh), 1560 (w), 1476 (vs), 1443 (m), 1430 (s), 1278 (m), 1203 (vs), 1116 (s), 1060 (vs), 913 (s), 758 (vs), 716 (m), 619 (m), 605 (m), 531 m) cm^{-1}.

Oligomerization of Ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. The preparation of the solution of the precatalyst is dependent on the nature and the amount of the cocatalyst.

When $AlEtCl_2$ in toluene was used as a cocatalyst, 4×10^{-2} mmol of Ni complex was dissolved in 14, 13, or 12 mL of cholorobenzene depending on the amount of the cocatalyst and injected into the reactor under an ethylene flux. Then 1, 2, or 3 mL of a cocatalyst solution, corresponding to 2, 4, or 6 equiv, respectively, was added to form a total volume of 15 mL with the precatalyst solution. When 10^{-2} mmol of precatalyst was used, a solution of the complex in 14 mL of chlorobenzene was injected into the reactor, followed by 0.75 mL of a solution of the cocatalyst (6 equiv).

With MAO in toluene as a cocatalyst, 1×10^{-2} or 4×10^{-2} mmol of Ni complex was dissolved in 10 mL in chlorobenzene and injected into the reactor under an ethylene flux. Then 0.5, 1, 2, 4, 8, or 16 mL of a cocatalyst solution, corresponding to 12.5, 25, 50, 100 (4 mL for 4×10^{-2} mmol of Ni complex or 1 mL for 10^{-2} mmol of Ni complex), 200, or 400 equiv of MAO, respectively, was added.

All catalytic tests were started between 25 and 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 or 30 bar. A temperature increase was observed, which resulted solely from the exothermicity of the reaction. The 10 or 30 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 or 120 min) a dry ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool the reactor, thus stopping the reaction. When the inner temperature reached 0 °C, the ice bath was removed, allowing the temperature to slowly rise to 10 °C. The gaseous phase was then 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 amount of ethylene not consumed was thus determined. Although this method is of limited accuracy, it was used throughout and gave satisfactory reproducibility. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid loss of product.

Crystal Structure Determinations. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (Table 7).

Data were collected using phi-scans, the structures were solved by direct methods using the SHELX 97 software,[79,80] and the refinement was 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 ($d_{C\text{-}H}$ =

(79) *Kappa CCD Operation Manual*, Nonius BV: Delft, The Netherlands, 1997.

(80) Sheldrick, G. M. *SHELXL97, Program for the refinement of crystal structures*; University of Göttingen: Germany, 1997.

0.95 Å, $U_{11} = 0.04$). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication no. CCDC 668689 and 668690. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files giving crystal data for the complexes **18** and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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