Nickel Complexes with Oxazoline-Based *P,N*-Chelate Ligands: Synthesis, Structures, and Catalytic Ethylene Oligomerization Behavior†

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The phosphinooxazoline ligands **9**−**12** have been prepared and used to examine and compare the catalytic properties of their corresponding Ni(II) complexes in ethylene oligomerization. The molecular structure of *rac*-2-[1′-(diphenylphosphanyl)ethyl]-4,4-dimethyl-4,5-dihydrooxazole (**10**) has been determined by X-ray diffraction. The paramagnetic Ni(II) complexes $[NiX(\mu\text{-}X)(P,N)]_2$ (**19**, X = Br, P,N = 2-[(diphenylphosphanyl)methyl]-4,4-dimethyl-4,5-dihydrooxazole (**9**)); **20**, X = Cl, P,N = **9**; **21**, X = Cl, P,N = **10**); **22**, X = Cl; P,N = 2-[(diphenylphosphanyl)methyl]-4-(*R*)-phenyl-4,5-dihydrooxazole (**12**)); **23**, X = Br, P,N = **12**) and $[NiCl_2(P,N)]$ (**24**; P,N = 2-[1′-(diphenylphosphanyl)-1′-methylethyl]-4,4-dimethyl-4,5-dihydrooxazole (**11**)) were prepared in yields of 79−90%, and **19** and **24** have been characterized by X-ray diffraction. The former is a dinuclear complex with distorted-trigonal-bipyramidal geometry around the Ni(II) centers, whereas **24** is a mononuclear, tetrahedral complex, which underlines the strong influence of a substituent on the carbon atom α to P. The metal coordination sphere in complexes **19**−**24** was determined in solution by the Evans method to be trigonal bipyramidal for **19**−**23** and tetrahedral for **24**. Whereas complexes **19**−**23** and $[NiCl_2(PCy_3)_2]$ were inactive for ethylene polymerization in the presence of methylaluminoxane (MAO), the mononuclear complex **24** gave a TOF of 7900 mol of C_2H_4/((mol of Ni) h) with a selectivity for 1-butene of 38%. Complexes **19**, **20**, and **22** were inactive for the oligomerization of ethylene in the presence of $NaBH_4$, but **19**, **21**, and **24** were active with $AlEtCl_2$ as a cocatalyst. Activities and selectivities were compared to those of $[NiCl_2(PCy_3)_2]$, a typical precatalyst used in the dimerization of α-olefins. Complex **19** yielded a turnover frequency of 36 300 mol of C_2H_4/((mol of Ni) h) in the presence of 14 equiv of $AlEtCl_2$. In the presence of only 6 equiv of cocatalyst, the Ni complexes **21** and **24** showed TOF values of 38 100 and 45 900 mol of C_2H_4/((mol of Ni) h), respectively, higher than that of 27 200 mol of C_2H_4/((mol of Ni) h) obtained with $[NiCl_2(PCy_3)_2]$.

Introduction

Unsymmetrical bidentate ligands with a nitrogen and a phosphorus donor atom, referred to as P,N ligands in the following, can chelate a metal center or bridge two identical or different metal centers. Owing to their bonding versatility and the relative ease with which the electronic and steric properties of the donor atoms can be modified, P,N ligands play an important role in the coordination chemistry of transition metals and in homogeneous catalysis.[1−6] These heterofunctional systems often display unique dynamic features, such as hemilability, which represents an efficient way to control the selectivity of catalytic processes.[1]

Despite their widespread application in asymmetric catalysis,[6] phosphinoimine ligands have only recently attracted attention for the late-transition-metal-catalyzed oligomerization, polymerization, and copolymerization of ethylene.[7−10] This includes the phosphinoimine ligands **1**−**4**, which were developed by the

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† Dedicated to Prof. H. Werner on the occasion of his 70th birthday, with our warmest congratulations for his scientific achievements and best wishes.

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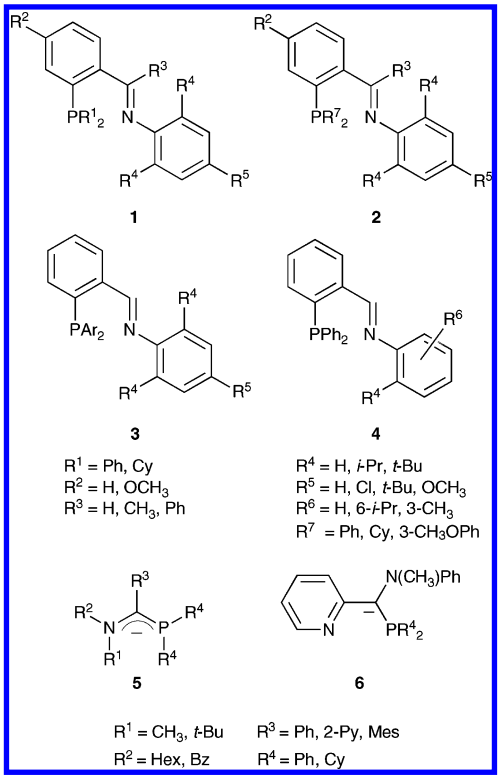
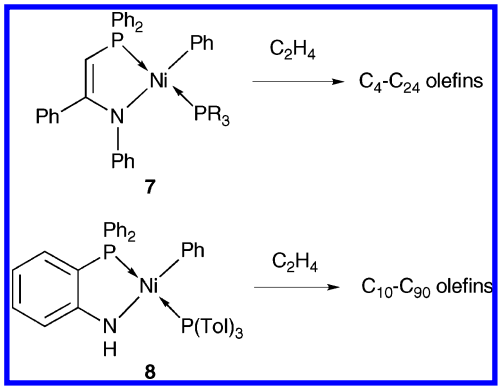


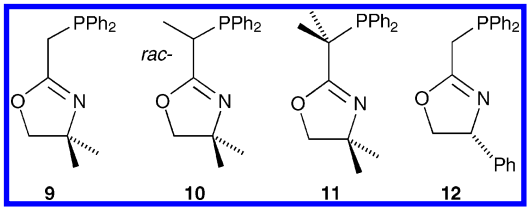
Eastman Chemical Corporation (**1**),[11] Shell (**2**),[12] and Rush and co-workers (**3**)[13] with varying R groups on either the phosphorus- or nitrogen-bound phenyl substituent. Asahi Industries published the similar system **4** with only one bulky substituent in the position ortho to the imine nitrogen.[14] The corresponding Ni and Pd complexes were used for the catalytic polymerization of ethylene.[7,9−14] Other P,N systems used in the oligomerization or polymerization of α-olefins include the anionic ligands **5** and **6**, developed by Symyx Technologies.[15]

Catalytic olefin oligomerization represents a major industrial process, and suitable ligand design has led to high-performance Ni catalysts.[16] In particular, ethylene oligomerization providing α-olefins in the C_6−C_{20} range is highly desirable, since they are used for the preparation of detergents, plasticizers, and fine chemicals and as comonomers for the synthesis of linear low-density polyethylene. In particular, the dimerization of olefins catalyzed by transition-metal complexes is of considerable industrial relevance.[16c,d] Following our recent studies on the synthesis and application of the Ni complexes **7** and **8** bearing anionic phosphinoamide ligands[17b,c] and on SHOP-type P,O systems[17a,c,18,19] for the oligomerization of ethylene (Scheme 1), we were interested in obtaining short-chain oligomers using Ni complexes with other P,N donor ligands. The stronger binding ability of the phosphine may lead to improved thermal stability of the catalysts. Furthermore, the use of nonenolizable imine donors should also be beneficial to catalyst thermal stability.[10c,f]

Scheme 1



The phosphinooxazolines **9**−**12** fulfill these requirements and were selected also because their stereoelectronic properties can be modulated in a systematic manner. The CH_2 group in a position α to the phosphorus atom is well suited for introducing substituents in the vicinity of the P donor atom and thereby fine-tuning its electronic properties (see **10** and **11**). Furthermore, the oxazoline heterocycle provides a rigid backbone with the possibility of introducing chirality and steric hin-



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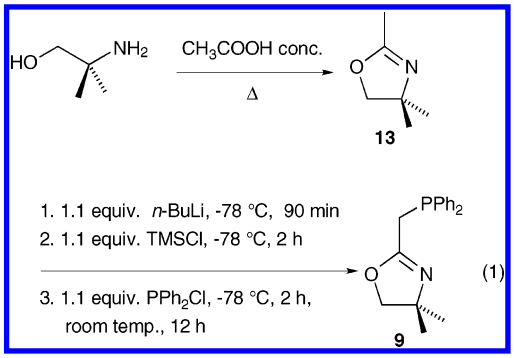
drance, as in the case of **12**. In addition to the possible variations at the P substituents, which we did not perform in the present work, changing the basicity and the donor strength of the P,N ligand could have a significant influence on complex stability and catalytic activity.

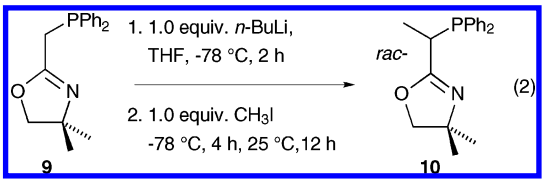
Results and Discussion

1. Ligand Synthesis. The phosphinooxazoline ligand **9** was prepared from the oxazoline **13**, itself obtained by heating 2-amino-2-methylpropan-1-ol in glacial acetic acid, followed by azeotropic distillation of the product (eq 1).[20] Lithiation of the oxazoline **13** in THF was

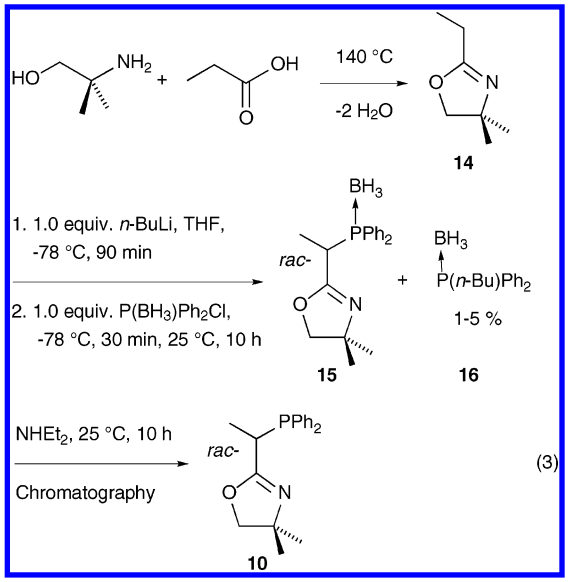


performed with 1.1 equiv of *n*-BuLi at −78 °C. The solution must be kept at −78 °C in order to avoid metalation on the heterocycle.[21] After the oxazoline was lithiated, 1.1 equiv of TMSCl was added, which allows a clean reaction.[8] In the final step, 1.1 equiv of PPh_2Cl was added and the solution was brought to room temperature overnight (eq 1). Small amounts of oxidized phosphinooxazoline were separated by column chromatography over silica gel under a nitrogen atmosphere, which afforded the product in 73% yield.

The ligand *rac*-2-[1′-(diphenyl-phosphanyl)ethyl]-4,4-dimethyl-4,5-dihydrooxazole (**10**) was synthesized by monolithiation of the PCH_2 group of **9** with 1.0 equiv of *n*-BuLi, followed by the addition of 1.0 equiv of CH_3I (eq 2). After workup, **10** was isolated in 83% yield as a

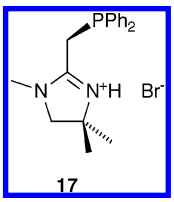


slightly yellow, transparent oil. An alternative and more efficient synthesis of **10** was developed, using the 2-ethyl-4,4-dimethyl-4,5-dihydrooxazole **14** as precursor (eq 3). This method reduces the number of reaction steps and introduces the phosphine moiety in the final step, which facilitates the isolation of a pure product, since phosphinooxazolines are readily oxidized by small



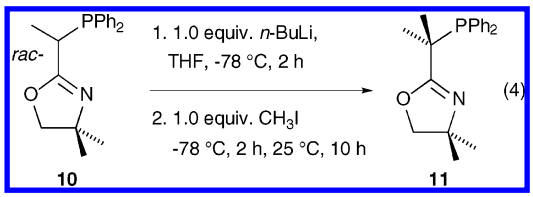
amounts of adventitious oxygen. Addition of 1 equiv of *n*-BuLi to oxazoline **14** and 1 equiv of $P(BH_3)Ph_2Cl$ at −78 °C, followed by deprotection of **15**, afforded ligand **10** as a slightly yellow oil, which solidifies upon standing, in 65% yield after column chromatography. The borane-protected phosphine $P(BH_3)(n\text{-Bu})Ph_2$ (**16**) was formed as a byproduct and separated by column chromatography.

Ligand **10** was characterized by ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectroscopy and X-ray diffraction. A view of the crystal structure is shown in Figure 1, and selected bond distances and angles are given in Table 1. Both enantiomers of the racemate crystallize in the unit cell. The P−C(6) bond is almost orthogonal to the plane of the heterocycle, which minimizes the repulsion between the lone pairs on the nitrogen and oxygen atoms and that on phosphorus. A similar orientation was observed in the X-ray structure of 2-[(diphenylphosphanyl)methyl]-3,5,5-trimethyl-4,5-dihydro-3*H*-imidazol-1-ium bromide (**17**).[22] The C(1)−N bond length of 1.259(3) Å in **10** is in



accordance with a double bond[23] and is shorter than the corresponding bond distance of 1.335(4) Å in **17**.[22]

For the synthesis of 2-[1′-(diphenylphosphanyl)-1′-methylethyl]-4,4-dimethyl-4,5-dihydrooxazole (**11**), the phosphinooxazoline **10** was first reacted with 1 equiv of n-BuLi and then CH_3I, yielding **11** as a yellow-white solid (eq 4). Care has to be taken during the addition of



CH_3I, since an excess leads to quaternization of the phosphorus atom. Ligand **11** was isolated after column chromatography in 50% yield. This modest yield is due

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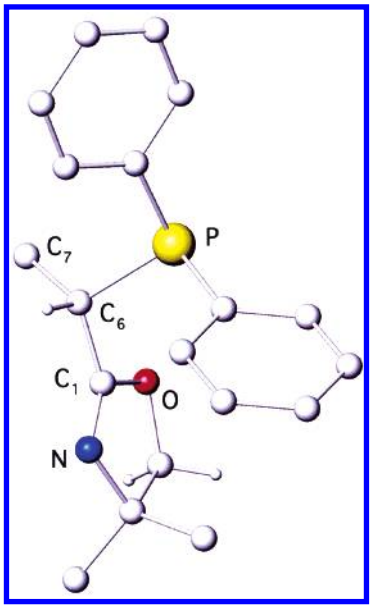


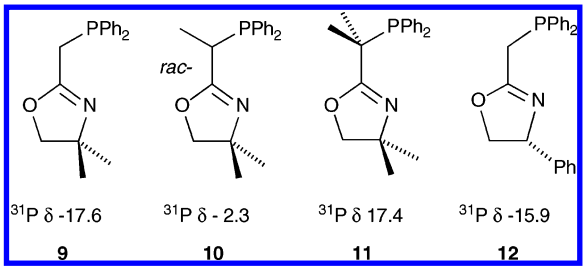
Figure 1. View of the molecular structure of 2-[1-(diphenylphosphanyl)ethyl]-4,4-dimethyl-4,5-dihydrooxazole (**10**).

Table 1. Selected Bond Distances (Å) and Angles (deg) in 10

C(1)−O	1.359(2)	C(6)−P	1.873(2)
C(1)−N	1.259(3)	C(6)−C(7)	1.531(3)
C(1)−C(6)	1.486(3)		
C(1)−C(6)−P	108.1(1)	C(1)−C(6)−C(7)	109.5(1)
C(1)−C(6)−C(7)	112.3(2)	N−C(1)−O	118.2(2)

in part to the insufficient basicity of the reagent used and to a difficult separation by column chromatography between residual **10** and **11**. However, when stronger bases such as *t*-BuLi or the Lochmann−Schlosser base were used, decomposition of the starting material or formation of a product mixture was observed.[20,24]

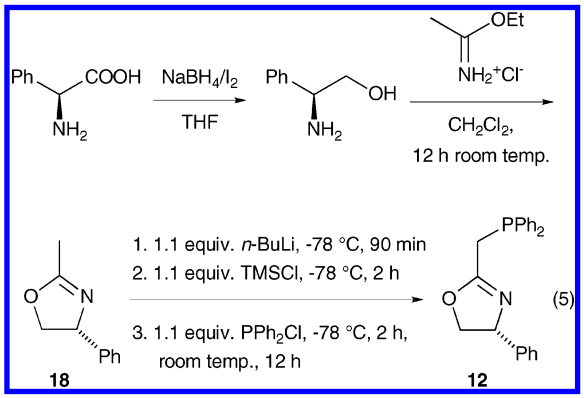
To prepare the *R*-enantiopure ligand **12**, D-phenylglycinol, which is readily derived from D-phenylglycine by reduction with $NaBH_4/I_2$ in THF in good yields (eq 5),[25] was reacted with ethyliminoacetate hydrochloride to give the oxazoline **18**.[26] The latter was then functionalized to give **12**, following the procedure used to prepare **9** (eq 5). Ni(II) and Pd(II) complexes of chiral phosphinooxazolines related to **12** have been successfully used as catalysts in asymmetric Grignard reactions or allylic alkylations,[6,27] and we have shown that such ligands can also be used as assembling ligands in bimetallic chemistry[28a,b] and that their deprotonated form (phosphinoiminolate) leads to novel Pd(II) complexes[28c] and Ru(II) catalysts for the transfer hydrogenation of ketones.[28d] The phosphinooxazolines **9**−**12** show characteristic signals in $^{31}P\{^1H\}$ NMR which are sensitive to the degree of substitution in the position α to the phosphorus moiety. The unsubstituted phosphines **9**



and **12** give rise to singlets at δ −17.6 and −15.9, respectively. A low-field shift to δ −2.3 ppm is observed for the racemic phosphinooxazoline **10**. This trend extends further to the tetramethylated phosphinooxazoline **11** with a resonance at δ 17.4. The assignment of the ^1H NMR spectrum of **12** resulted from COSY and selective decoupling experiments, and the fact that both the $^1H\{^{31}P\}$ and ^1H spectra were identical established that the $^2J(PH)$ coupling is zero. Also, the diastereotopic PCH_2 protons show a $^5J(HH)$ coupling with the CHPh proton (see Experimental Section).

2. Preparation of the Ni(II) Complexes. The P,N ligands were reacted with Ni(II) precursor complexes, as indicated in Scheme 2. The reactions were clean and rapid. After the reagents were stirred for 2 h at room temperature in CH_2Cl_2, all NiX_2 or $[NiX_2(DME)]$ (X = Cl, Br) has dissolved, yielding a dark violet solution. Solutions of the Ni(II) complexes were finally purified by filtration through Celite, to separate unreacted $[NiCl_2(DME)]$ or NiX_2.

Low-temperature ^1H and ^{31}P NMR spectra indicate the paramagnetic nature of the Ni complexes. In all of the cases, the proton resonances underwent dramatic shifts to either lower or higher field compared to the free ligand. Coordination of the phosphinooxazoline is evidenced by a sharp absorption in the IR spectrum between 1650 and 1620 cm^{-1} for the ν(C=N) vibration, which is significantly shifted compared to that in the free ligand (1660−1680 cm^{-1}).[8] All complexes were characterized in solution by the Evans method,[29] and the magnetic moments of complexes **19**−**23** were found in the range 3.21−3.90 μ_B, which corresponds to the presence of two unpaired electrons in a trigonal-bipyramidal coordination sphere of the metal[30−32] (see the X-ray structure determination of **19** below). In rare cases, diamagnetism has been observed for cationic trigonal-bipyramidal Ni(II) complexes.[32] The magnetic moment of 2.15 μ_B



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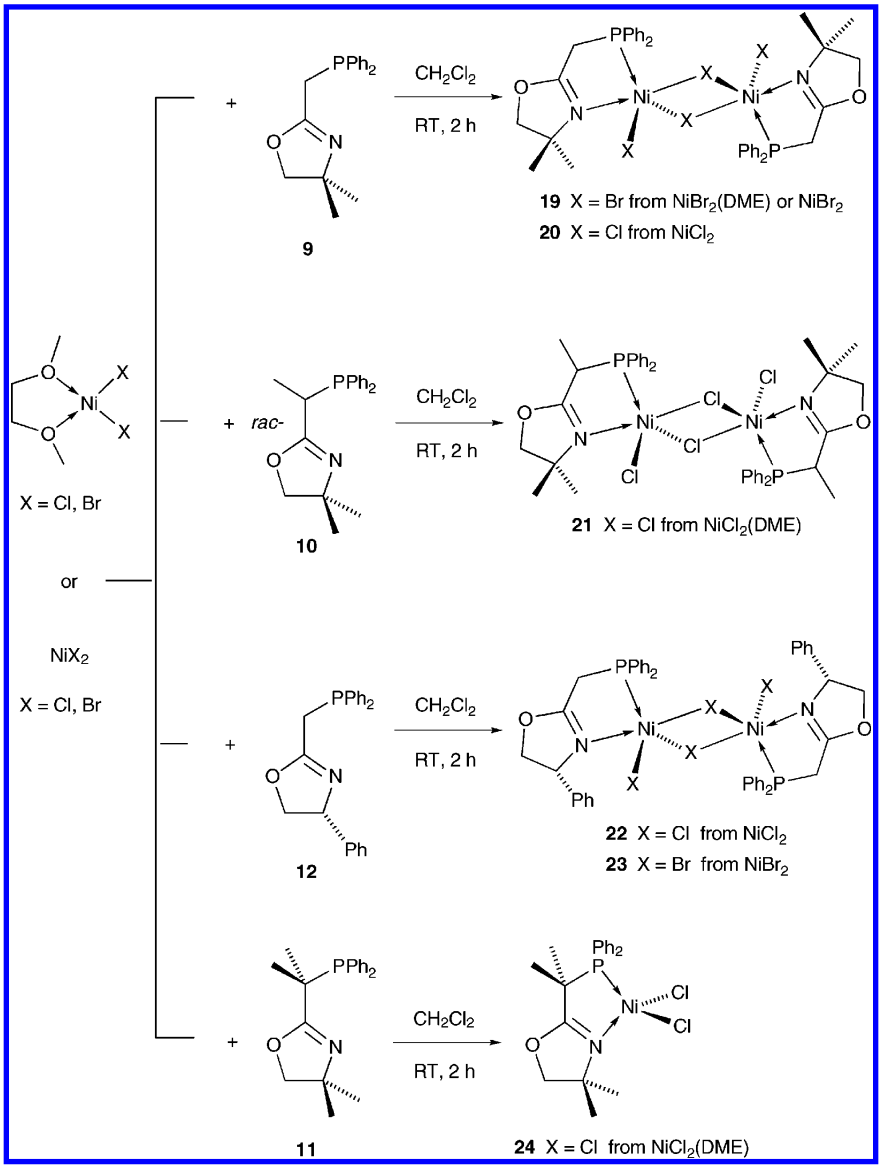
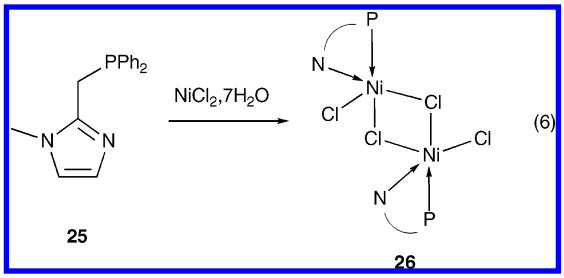
Scheme 2



found in solution for the mononuclear complex **24** is smaller than is usually observed for a tetrahedral coordination geometry (3.5−4.0 μ_B[30,31,33]) (see the X-ray structure determination of **24** below), but magnetic properties are strongly dependent on the ligand field and considerable fluctuations of the magnetic moments are often observed, due to the occurrence of structural equilibria in solution.[30,34−36]

Complexes **19** and **24** have been fully characterized by X-ray diffraction. A view of the centrosymmetric dinuclear complex **19** is shown in Figure 2, and selected bond distances and angles are given in Table 2. The Ni centers are in a distorted-trigonal-bipyramidal environment,[37] and according to the Cambridge Structure Database, **19** appears to be the first dinuclear complex of the type [Ni(μ-X)X(P,N)]$_2$ characterized by X-ray crystallography. The angle P−Ni−N found for the coordinated ligand is rather small, 80.83(7)°, compared to that in related ligands whose bite angles range from 83.0(1)°[38,39] to 84.4(3)°.[22] The Ni−N distance (2.098(2) Å) and Ni−P distance (2.3418(9) Å) are longer than in related complexes, where they range from 1.918(4) to 1.937(4) Å and from 2.176(1) to 2.180(1) Å, respectively.[22,39]

Complexes of the type [Ni(μ-X)X(P,N)]$_2$ (X = Cl) have been reported by Nishikawa and co-workers,[22] in which the P,N ligand is 2-[(diphenylphosphanyl)methyl]-1-methyl-1*H*-imidazole (**25**) (eq 6). The dinuclear nature



of complex **26** and the trigonal-bipyramidal coordination

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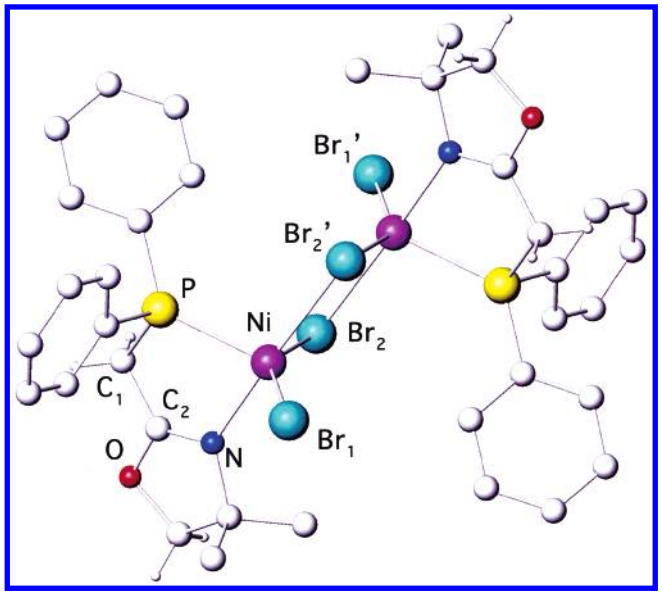
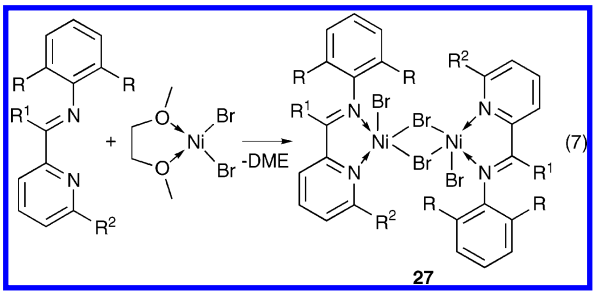


Figure 2. View of the molecular structure of [Ni(μ-Br)-Br{2-[(diphenylphosphanyl)methyl]-4,4-dimethyl-4,5-dihydrooxazole}]$_2$ (**19**).

Table 2. Selected Bond Distances (Å) and Angles (deg) in 19

Ni−P	2.3418(9)	Ni−Br(2)	2.6028(5)
Ni−N	2.098(2)	P−C(1)	1.843(3)
Ni−Br(1)	2.4177(5)	C(1)−C(2)	1.491(5)
Ni−Br(2)	2.5043(6)	C(2)−N	1.282(4)
Br(1)−Ni−Br(2)	145.88(2)	Br(2)−Ni−P	100.34(3)
Br(1)−Ni−Br(2)	89.30(2)	Br(2)−Ni−N	89.05(8)
Br(1)−Ni−P	113.78(3)	Br(2)−Ni−P	101.53(2)
Br(1)−Ni−N	95.42(7)	Br(2)−Ni−N	173.37(9)
P−Ni−N	80.83(7)		

geometry about the Ni centers were suggested on the basis of solid-state electronic spectra, mass spectrometry, and magnetic moment.[22] Recently Laine and coworkers have characterized binuclear Ni(II) complexes of type **27** bearing an iminopyridine-type ligand (eq 7) and used them in the polymerization of ethylene with methylalumoxane (MAO) as cocatalyst.[40,41]



The Ni(II) center in complex **24** adopts a tetrahedral coordination geometry (Figure 3; selected bond lengths

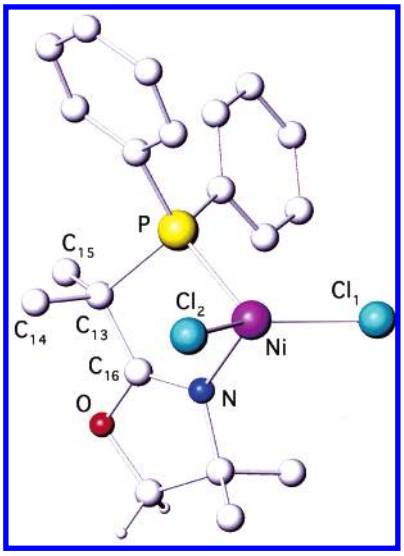


Figure 3. View of the molecular structure of [NiCl$_2${2-[1-(diphenylphosphanyl)-1-methylethyl]-4,4-dimethyl-4,5-dihydrooxazole}] (**24**).

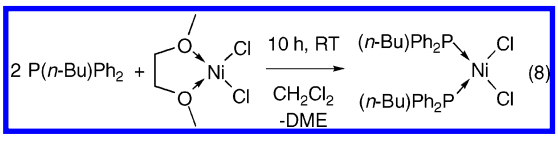
Table 3. Selected Bond Distances (Å) and Angles (deg) in 24

Ni−P	2.307(1)	P−C(13)	1.882(4)
Ni−N	1.987(3)	C(13)−C(16)	1.511(6)
Ni−Cl(1)	2.191(1)	C(16)−N	1.269(5)
Ni−Cl(2)	2.217(1)		
Cl(1)−Ni−Cl(2)	124.35(5)	P−Ni−N	82.7(1)
Cl(1)−Ni−P	120.40(2)	Ni−P−C(13)	97.23(6)
Cl(1)−Ni−N	112.1(1)	P−C(13)−C(16)	104.1(3)
Cl(2)−Ni−P	103.25(5)	Ni−N−C(16)	118.62(9)
Cl(2)−Ni−N	105.7(1)	C(13)−C(16)−N	125.4(3)

and angles are given in Table 3). Except for the angles around the metal, most structural parameters are similar to those observed for the dinuclear complex **19**. The P,N bite angle is increased to 82.7(1)°, in comparison to 80.83(7)° for complex **19**. According to the Cambridge Structure Database, **24** is the first [NiX$_2$-(phosphinooxazoline)] complex to be characterized by X-ray crystallography. Therefore, no comparative structural data are available.

When the structures of **19** and **24** and the changes in coordination geometries about the metal center solely induced by substitution at the α-position to the phosphorus atom are considered, the versatility of the ligand system appears remarkable. We shall examine below its influence on the activity or selectivity of the complexes in the catalytic oligomerization of ethylene.

In the course of the preparation of **21**, the complex [NiCl$_2${P(*n*-Bu)Ph$_2$}$_2$] was obtained unexpectedly, owing to contamination of the phosphinooxazoline **10** with P(*n*-Bu)Ph$_2$ (eq 8). This complex was then prepared more



rationally by reaction of P(*n*-Bu)Ph$_2$, isolated by column chromatography, with [NiCl$_2$(DME)] and was characterized by X-ray diffraction. The tetrahedral coordination of the Ni center indicates that P(*n*-Bu)Ph$_2$ behaves more like an arylphosphine than an alkylphosphine (Figure 4, Table 4).

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(41) Laine, T. V.; Piironen, U.; Lappalainen, K.; Klinga, M.; Aitola, E.; Leskelä, M. *J. Organomet. Chem.* **2000**, *606*, 112.

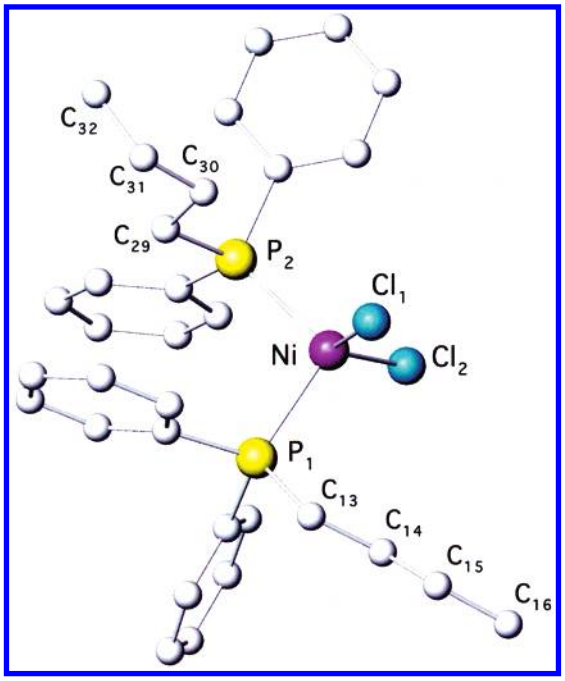


Figure 4. View of the molecular structure of $[NiCl_2\{P(n\text{-}Bu)Ph_2\}_2]$.

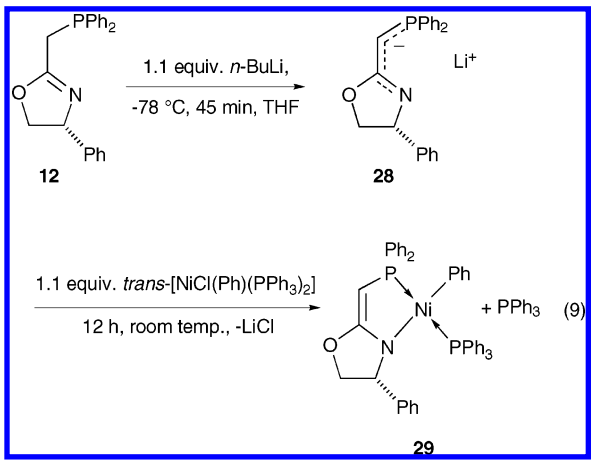
Table 4. Selected Bond Distances (Å) and Angles (deg) in $[NiCl_2\{P(n\text{-}Bu)Ph_2\}_2]$

Ni−P(1)	2.314(2)	Ni−Cl(1)	2.229(2)
Ni−P(2)	2.316(2)	Ni−Cl(2)	2.214(1)
Cl(1)−Ni−Cl(2)	123.64(7)	Cl(2)−Ni−P(1)	114.22(5)
Cl(1)−Ni−P(1)	97.96(5)	Cl(2)−Ni−P(2)	107.68(6)
Cl(1)−Ni−P(2)	107.61(6)	P(1)−Ni−P (2)	103.87(6)

3. Alkylation of the $[Ni(\mu\text{-}X)X(P,N)]_2$ Complexes. Ni alkyls are known to be active species in the catalytic oligomerization and polymerization of ethylene, and numerous studies have been reported on the role of neutral or cationic Ni−alkyl complexes in these reactions.[7,9,42−44] The nickel complexes **19**, **20**, and **22** were treated with $LiCH_3$ (2 or 4 equiv), Grignard reagents (1, 2, or 4 equiv of CH_3MgCl or $PhCH_2MgCl$), $Sn(CH_3)_4$ (1, 2, or 4 equiv), or $Zn(CH_3)_2$ (1, 2, or 4 equiv), at different temperatures with various stoichiometries of the alkylating reagent. No reaction was observed with $Sn(CH_3)_4$. The different basicities of these alkylating reagents need to be considered, since the PCH_2 protons exhibit enhanced acidity upon P coordination to the metal and are therefore sensitive to basic reagents such as CH_3Li. Surprisingly, these reagents afforded products with similar NMR and IR spectra. All reaction products were only soluble in DMSO. Formation of a complex resulting from deprotonation of the PCH_2 group could be generally ruled out, since deprotonation of coordinated phosphinooxazolines leads to a shift of the ν(C=N) infrared absorption of about 100 cm^{-1} to smaller wavenumbers.[45] For all products the characteristic ν-(C=N) absorption was observed around 1660 cm^{-1}.[8,45] The phosphorus atom is still coordinated to the Ni center, as indicated by the $^{31}P\{^1H\}$ NMR singlets observed between δ 26.1 and 26.6 ppm, but the exact nature of this compound could not be determined.

The problems encountered in the alkylation reactions of the complexes **19**, **20**, and **22** were no longer observed with the Ni complex **21** (which has a methyl group in a position α to P) when it was reacted with the Grignard reagents CH_3MgCl, $PhCH_2MgCl$, and EtMgCl. Preliminary studies on the alkylation of **21** showed that the reaction products were thermally unstable and sensitive toward traces of air and moisture. In view of the paramagnetic nature of the products and their high sensitivity toward oxygen, water, and temperature, their characterization proved to be extremely difficult and therefore remains incomplete. In the catalytic experiments (see below), alkylation was performed in situ.

4. Reaction of Metalated and Neutral Phosphinooxazoline Ligands with *trans*-$[NiCl(Ph)(PPh_3)_2]$. An alternative way to generate a Ni−carbon bond was explored, and *trans*-$[NiCl(Ph)(PPh_3)_2]$ was used as a precursor for the preparation of Ni−aryl complexes, which after chloride abstraction should afford cationic Ni(II) complexes of potential interest in catalysis. *trans*-$[NiCl(Ph)(PPh_3)_2]$[46] was reacted with the ligands **9** and **12** under different reaction conditions. Neither at room temperature nor at 80 °C in toluene could any reaction be observed by ^{31}P NMR spectroscopy. The complex *trans*-$[NiCl(Ph)(PPh_3)_2]$ was then reacted at room temperature with 1 equiv of the metalated phosphinooxazoline **28** prepared in situ at room temperature (eq 9).



After the reaction mixture was stirred for 12 h and workup, an impure product could be isolated which contained PPh_3 and the desired reaction product **29**, as indicated by the ^{31}P NMR resonance at 25.5 ppm for the deprotonated, coordinated phosphinooxazoline. This reaction has not yet been optimized.

5. Reaction Between Ligand 9 and Ni(0) Complexes. Early results by Wilke et al.[47] have shown that Ni(0) complexes such as $[Ni(COD)_2]$ or Ni−allyl species catalyze the oligomerization of ethylene. Therefore, we envisaged the preparation of Ni(0) complexes containing the phosphinooxazoline **9** from $[Ni(COD)_2]$. After the ligand and $[Ni(COD)_2]$ were mixed in toluene at room

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Table 5. Catalytic Results for the Dinuclear Complexes 19 and 21 and the Mononuclear Complexes 24 and $[NiCl_2(PCy_3)_2]$ in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	19			**21**	**24**		$NiCl_2(PCy_3)_2$	
amt of $AlEtCl_2$ (equiv)	6	12	14	6	2	6	2	6
selectivity C_4 (%)	100	62	56	64	67	54	88	86
selectivity C_6 (%)		36	41	33	28	40	12	14
selectivity C_8 (%)		2	2	3	3	1		0.5
selectivity C_{10} (%)			2		2	2		
selectivity C_{12} (%)					1	3.5		
productivity (g of C_2H_4/((g of Ni) h))	traces	16 300	17 500	18 400	12 300	22 000	800	13 000
TOF (mol of C_2H_4/((mol of Ni) h))	traces	33 800	36 300	38 100	25 400	45 900	1600	27 200
α-olefin (C_4) (%)		3	3	13	25	20	12	9
k_α[b]		0.39	0.49	0.34	0.28	0.50	0.09	0.11

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

temperature, a color change from yellow to dark red was observed, followed by rapid formation of a black precipitate (zerovalent nickel). The phosphinooxazoline **9** proved unable to stabilize a Ni(0) complex. Because of the lability of the COD ligand, a Ni complex with more strongly bound ligands was chosen and $[Ni(PPh_3)_4]$ was therefore employed for the synthesis of $[Ni(P,N)(PPh_3)_2]$-type complexes. Ligand **9** was reacted either at room temperature in toluene with $[Ni(PPh_3)_4]$ or at 80 °C. In neither case could any reaction be observed. Only uncoordinated PPh_3 and unreacted **9** could be detected by ^{31}P NMR spectroscopy. This may indicate that two PPh_3 ligands have better stabilizing properties toward Ni(0) than the bidentate phosphinooxazoline. When **9** was reacted with $[Ni(PPh_3)_4]$ in the presence of PhCl in toluene with the hope of forming a substituted Ni aryl complex, only formation of *trans*-$[NiCl(Ph)(PPh_3)_2]$ could be identified by ^1H and ^{31}P NMR and IR spectroscopy.

6. Catalytic Oligomerization of Ethylene Using Complexes 19−24. Ni complexes have long been studied as catalysts for the oligomerization and polymerization of ethylene.[7−9,48] In particular, the groups of Keim[18] and Ostoja Starzewski[19] have used P,O chelate complexes which afford highly linear α-olefins (C_6−C_{20}).[49] The chain length distribution strongly depends on the steric properties of the substituents on the phosphorus atom of the chelate ligand. With increasing steric hindrance, longer chain lengths were obtained. Various modifications have been developed around these $[NiX_2(P,O)]$-type catalysts (X = Cl), such as a $NaBH_4$ (1−2 equiv)/1,4-butanediol system.[49,50] The diol allows an easy separation of the oligomerization products by either evaporation or distillation. In the IFP Dimersol process, Ni(II) salts are applied in combination with halogenoalkylaluminum compounds as activators (Al:Ni > 10) in a nonpolar solvent and butenes and dimethylbutenes are formed, depending on the α-olefin.[51a] Brookhart and co-workers[7,42−44] used a large excess of methylaluminoxane (MAO; 300−1000 equiv) with the $[NiX_2(diimine)]$ complexes, which led to ethylene polymerization and oligomerization catalysts with turnover frequencies up to 3×10^6 mol of C_2H_4/((mol of Ni) h). Some catalysts produced oligomers ranging from C_6 to C_{24} with a high selectivity for α-olefins (94%).[44] A range of Ni(II) six-membered chelate complexes bearing the phosphinoimine ligands **1**−**4** have been reported for the polymerization of ethylene, and the active species were generated in situ upon addition of a large amount of MAO (100−350 equiv).[11−14]

We have evaluated complexes **19**−**22** and **24** for the oligomerization of ethylene with the aim of producing short-chain oligomers in the presence, if possible, of only small quantities of cocatalyst. Different activators and experimental conditions have been used to improve the productivity and selectivity of the catalysts. The complexes were treated with different quantities of $AlEtCl_2$ or MAO as cocatalysts. To evaluate the transferability of the catalyst/cocatalyst system developed by Keim and co-workers[18] to the Ni(II) complexes **19**, **20**, and **22**, $NaBH_4$ was used as activator for the oligomerization of ethylene. The catalytic reactions have been carried out at either 65 or 85 °C, but these complexes were almost inactive. Only small amounts of C_4 oligomers could be detected by GC analysis.

Therefore, Lewis acidic cocatalysts such as $AlEtCl_2$, $AlEt_3$, and methylaluminoxane (MAO) were chosen. $AlRCl_2$ compounds are used in the Dimersol process, where in situ formation of a Ni−alkyl complex leads to the active Ni−hydride species after β-elimination.[51b] The $[Ni(\mu\text{-}Cl)Cl(phosphinooxazoline)]_2$ dinuclear complexes **19** and **21** and the mononuclear complex **24** were tested in the presence of different quantities of $AlEtCl_2$. Preliminary results with **22** have shown that introduction of steric hindrance on the oxazoline heterocycle did not have any significant influence on either activity or selectivity. Therefore, only the results with complexes **19**, **21**, and **24** will be detailed below. To compare the activities and selectivities in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst, $[NiCl_2(PCy_3)_2]$ was chosen as a reference, because it is a typical catalyst for the Ni-catalyzed dimerization of α-olefins.[51] All selectivities reported in the following refer to the total amount of products formed in each catalytic test.

The dinuclear compound **19** was inactive when less than 6 equiv of cocatalyst was added. However, turnover frequencies of 33 800 and 36 300 mol of C_2H_4/((mol of Ni) h) were obtained in the presence of 12 and 14 equiv of cocatalyst, respectively (Table 5). Complex $[NiCl_2(PCy_3)_2]$ is less active with small amounts of $AlEtCl_2$. Dinuclear **21** and mononuclear **24** were inactive in the presence of 1.3 equiv of $AlEtCl_2$. However, when 2 equiv

(48) (a) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123. (b) Klabunde, U.; Mühlhaupt, R.; Herskowitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D. *J. Polym. Sci., A: Polym. Chem.* **1987**, *25*, 1989.

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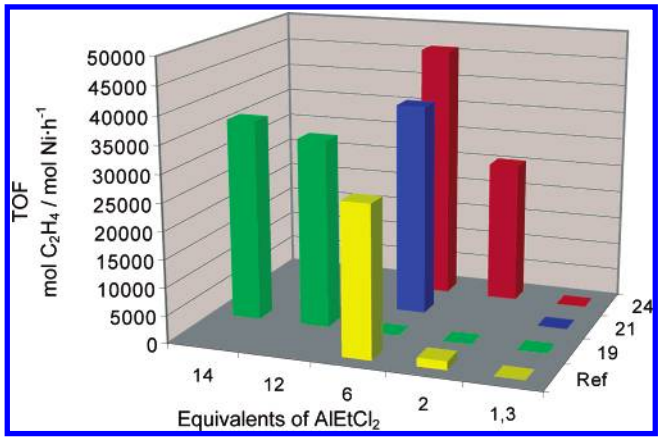

Figure 5. Catalytic activities of the complexes **19**, **21**, and **24** in the oligomerization of ethylene using $AlEtCl_2$ as activator ($[NiCl_2(PCy_3)_2]$ reference). Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-2} mmol of Ni, 15 mL of toluene.

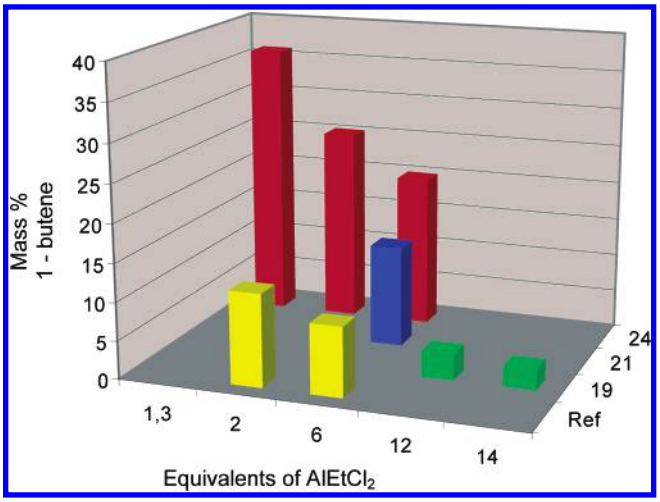

Figure 6. Selectivities for 1-butene within the C_4 fraction of the complexes **19**, **21**, and **24** ($[NiCl_2(PCy_3)_2]$ reference). Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-2} mmol of Ni, 15 mL of toluene.

was used, a turnover frequency (TOF) of 25 400 mol of C_2H_4/((mol of Ni) h) was observed for **24**. The turnover frequencies could be increased to 38 100 (**21**) and 45 900 mol of C_2H_4/((mol of Ni) h) (**24**) upon addition of 6 equiv of cocatalyst (Table 5 and Figure 5). These results are much better than those obtained with $[NiCl_2(PCy_3)_2]$ under similar conditions.

The catalytic results with **19**, **21**, and **24** indicate increased activity on going from ligand **9** < **10** < **11**, which parallels the degree of substitution at the carbon α to phosphorus and therefore the ligand basicity (see also ^{31}P chemical shifts; Figure 5). The main products formed during the oligomerization reactions were C_4 and C_6 oligomers. When 2 or 6 equiv of $AlEtCl_2$ was used, the mononuclear Ni complex **24** yielded 67% or 54% of C_4 and 28% or 40% of C_6 oligomers, respectively. Only small quantities of octenes and decenes were observed. Precatalysts **19** and **21** provided almost the same product distribution. An increase in the amount of cocatalyst displaced the product distribution toward the formation of C_6 oligomers.

Since butenes proved to be the main products in the oligomerization of ethylene using precatalysts **19**, **21,** and **24**, we focused on 1-butene formation, knowing that nickel complexes tend to isomerize α-olefins.[51,52a] The selectivity for 1-butene within the C_4 fraction (Figure 6) follows a trend similar to that for the turnover frequencies of the complexes (Figure 5). An increase in the basicity of the P,N chelate leads to a better selectivity for 1-butene within the C_4 fraction: 9% ($[NiCl_2(PCy_3)]$) < 13% (**21**) < 20% (**24**) (in the presence of 6 equiv of $AlEtCl_2$).

When MAO was used as a cocatalyst in the oligomerization of ethylene, complexes **19**, **21**, and $[NiCl_2(PCy_3)_2]$ decomposed, whereas the mononuclear complex **24** showed a TOF of 7900 mol of C_2H_4/((mol of Ni) h) (Table 6). Dimerization (72%) and trimerization (23%) of ethylene dominated, and a selectivity for 1-butene within the C_4 fraction of 38% was observed. It thus appears that, although MAO is a less suitable cocatalyst than $AlEtCl_2$, it leads to a higher selectivity for 1-butene within the C_4 fraction.

Table 6. Catalytic Results for 24 in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

amt of MAO (equiv)	800
selectivity C_4 (%)	72
selectivity C_6 (%)	23
selectivity C_8 (%)	5
selectivity C_{10} (%)	1
selectivity C_{12} (%)	–
productivity (g of C_2H_4/((g of Ni) h))	3800
TOF (mol of C_2H_4/((mol of Ni) h))	7900
α-olefin (C_4) (%)	38
k_α[b]	0.21

[a] Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-2} mmol of Ni complex, solvent 20 mL of toluene. [b] k_α = hexenes [mol]/butenes [mol].

The k_α values given in the Tables 5 and 6 correspond to the ratio hexenes [mol]/butenes [mol] and not to the Schultz−Flory constant, since our catalysts are mainly dimerization and trimerization catalysts.

Conclusion

The Ni(II) complexes prepared from the phosphinooxazoline ligands **9**−**12** have been evaluated in the catalytic oligomerization of ethylene. The molecular structure of the ligand *rac*-2-[1′-(diphenylphosphanyl)-ethyl]-4,4-dimethyl-4,5-dihydrooxazole (**10**) has been determined by X-ray diffraction. The Ni(II) phosphinooxazoline complexes **19**−**24** have been prepared in 79−90% yields, and **19** and **24** have also been characterized by X-ray diffraction. The former is a dinuclear complex with distorted-trigonal-bipyramidal Ni(II) centers, whereas **24** is a mononuclear, tetrahedral complex, which underlines the strong influence of a substituent on the carbon atom α to P. The coordination geometry of the Ni(II) center in complexes **19**−**24** in solution was determined by the Evans method to be trigonal bipyramidal in **19**−**23** and tetrahedral in **24**.

The precatalysts **19**, **21**, and **22** were inactive for the oligomerization of ethylene in the presence of $NaBH_4$. However, with $AlEtCl_2$ as a cocatalyst, complexes **19**, **21**, and **24** were active and activities and selectivities

(52) (a) See for exemple: Birdwhistell, K. R.; Lanza, J. *J. Chem. Educ.* **1997**, *74*, 579. (b) Chen, H.-P.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2003**, *22*, 4893. (c) Kunrath, F. A.; de Souza, R. F.; Casagrande, O. L., Jr.; Brooks, N. R.; Young, V. G., Jr. *Organometallics* **2003**, *22*, 4739.

have been compared to those of $[NiCl_2(PCy_3)_2]$, a typical precatalyst used in the dimerization of α-olefins. Complex **19** yielded a turnover frequency of 36 300 mol of C_2H_4/((mol of Ni) h) in the presence of 14 equiv of cocatalyst. In the presence of only 6 equiv of $AlEtCl_2$, the Ni complexes **21** and **24** showed TOF values of 38 100 and 45 900, respectively, higher than that of 27 200 mol of C_2H_4/((mol of Ni) h) obtained with $[NiCl_2(PCy_3)_2]$. The dinuclear complexes **19** and **21** led to selectivities for 1-butene within the C_4 fraction lower than the mononuclear complex **24**. In the presence of MAO, the complexes **19**−**23** and $[NiCl_2(PCy_3)_2]$ were inactive, whereas **24** showed a TOF of 7900 mol of C_2H_4/((mol of Ni) h) and a selectivity for 1-butene within the C_4 fraction of 38%. The fact that the k_α value varies for a given catalyst as a function of the nature or quantity of cocatalysts used suggests that some incorporation of the butene formed occurs during chain growth (consecutive reaction). We have not yet studied the reasons for the limited selectivity for α-olefins which could 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 re-uptake mechanism leading to isomerization of 1-butene. The ability of Ni(II) complexes to isomerize α-olefins is well-known[52a] and has again been recently evidenced in the case of phosphinopyridine chelates.[52b]

It has recently been reported that mononuclear Ni(II) complexes with bulky tris(pyrazolyl)borate ligands were active for ethylene oligomerization, in contrast to the chloride-bridged dinuclear complex.[52c] In our case, the catalytic results obtained with the dinuclear complexes could be due to their specific ligand sphere or to a likely cocatalyst-induced dissociation in solution. The observation that the dinuclear complexes require more than 2 equiv of cocatalyst to display significant activity, in contrast to **24**, could be related to the need to use this Lewis acid to break the halide bridges before generating the active species.

Experimental Section

General Considerations. All solvents were dried and distilled using common techniques unless otherwise stated. All manipulations were carried out using Schlenk techniques. $NiCl_2 \cdot 6H_2O$ was dried by heating for 6 h at 160 °C under vacuum to give anhydrous $NiCl_2$. The complexes $[NiX_2(DME)]$ (X = Cl, Br),[53a] $[Ni(PPh_3)_4]$,[53b,54] and *trans*-$[NiCl(Ph)(PPh_3)_2]$[46] and 2,4,4′-trimethyloxazoline (**13**),[20] 2-[(diphenylphosphanyl)-methyl]-4,4-dimethyl-4,5-dihydrooxazole (**9**),[8] 2-ethyl-4,4-dimethyl-4,5-dihydrooxazole,[20] D-phenylglycinol,[25] and 2-methyl-4-phenyl-4,5-dihydrooxazole (**18**)[26] were prepared according to literature procedures. 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).

(53) (a) Cotton, F. A. *Inorg. Synth.* **1971**, *13*, 160. (b) Cotton, F. A. *Inorg. Synth.* **1971**, *13*, 124.
(54) MacDiarmid, A. G. *Inorg. Synth.* **1977**, *17*, 120.

Preparation of *rac*-2-[1′-(Diphenylphosphanyl)ethyl]-4,4-dimethyl-4,5-dihydrooxazole (10). A solution of **9** (4.86 g, 0.016 mol) in THF (150 mL) was cooled to −78 °C, and 1.0 equiv of *n*-BuLi was added (1.6 M solution in hexane, 10.00 mL, 0.016 mol). After the solution was stirred for 1 h at −78 °C, 1.0 equiv of CH_3I (0.93 mL, 0.016 mol) was added dropwise at −78 °C. The reaction mixture was stirred for 2 h at −78 °C and warmed to room temperature overnight. The solution was hydrolyzed with degassed water (30 mL) and extracted with diethyl ether (3 × 30 mL). Finally the organic phase was separated and dried over degassed $MgSO_4$. After evaporation of the diethyl ether, the product was isolated as a slightly yellow oil. Yield: 4.23 g, 0.013 mol, 83%.

Alternatively, **10** can be prepared by adding 1 equiv of *n*-BuLi (1.6 M solution in hexane, 76.71 mL, 0.12 mol) to a cold solution of **14** (15.00 g, 0.12 mol) in THF (200 mL) at −78 °C and stirring for 2 h at −78 °C. After addition of 1.1 equiv of $P(BH_3)Ph_2Cl$ (29.12 g, 0.132 mol), the solution was stirred for 2 h at −78 °C and then slowly warmed to room temperature and stirred overnight. The reaction mixture was hydrolyzed with degassed water (100 mL). The organic phase was separated with a cannula, and the aqueous phase was extracted with diethyl ether (2 × 50 mL). The organic fractions were pooled and dried over degassed $MgSO_4$ and filtered through a cannula equipped with a filter cap. The solvent was evaporated under reduced pressure, yielding the borane-protected ligand **15** as a slightly yellow oil. Deprotection by stirring in degassed diethylamine (120 mL) for 10 h at room temperature afforded the phosphinooxazoline **10**. All volatiles were evaporated, and the product mixture was separated by column chromatography (length of the stationary phase 60 cm, diameter 8 cm) over silica gel using hexane (5% diethylamine). Yield: 24.38 g, 0.078 mol, 65%. IR (CH_2Cl_2): 1655 cm^{-1} (ν(C═N)). ^1H NMR ($CDCl_3$) δ: 0.97 (s, 3H, C(CH_3)$_2$), 1.11 (s, 3H, C(CH_3)$_2$), 1.36 (dd, 3H, CHCH_3, ^3J(H,H) = 7.0 Hz, ^3J(P,H) = 14 Hz), 3.38 (dq, 1 H, CHCH$_3$, ^3J(H,H) = 7.0 Hz, ^2J(P,H) = 4.9 Hz), 3.71 and 3.73 (AB spin system, 2H, OCH_2, ^2J(H,H) = 8 Hz), 7.26−7.36 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.9 (d, PC(CH_3), ^1J(P,C) = 23.0 Hz), 28.0 (s, NC(CH_3)$_2$), 32.5 (d, ^2J(P,C) = 10.5 Hz, PC(CH_3)), 66.6 (s, NC(CH_3)$_2$), 78.3 (s, OCH_2), 127.9−136.5 (m, PPh_2), 166.3 (d, ^2J(P,C) = 4.1 Hz, CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −1.0 (s). Anal. Calcd for $C_{19}H_{22}NOP$: C, 73.29; H, 7.12; N, 4.50. Found: C, 73.50; H, 7.30; N, 4.73.

Synthesis of 2-[1′-(Diphenylphosphanyl)-1′-methylethyl]-4,4-dimethyl-4,5-dihydrooxazole (11). A solution of **10** (4.43 g, 0.014 mol) in THF (100 mL) was cooled to −78 °C, and 1.1 equiv of *n*-BuLi was added (1.6 M solution in hexanes, 9.8 mL, 0.016 mol). The color changed from yellow to dark red. The reaction mixture was stirred for 90 min before 1.1 equiv of degassed CH_3I (0.97 mL, 0.016 mol) was added. The solution was further stirred for 4 h at −78 °C before it was warmed to room temperature overnight. The reaction was quenched by addition of degassed water (20 mL), and the hydrolyzed reaction mixture was extracted with Et_2O (2 × 30 mL). The organic phase was separated by a cannula, dried over degassed $MgSO_4$, and filtered via a cannula equipped with a filter cap, and the solvent was evaporated under vacuum, giving the product as a yellow-white solid. Yield: 2.27 g, 50%. IR (CH_2Cl_2): 1663 cm^{-1} (ν(C═N)). ^1H NMR ($CDCl_3$): δ 1.21 (s, 6H, NC(CH_3)$_2$), 1.39 (d, 6H, ^3J(P,H) = 12.6 Hz, PC(CH_3)$_2$), 3.71 (s, 2H, OCH_2), 7.32−7.62 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.4 (d, ^2J(P,C) = 10.0 Hz, PC(CH_3)$_2$), 28.4 (s, NC(CH_3)$_2$), 36.4 (s, PC(CH_3)$_2$, ^1J(P,C) = 22.0 Hz), 66.8 (s, NC(CH_3)$_2$), 79.3 (s, OCH_2), 128.1 (d, ^3J(P,C) = 4.0 Hz, m-aryl), 128.9 (s, p-aryl), 134.6 (d, o-aryl, ^2J(P,C) = 16.7 Hz), 135.7 (d, ^1J(P,C) = 11.2 Hz, ipso-aryl), 169.9 (s, OCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.4 (s). Anal. Calcd for $C_{20}H_{24}NOP$: C, 73.83; H, 7.43; N, 4.30. Found: C, 74.00; H, 7.55; N, 4.41.

Preparation of 2-[(Diphenylphosphanyl)methyl]-4-(*R*)-phenyl-4,5-dihydrooxazole (12). To a solution of *n*-BuLi (0.014 mol, 8.6 mL) cooled to −78 °C was added a solution of

the oxazoline **18** (2.00 g, 0.012 mol) in THF (20 mL) over a period of 10 min. After the solution was stirred for 1 h at −78 °C, 1 equiv of TMSCl (1.68 mL, 1.44 g, 0.012 mol) was added dropwise over a period of 10 min. The reaction mixture was stirred for 90 min at −78 °C before 1 equiv of PPh_2Cl (2.64 g, 0.12 mol) was reacted with the silylated oxazoline. The solution was further stirred for 90 min at −78 °C and slowly warmed to room temperature overnight. All volatiles were evaporated under reduced pressure to give a yellow oil, which was extracted with toluene. This solution was filtered and the solvent evaporated under reduced pressure, leaving an oil that solidifies in the refrigerator. Alternatively, purification can be performed by column chromatography over silica gel (pentane/ethyl acetate 3:1, 5% diethylamine). The product was isolated as a yellow solid. Yield: 3.23 g, 0.009 mol, 78%. R_f (pentane: ethyl acetate 3:1): 0.53. ^{1}H NMR ($CDCl_3$; assignments based on selective decoupling experiments and comparison between ^{1}H and ^{1}H{^{31}P} spectra): δ_A 3.23 and δ_B 3.30 (ABM (M = H) spin system, 2H, ^2J(H,H) = 14.1 Hz, $^5J(H_A,H)$ = 1.2 Hz, $^5J(H_B,H)$ = 0.7 Hz, PCH_AH_B), 4.00 (t, 1H, ^2J(H,H) = ^3J(H,H) = 8.3 Hz, OC*H*H), 4.58 (dd, 1H, ^2J(H,H) = 8.3 Hz, ^3J(H,H) = 10.1 Hz, OCH*H*), 5.12 (overlaping dd, 1H, ^3J(H,H) = 8.3 and 10.1 Hz, C*H*Ph), 6.9−7.7 (m, 15H, aryl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.4 (δ, ^1J(P,C) = 19.2 Hz, PCH_2), 69.7 (s, *C*HPh), 75.1 (s, OCH_2), 165.7 (d, ^2J(P,C) = 7.4 Hz, C=N), 125−138 (aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −15.9 (s).

Preparation of [Ni(μ-Br)Br{2-[(diphenylphosphanyl)-methyl]-4,4-dimethyl-4,5-dihydrooxazole}]$_2$ (19). Ligand **9** (0.220 g, 0.74 mmol) was added to a solution of [$NiBr_2$(DME)] (0.55 g, 1.76 mmol) in CH_2Cl_2 (40 mL). After the mixture was stirred for 2 h at room temperature, the dark violet solution was separated from the remaining nickel salt by cannula. The solvent was evaporated under reduced pressure. The crude product was dissolved in toluene (20 mL) and reprecipitated by addition of hexane (50 mL). The supernatant organic phase (in which the free ligand is well soluble) was filtered off by cannula, and the solid product **19** was dried under vacuum. Alternatively, this product can be prepared by heating [$NiBr_2$-(DME)] (0.228 g, 0.74 mmol) or $NiBr_2$ (0.10 g, 0.46 mmol) and **9** (0.220 g, 0.74 mmol or 0.136 g, 0.46 mmol for $NiBr_2$) in degassed ethanol or *n*-butanol (30 mL) for 45 min until all the metal salt had dissolved. Workup of the product **19** was as described above. Yield: 0.200 g, 85%. IR (KBr): 1642 cm^{-1} (ν(C=N)). Magnetic moment in solution (Evans method): 3.82 μ_B. Anal. Calcd for $C_{36}H_{40}Br_4N_2Ni_2O_2P_2$: C, 41.91; H, 3.91; N, 2.72. Found: C, 42.3; H, 4.28; N, 2.78.

Preparation of [Ni(μ-Cl)Cl{2′-[(diphenylphosphanyl)-methyl]-4,4-dimethyl-4,5-dihydrooxazole}]$_2$ (20). Solid anhydrous $NiCl_2$ (0.194 g, 1.51 mmol) was added to a solution of **9** (0.450 g, 1.51 mmol) in CH_2Cl_2 (20 mL). The suspension was stirred for 2 h until all $NiCl_2$ had dissolved. The organic phase was evaporated under reduced pressure, yielding a brown solid. To eliminate the more soluble fraction, the crude product was partially dissolved in toluene (15 mL) and reprecipitated by addition of hexane (30 mL) and, after decantation and removal of the solvent, the solid was dissolved in CH_2Cl_2 (30 mL) and the solution filtered over Celite in order to remove unreacted $NiCl_2$. The product was dried under vacuum for 24 h, giving a light brown solid. Yield: 0.510 g, 1.19 mmol, 79%. IR (KBr): 1635 cm^{-1} (ν(C=N)). Magnetic moment in solution (Evans method): 3.90 μ_B. Anal. Calcd for $C_{36}H_{40}Cl_4N_2Ni_2O_2P_2$: C, 50.64 H, 4.72; N, 3.28. Found: C, 50.35, H, 4.48, N, 3.41.

Preparation of [Ni(μ-Cl)Cl{2′-[1′-(diphenylphosphanyl)ethyl]-4,4-dimethyl-4,5-dihydrooxazole}]$_2$ (21). To a solution of **10** (2.81 g, 9 mmol) in CH_2Cl_2 (40 mL) was added 1.2 equiv of [$NiCl_2$(DME)] (2.36 g, 11 mmol). While the reaction mixture was stirred for 2 h at room temperature, a color change from orange to dark green was observed. The reaction mixture was filtered through Celite in order to remove unreacted [$NiCl_2$(DME)]. The organic phase was again evaporated, and the resulting green solid was washed with hexane (2 × 15 mL) in order to separate remaining **10**. Finally, the product was dried under vacuum for 12 h, giving the nickel complex **21** as a green-gray powder. Yield: 7.10 g, 4.05 mmol, 90%. IR (KBr): 1624 cm^{-1} (ν(C=N)). Magnetic moment in solution (Evans method): 3.21 μ_B. Since NMR measurements were not possible, no attempt was made to identify or separate the diastereomers expected from the use of a racemic ligand. Anal. Calcd for $C_{38}H_{44}Cl_4N_2Ni_2O_2P_2$: C, 51.75; H, 5.03; N, 3.18. Found: C, 50.43; H, 4.57; N, 2.89 (we have no explanation for these poor results).

Preparation of [Ni(μ-X)X{2′-[(diphenylphosphanyl)-methyl]-4-(*R*)-phenyl-4,5-dihydrooxazole}]$_2$ (22, X = Cl; 23, X = Br). Solid, anhydrous $NiBr_2$ (0.190 g, 0.86 mmol) or [$NiCl_2$(DME)] (0.342 g, 0.86 mmol) was added to a solution of **12** (0.300 g, 0.86 mmol) in CH_2Cl_2 (30 mL). The suspension was stirred for 2 h at room temperature. The reaction progress was monitored by the dissolution of the Ni(II) precursors, and the color changed from yellow to violet. After the solvent was evaporated, the dark violet solid was dissolved in toluene (15 mL) in order to eliminate the more soluble fraction (which could contain residual ligand). Addition of hexane (30 mL) precipitated a solid, and the supernatant liquid was separated with the help of a cannula. To separate any unreacted nickel salt, the solid was dissolved in CH_2Cl_2 (30 mL) and the solution filtered through Celite. The solvent was evaporated, and the violet product was dried under vacuum. Yield of **22**: 0.424 g, 0.376 mmol, 87% based on [$NiCl_2$(DME)]; IR (KBr): 1637 cm^{-1} (ν(C=N)). Magnetic moment in solution (Evans method) 3.79 μ_B. Anal. Calcd for **22**, $C_{44}H_{40}Cl_4N_2Ni_2O_2P_2$: C, 55.63; H, 4.24; N, 2.95. Found: C, 57.35; H, 5.38; N, 2.19.

Yield of **23**: 0.447 g, 0.397 mmol, 92% based on $NiBr_2$. IR (KBr): 1635 cm^{-1} (ν(C=N)). Magnetic moment in solution (Evans method): 3.89 μ_B. Anal. Calcd for $C_{44}H_{40}Br_4N_2Ni_2O_2P_2$: C, 46.86; H, 3.58; N, 2.48. Found: C, 46.45; H, 3.28; N, 2.19.

Synthesis of [$NiCl_2${2′-[1′-(diphenylphosphanyl)-1′-methylethyl]-4,4-dimethyl-4,5-dihydrooxazole}] (24). To a solution of **11** (0.214 g, 0.658 mmol) in degassed ethanol (20 mL) was added 0.9 equiv of [$NiCl_2$(DME)] (0.129 g, 0.592 mmol), and the solution was stirred for 24 h at room temperature. After 1 h a color change from yellow-green to violet was observed. The solvent was evaporated under reduced pressure. The violet residue was dissolved in CH_2Cl_2 (15 mL), this solution was filtered through Celite, and the Celite was washed with CH_2Cl_2 (10 mL). The filtrate was evaporated to dryness, giving the product as a violet solid which was dried in vacuo overnight. Yield: 0.210 g, 0.462 mmol, 78%. IR (CH_2Cl_2): 1627 cm^{-1} (ν(C=N)). Anal. Calcd for $C_{20}H_{24}Cl_2NNiOP$: C, 52.80; H, 5.32; N, 3.08. Found: C, 52.70; H, 5.22; N, 2.99.

Synthesis of [$NiCl_2${P(*n*-Bu)Ph_2}$_2$]. To a solution of P(*n*-Bu)Ph_2 (0.458 g, 1.89 mmol) in CH_2Cl_2 (20 mL) was added 0.9 equiv of [$NiCl_2$(DME)] (0.373 g, 1.70 mmol), and the solution was stirred for 2 h at room temperature. After 5 min, a color change from yellow-green to violet was observed. The solvent was evaporated under reduced pressure. The violet residue was dissolved in CH_2Cl_2 (15 mL), this solution was filtered through Celite, and the Celite was washed with CH_2Cl_2 (10 mL). The filtrate was evaporated, giving the product as a violet solid, which was dried in vacuo overnight. Yield: 0.924 g, 1.51 mmol, 88%. Anal. Calcd for $C_{32}H_{38}Cl_2NiP_2$: C, 62.58; H, 6.24. Found: C, 62.90; H, 6.30.

Reaction of Lithiated 12 with *trans*-[NiCl(Ph)(PPh_3)$_2$]. A solution of **12** (0.645 g, 1.86 mmol) in THF (30 mL) was cooled to −78 °C. After 15 min, 1.1 equiv of *n*-BuLi (1.6 molar solution in hexane, 1.28 mL, 2.05 mmol) was added and the reaction mixture was stirred for 30 min. A solution of *trans*-[NiCl(Ph)(PPh_3)$_2$] (1.29 g, 2.05 mmol) in toluene (30 mL) was transferred to the solution of the deprotonated ligand **28**. The solution was stirred for 12 h at room temperature. The dark red reaction mixture was filtered over Celite, and the solvent

Table 7. X-ray Experimental Data

	10	**19**	**24**	$[NiCl_2\{P(n\text{-}Bu)Ph_2\}_2]$
formula	$C_{19}H_{22}NOP$	$C_{36}H_{40}Br_4N_2Ni_2O_2P_2$	$C_{20}H_{24}Cl_2NNiOP$	$C_{32}H_{38}Cl_2NiP_2$
fw	311.37	1031.74	455.01	614.18
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$Pca2_1$	$P2_1/n$	$Pna2_1$	$Pna2_1$
a, Å	10.7839(3)	11.7810(9)	17.9824(2)	16.152(1)
b, Å	9.4726(4)	12.447(1)	8.0761(8)	19.663(1)
c, Å	17.2463(8)	13.2950(8)	14.753(1)	9.794(1)
β, deg		95.859(4)		
V, Å^3	1761.7(2)	1939.4(4)	2142.5(3)	3110.4(4)
Z	4	2	4	4
color	colorless	violet	violet	blue
cryst dimens (mm)	0.20 × 0.20 × 0.16	0.20 × 0.14 × 0.12	0.14 × 0.10 × 0.06	0.15 × 0.12 × 0.10
ρ(calcd), g cm^{-3}	1.17	1.77	1.41	1.312
μ(Mo Kα), mm^{-1}	1.17	5.208	1.238	0.918
T, K	173	173	294	293
θ limits (deg)	2.5−27.47	2.5−27.50	2.5−27.49	2.07−30.08
no. of data measd	4053	14942	4920	8843
no. of data, $I > 3\sigma(I)$	2662	3073	3044	6162
no. of variables	198	217	234	334
R	0.035	0.030	0.035	0.0714
R_w	0.043	0.038	0.046	0.1769
GOF	1.009	1.025	1.052	1.043
largest peak in final diff map (e Å^{-3})	0.249	0.762	0.553	0.997

was evaporated under reduced pressure. The orange-red solid collected after cooling was washed with hexane (50 mL) and dried under vacuum for 24 h. $^{31}P\{^1H\}$ NMR ($CDCl_3$; selected data): δ 25.5 (s, $CHPPh_2$).

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 was used. The necessary amount of complex for six catalytic runs was dissolved in 60 mL of toluene. For each catalysis, 10 mL of this solution was injected into the reactor. Depending on the amount of cocatalyst added, between 0 and 5 mL of solvent was added so that the total volume of all solutions was 15 mL. This can be summarized by the equation

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

When MAO was used as cocatalyst, the total volume was increased to 20 mL. After injection of the catalyst solution under a constant low flow of ethylene, the reactor was brought to working pressure and continuously fed with ethylene, using a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. The temperature increase observed resulted solely from the exothermicity of the reaction. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test, the reactor was cooled to 10 °C before 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 to 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. The catalytic results are presented in Tables 5 and 6.

Crystal Structure Determinations of 10, 19, 24, and $[NiCl_2\{P(n\text{-}Bu)Ph_2\}_2]$. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The relevant data are summarized in Table 7. Data were collected using ψ scans, the structures were solved by direct methods using the SHELX 97 software,[55,56] 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-H} = 0.95 Å, U_{11} = 0.04). Full data collection parameters and structural data are available as Supporting Information. Crystallographic data for all structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 227819−227822. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (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 and angles, and anisotropic thermal parameters and ORTEP views for **10**, **19**, **24** and $[NiCl_2\{P(n\text{-}Bu)Ph_2\}_2]$; X-ray data as CIF files are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034197Q

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