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Dinuclear Nickel Complexes with Bidentate N,O Ligands: Synthesis, Structure, and Catalytic Oligomerization of Ethylene[†]

Fredy Speiser and Pierre Braunstein*

Laboratoire de Chimie de Coordination (UMR 7513 CNRS), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France

Lucien Saussine

Institut Français du Pétrole, Direction Catalyse et Séparation, CEDI René Navarre, BP 3, F-69390 Vernaison, France

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The new dicationic dinuclear complexes $[Ni(\mu\text{-}Cl)_2(N,OH)_2]Cl_2$ (**11**, N,OH = 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-propan-2-ol; **12**, N,OH = 2-pyridin-2-yl-propan-2-ol) were prepared in good yields and evaluated as precatalyts in the oligomerization of ethylene, using MAO or $AlEtCl_2$ as cocatalyst. These paramagnetic complexes were characterized by single-crystal X-ray diffraction in the solid state and in solution with the help of the Evans method, which revealed agreement between the octahedral coordination spheres found in solution and in the solid state. The N donor atoms of each chelating ligand are in mutual cis position, and the OH donors are mutually trans situated. Selectivities for 1-butene within the C_4 fraction of 61% (**11**) and 58% (**12**) were observed in the presence of 200 equiv of MAO, but better turnover frequencies (28 300 (**11**) and 20 400 (**12**) mol of C_2H_4/(mol of Ni•h)) were obtained when 800 equiv of MAO was used. In the presence of 6 equiv of $AlEtCl_2$, the activities were considerably increased, up to 174 300 (**11**) and 97 100 (**12**) mol of C_2H_4/(mol of Ni•h), and the selectivity for C_4 olefins was 70% and 64%, respectively.

Introduction

Chelating ligands play a central role in the development of late transition metal catalysts for oligomerization and polymerization of olefins in both academic and industrial sectors.[1−4] They allow one to fix the active coordination sites of tetracoordinated Ni(II) or Pd(II) complexes in a cis-arrangement, which favors the migratory insertion of an olefin in the metal−alkyl bond and thus chain growth. Chain transfer can then result from an associative displacement step following β-H transfer to the metal or from direct β-H transfer to the incoming monomer. The metal−hydride intermediate can lead to the formation of terminal or internal olefins. Both the catalytic ethylene oligomerization providing α-olefins in the highly desirable C_6-C_{20} range for their use in the preparation of detergents, plasticizers, and fine chemicals and as comonomers for the synthesis of linear low-density polyethylene and the dimerization of olefins catalyzed by transition metal complexes are of considerable industrial relevance.[5] Anionic bidentate P,O and neutral N,N chelating ligands occupy central positions due to the successful developments of the SHOP system **1**[1d,k−n,p] and the DuPont Versipol diimine N,N system **2**.[1e,f,j,k,o,q] Since Grubbs and co-workers reported the synthesis of N,O salicylaldiminate Ni complexes of type **3** which are able to polymerize olefins even in water,[3] anionic N,O chelating ligands are receiving increased attention in ethylene chemistry.[2−4] Increasing the steric bulk around the axial sites of the nickel center changes the nature of the products from butenes (rapid chain transfer reaction) to oligomers or polymers.[2p,q] Brookhart's group also reported the preparation of Ni(II) systems **4** bearing an anionic, amide-type five-membered N,O chelate,[4] in contrast to the six-membered ring of the Grubbs systems **3**. Complexes **3** and **4** are very active catalysts for the polymerization of ethylene, even when no cocatalyst is added.[3b,4] Very recently, a binuclear Ni(II) 2,5-disubstituted amino-*p*-benzoquinone complex was reported which shows high activity for ethylene polymerization without any cocatalyst[6] whereas

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[*] Author to whom correspondence should be addressed. E-mail: braunst@chimie.u-strasbg.fr. Fax: +33-390 241 322.

[†] Dedicated to Professor R. Schmutzler on the occasion of his 70th birthday, with our congratulations and best wishes.

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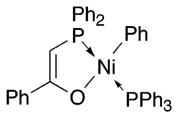
a binuclear Ni(II) cyclotetraphosphine complex activated with methylalumoxane (MAO) oligomerized ethylene to C_4-C_{14} olefins.[7]



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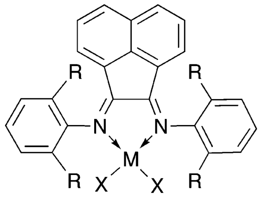
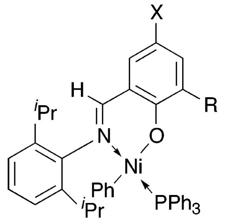


2

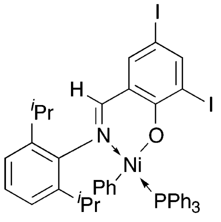
R = H, CH_3, ^{i}Pr



3 a

R = H, CH_3, ^{t}Bu, 9-phenanthrenyl

X = H, OCH_3, NO_2



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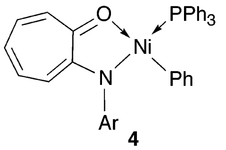
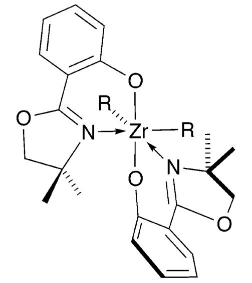


4

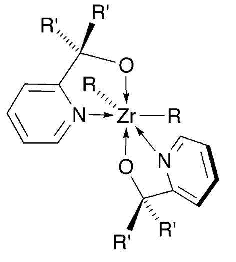
Ar = $C_6H_3(^i\mathrm{Pr})_2$

In contrast, the Zr complexes **5** and **6** with anionic N,O ligands derived from oxazoline– and pyridine–alcohols were reported to have low activities in ethylene polymerization.[8]



5

R = CH_2Ph



6

R = CH_2Ph

R' = CH_3, CF_3, $Si(CH_3)_3$

Following our recent studies on the catalytic oligomerization of ethylene involving Ni(II) complexes with *anionic* phosphinoamide P,N ligands, such as **7** and **8**,[9a,b] or SHOP-type P,O chelates,[9b,c] or Ni(II) complexes with *neutral* P,N chelates (where N belongs to a pyridine or oxazoline moiety),[10] we were interested in obtaining short-chain oligomers using Ni(II) complexes with other heterobidentate chelating ligands. As part of our more general interest in

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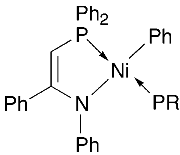
the synthesis and catalytic applications of hybrid ligands containing an oxygen-based functionality,[11] we have considered in this work N,O ligands, which tend to show a preference for the formation of longer chain oligomers,[12,13] to gain a better insight into the influence of the donor atoms bound to the Ni(II) center.



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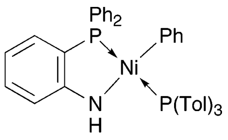


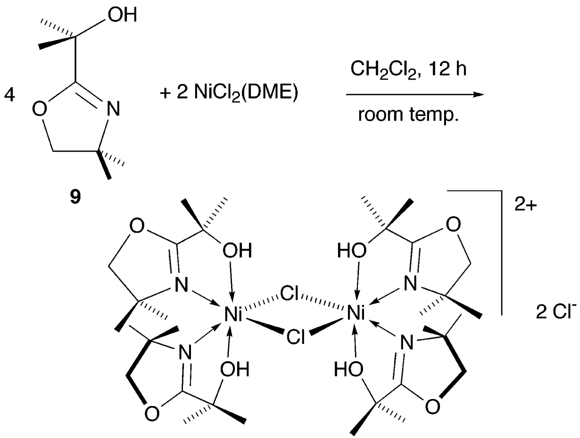
8

We have used the ligands 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propan-2-ol (**9**)[14] and 2-pyridin-2-yl-propan-2-ol (**10**)[15] and characterized the new dinuclear nickel complexes $[\mathrm{Ni}(\mu\text{-Cl})_2(\mathrm{N,OH})_2]\mathrm{Cl}_2$ (**11**, N,OH = oxazoline−alcohol **9**; **12** (N,OH = pyridine−alcohol **10**)) (see below), which were examined as precatalysts for the oligomerization of ethylene, using $\mathrm{AlEtCl_2}$ or methylalumoxane (MAO) as cocatalysts.

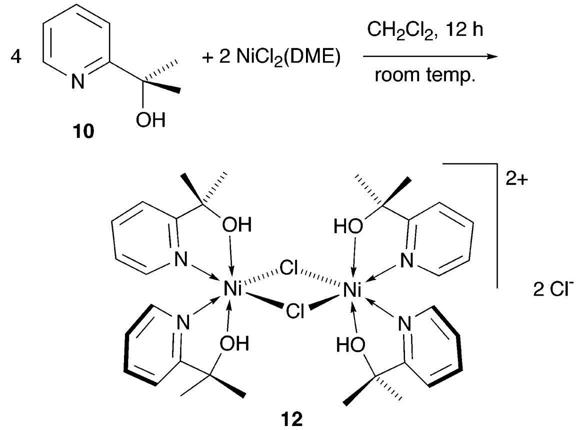
Results and Discussion

The ligand **9** was prepared by a slightly modified literature method,[14] by heating 2-hydroxyisobutyric acid and 2-amino-2-methylpropanol up to 170 °C in xylene until no further formation of water was observed in a Dean−Stark trap.[10a] The ligand **10** was prepared by metalation of 2-bromopyridine and subsequent reaction with acetone at −78 °C. After workup, it was isolated in 60% yield.[10a,15]

The Ni(II) complexes **11** and **12** were prepared by reacting 1 equiv of $[\mathrm{NiCl_2(DME)}]$ with 2 equiv of the corresponding alcohol for 12 h in $\mathrm{CH_2Cl_2}$ at 25 °C. After workup, the Ni complexes were isolated in 75 and 79% yields, respectively (eqs 1 and 2). All the complexes are paramagnetic and were therefore best characterized by X-ray diffraction (Figures 1 and 2). Their magnetic moment was determined by the Evans method.[16−18] Magnetic moments of 2.92 and 3.12 μ_B were found for complexes **11** and **12**, respectively, consistent with an octahedral coordination geometry in solution for which literature values are usually found in the range 2.9−3.2 μ_B.[19−23]



(1)



(2)

The X-ray structure of the oxazoline alcohol complex **11** (Figure 1) shows a dinuclear, centrosymmetric molecule containing two chloride bridges and mutually cis nitrogen and trans OH donors, respectively. The Ni−O(1) and Ni−O(2) distances of 2.124(2) and 2.104(2) Å, respectively, correspond to those found in the literature (2.093 ± 0.073 Å)[24] for a dative bond between an alcohol and Ni(II). All other distances and angles are in the expected range (Table 1). The octahedral coordination sphere of the Ni centers is distorted, as indicated by the bond angles around the metal (Table 1). Two chloride ions are present in the asymmetric unit to compensate for the doubly positive charge of the complex. They display no significant bonding interaction with the complex (Ni−Cl(2)/Cl(2′) = 4.26 Å).

The X-ray structure of the pyridine alcohol complex $\mathbf{12}\cdot 2\mathrm{CH_2Cl_2}$ (Figure 2) also shows, like in **11**, a centrosymmetric

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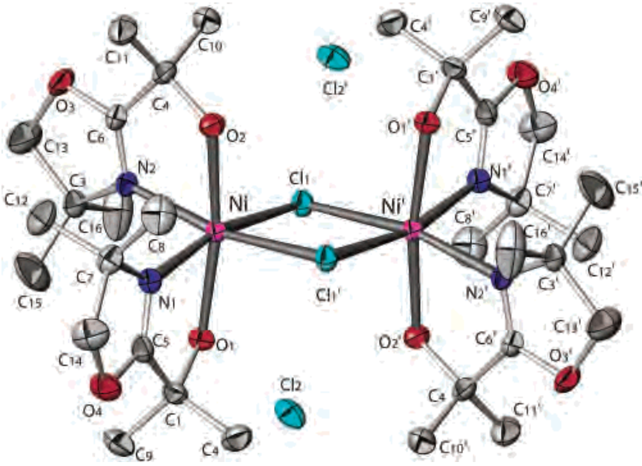

Figure 1. ORTEP view of the structure of the oxazoline alcohol complex **11** with thermal ellipsoids drawn at the 50% probability level.

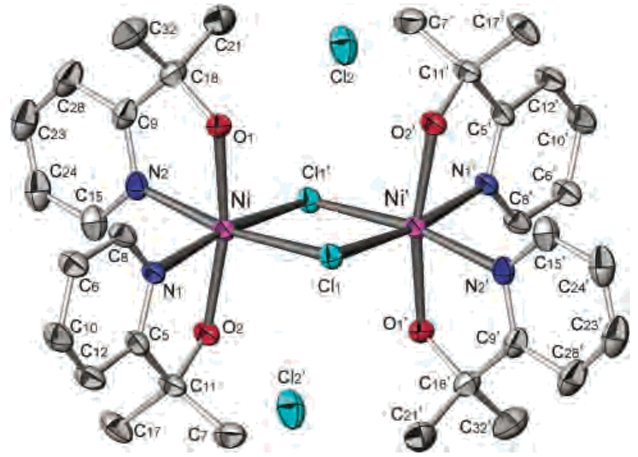

Figure 2. ORTEP view of the structure of the pyridine alcohol complex **12** in **12**·2CH$_2$Cl$_2$ with thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) in Complex **11**

Ni−O(1)	2.124(2)	C(1)−O(1)	1.438(3)
Ni−N(1)	2.098(2)	Ni−O(2)	2.104(2)
Ni−Cl(1)	2.420(1)	Ni−N(2)	2.101(2)
Ni−Cl(1′)	2.440(1)	N(2)−C(6)	1.266(3)
N(1)−C(5)	1.270(3)	C(6)−C(2)	1.503(4)
C(5)−C(1)	1.504(4)	C(2)−O(2)	1.438(3)
Cl(1)−Ni−Cl(1′)	83.15(3)	N(1)−Ni−N(2)	93.01(8)
Cl(1)−Ni−O(1)	95.53(6)	O(2)−Ni−O(1)	170.92(7)
C(1)−O(1)−Ni	117.9(2)	Cl(1)−Ni−O(2)	95.58(6)
O(1)−C(1)−C(5)	103.7(2)	C(2)−O(2)−Ni	118.3(1)
C(1)−C(5)−N(1)	125.0(2)	O(2)−C(2)−C(6)	103.6(2)
C(5)−N(1)−Ni	114.3(2)	C(2)−C(6)−N(2)	124.8(2)
N(1)−Ni−O(1)	76.23(8)	N(2)−Ni−Cl(1′)	167.12(6)
N(1)−Ni−Cl(1′)	166.42(6)	N(2)−Ni−Cl(1)	94.66(7)
N(1)−Ni−Cl(1)	91.76(6)	N(2)−Ni−O(2)	76.54(8)

Table 2. Selected Bond Distances (Å) and Angles (deg) in Complex **12**·2CH$_2$Cl$_2$

Ni−O(1)	2.054(4)	C(11)−O(2)	1.432(6)
Ni−O(2)	2.057(3)	Ni−O(2)	2.057(3)
Ni−N(1)	2.080(4)	Ni−N(2)	2.075(5)
Ni−Cl(1)	2.401(2)	N(2)−C(9)	1.361(7)
Ni−Cl(1′)	2.430(2)	C(9)−C(18)	1.490(9)
N(1)−C(5)	1.340(6)	C(18)−O(1)	1.439(7)
C(5)−C(11)	1.497(7)		
Cl(1′)−Ni−Cl(1)	85.26(5)	O(2)−Ni−O(1)	167.8(2)
Cl(1)−Ni−O(1)	95.4(1)	Cl(1)−Ni−O(2)	96.4(1)
C(11)−O(2)−Ni	119.8(3)	C(18)−O(1)−Ni	119.5(3)
O(2)−C(11)−C(5)	106.3(4)	O(1)−C(18)−C(9)	106.7(4)
C(11)−C(5)−N(1)	118.7(4)	C(18)−C(9)−N(2)	119.3(5)
C(5)−N(1)−NI	116.4(3)	C(9)−N(2)−Ni	115.3(4)
N(1)−Ni−O(1)	94.4(2)	N(2)−Ni−Cl(1)	169.3(1)
N(1)−Ni−Cl(1′)	170.1(1)	N(2)−Ni−Cl(1′)	92.7(11)
N(1)−Ni−Cl(1)	93.9(1)	N(1)−Ni−N(2)	89.9(2)
N(1)−Ni−N(2)	89.9(2)	N(2)−Ni−O(2)	94.21(8)

dinuclear molecule with two chloride bridges and mutually cis nitrogen and trans OH donors, respectively. The Ni−O distances of 2.054(4) and 2.057(3) Å, respectively, correspond to a dative bond between an alcohol and a Ni(II) center, as observed with complex **11** (Table 2). The metal coordination sphere in **12** is more distorted than in **11**, as shown by the O(1)−Ni−O(2) angle of 167.8(2)°.

Catalytic Oligomerization of Ethylene with the Ni(II) Complexes 11 and 12. Complexes **11** and **12** were evaluated and compared as precatalysts in the oligomerization of ethylene to examine the influence of the basicity of the nitrogen donor on the catalytic performances of the complexes. As cocatalysts 200, 400, or 800 equiv of MAO or 6 equiv of AlEtCl$_2$ was used. The ethylene dimerization catalyst [NiCl$_2$(PCy$_3$)$_2$] was used as reference.[25a,b]

Turnover frequencies of 15600 (**11**) and 5000 (**12**) mol of C$_2$H$_4$/(mol of Ni·h) were observed in the presence of 200 equiv of MAO which increased to 18 800 (**11**) and 6800 (**12**) mol of C$_2$H$_4$/(mol of Ni·h) when 400 equiv of MAO was used (Table 3). They increased up to 28 300 (**11**) and 20 400 (**12**) mol of C$_2$H$_4$/(mol of Ni·h) when 800 equiv of MAO was used (Figure 3). All catalysts were still active when the reactions were quenched by injection of 10 mL of ethanol since ethylene consumption was not finished. For comparison, [NiCl$_2$(PCy$_3$)$_2$] showed no catalytic activity in the presence of MAO.

Complexes **11** and **12** proved to be good ethylene dimerization catalysts as selectivities of 77−88% were observed for the C$_4$ products. Therefore, only 1-butene will be considered for the α-olefin selectivities.

Complexes **11** and **12** showed selectivities for 1-butene of 39% (**11**) and 42% (**12**) in the presence of 800 equiv of MAO, which increased to 56% (**11**) and 49% (**12**) when 400 equiv of cocatalyst was used. Selectivities for 1-butene within the C$_4$ fraction of 61% (**11**) and 58% (**12**) were obtained when 200 equiv of MAO was used (Figure 4).

The Ni complexes **11** and **12** were also tested in the oligomerization of ethylene using AlEtCl$_2$ as cocatalyst (Table 4). In the presence of 2 equiv of AlEtCl$_2$, all three complexes were inactive. However, activities of 27 200 ([NiCl$_2$(PCy$_3$)$_2$]), 174 300 (**11**), and 97 100 (**12**) mol of C$_2$H$_4$/(mol of Ni·h) were found in the presence of 6 equiv of AlEtCl$_2$. For **11**, **12**, and [NiCl$_2$(PCy$_3$)$_2$], C$_4$ and C$_6$ oligomers were the main products and C$_8$ olefins were only observed in small quantities. Selectivities for 1-butene within the C$_4$ fraction were 9% (**11**), 11% (**12**), and 9% ([NiCl$_2$(PCy$_3$)$_2$]).

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(25) (a) Commereuc, D.; Chauvin, Y.; Léger, G.; Gaillard, J. *Rev. Inst. Fr. Pet.* **1982**, *37*, 639−649. (b) Knudsen, R. D. *Prepr. Pap.*—*Am. Chem. Soc., Div. Pet. Chem.* **1989**, 572−576. (c) Birdwhistell, K. R.; Lanza, J. *J. Chem. Educ.* **1997**, *74*, 579. (d) Chen, H.-P.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2003**, *22*, 4893−4899.

Table 3. Catalytic Data for Complexes **11** and **12** in the Oligomerization of Ethylene Using MAO as Cocatalyst[a,b]

	11	**11**	**11**	**12**	**12**	**12**
MAO (equiv)	200	400	800	200	400	800
selectivity C_4 (mass %)	88	84	77	87	83	81
selectivity C_6 (mass %)	11	14	19	12	15	17
selectivity C_8 (mass %)	2	2	4	1.5	2.5	2
productivity (g of C_2H_4/(g of Ni·h))	7400	9000	13 500	2400	3200	9700
TOF (mol of C_2H_4/(mol of Ni·h))	15 600	18 800	28 300	5000	6800	20 400
α-olefin (C_4) (mol %)	61	56	39	58	49	42
k_α[c]	<0.10	0.11	0.16	<0.10	0.12	0.14

[a] Conditions: $T = 30$ °C; 10 bar C_2H_4; 35 min; 1.05×10^{-2} mmol of Ni complex; 20 mL of toluene solvent. [b] No $C_{10}-C_{12}$ oligomers were detected. [c] k_α = hexenes [mol]/butenes [mol].

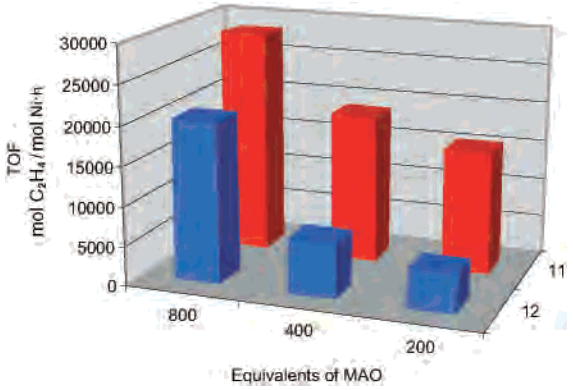

Figure 3. Activity of complexes **11** and **12** in the oligomerization of ethylene using different quantities of MAO as cocatalyst. Conditions: $T = 30$ °C; 10 bar C_2H_4; 35 min; 1.05×10^{-2} mmol of Ni; 20 mL of toluene.

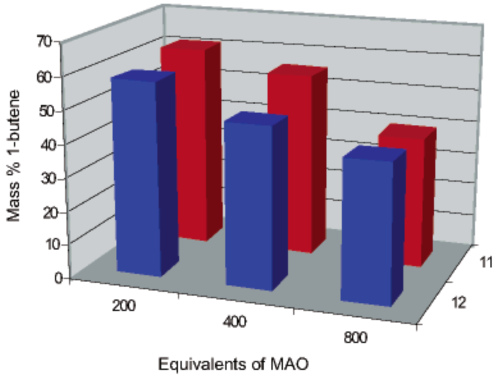

Figure 4. Selectivity of complexes **11** and **12** for 1-butene using different quantities of MAO. Conditions: $T = 30$ °C; 10 bar C_2H_4; 35 min, 1.05×10^{-2} mmol of Ni; 20 mL of toluene.

It is relevant to mention here that other dinuclear Ni(II) complexes have very recently been successfully studied for the catalytic oligomerization or polymerization of ethylene.[6,7]

Conclusion

The hexacoordinated dinuclear complexes **11** and **12**, containing two chelating oxazoline−alcohol or pyridine−alcohol ligands around each metal center, have been prepared in good yields and were characterized by single-crystal X-ray diffraction in the solid state and in solution by the Evans method to have octahedral Ni(II) centers in solution and in the solid state. They were evaluated as precatalysts for the oligomerization of ethylene using MAO or $AlEtCl_2$ as cocatalyst. In the presence of 200 equiv of MAO, precatalysts **11** and **12** led mostly to butenes, 88% and 87%, respectively, with a selectivity for 1-butene within the C_4 fraction of 61% (**11**) and 58% (**12**). Increasing the amount of MAO to 800 equiv led to an increase in the activity, with turnover frequencies up to 28 300 (**11**) and 20 400 (**12**) mol of C_2H_4/(mol of Ni·h). In the presence of 6 equiv of $AlEtCl_2$ the activities were considerably increased, to 174 300 (**11**) and 97 100 (**12**) mol of C_2H_4/(mol of Ni·h), with a selectivity for C_4 olefins of 70% and 64%, whereas the selectivity for 1-butene within the C_4 fraction decreased to 11% (**11**) and 9% (**12**), respectively. These low selectivities could be due to reversible β-H elimination after ethylene insertion and reinsertion of the olefin with the opposite regiochemistry to give 2-butene after chain transfer or to isomerization of 1-butene by a reuptake mechanism. Many Ni(II) complexes have been shown to isomerize α-olefins.[25c,d] It is likely that the dinuclear nature of our precatalysts is not retained during catalysis owing to the presence of the Lewis acid cocatalyst that will tend to open the chloride bridges. The nature of the cocatalyst could therefore be particularly sigificant,[26] as observed experimentally. However, these dinuclear structures provide an interesting "reservoir" of active species. The k_α values given in the Tables 3 and 4 correspond to the ratio hexenes [mol]/butenes [mol] and not to a Schultz−Flory constant since our catalysts are mainly dimerization and trimerization catalysts.

Table 4. Comparative Catalytic Data for Complexes **11**, **12**, and $[NiCl_2(PCy_3)_2]$ in the Oligomerization of Ethylene Using $AlEtCl_2$ as Cocatalyst[a,b]

	11	**12**	$[NiCl_2(PCy_3)_2]$
$AlEtCl_2$ (equiv)	6	6	6
selectivity C_4 (mass %)	70	64	86
selectivity C_6 (mass %)	28	33	14
selectivity C_8 (mass %)	2	3	0.5
productivity (g of C_2H_4/(g of Ni·h))	83 300	46 400	13 000
TOF (mol of C_2H_4/(mol of Ni·h))	174 300	97 100	27 200
α-olefin (C_4) (mol %)	9	11	9
k_α[c]	0.26	0.34	0.11

[a] Conditions: $T = 30$ °C; 10 bar C_2H_4; 35 min; 1.05×10^{-2} mmol of Ni; 4.0×10^{-2} mmol of $[NiCl_2(PCy_3)_2]$; 15 mL of toluene solvent. [b] No $C_{10}-C_{12}$ oligomers were detected. [c] k_α = hexenes [mol]/butenes [mol].

Our results also illustrate the influence of the basicity of the nitrogen donor and suggest that in these systems a less basic nitrogen moiety leads to an increased α-olefin selectivity and to higher turnover frequencies. A similar trend was observed when $AlEtCl_2$ was used instead of MAO. It remains difficult to generalize such considerations, and it was recently found with other Ni(II) complexes that phosphinitopyridine chelates (**13** and **14**) led to more active catalysts than

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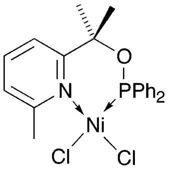
(26) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.

phosphinitooxazolines (**15**), in which the nitrogen donor is less basic, when 1.3 or 2 equiv of $AlEtCl_2$ was used, although no notable difference was observed in the presence of 6 equiv of the cocatalyst.[10a]



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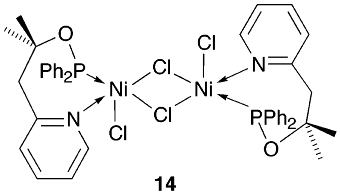

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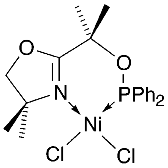

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Experimental Section

All solvents were dried and distilled using common techniques unless otherwise stated. $NiCl_2 \cdot 6H_2O$ was dried by heating for 6 h at 160 °C under vacuum. $[NiX_2(DME)]$ (X = Cl, Br)[27] and the ligands 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-propan-2-ol (**9**)[14] and 2-pyridin-2-ylpropan-2-ol (**10**)[15] were prepared according to the literature, with modifications in the latter cases.[10a] Other chemicals were obtained from commercial sources and were used without further purification unless otherwise described. IR spectra in the range 4000−400 cm^{-1} were recorded on a Bruker IFS66FT and a Perkin-Elmer 1600 Series FTIR. Gas chromatographic analyses were performed on an Thermoquest GC8000 Top Series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness).

Synthesis of [Ni(μ-Cl)$_2${2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propan-2-ol}$_2$]Cl$_2$ (11). To a solution of **9** (0.700 g, 4.45 mmol) in CH_2Cl_2 (30 mL) was added 0.5 equiv of $[NiCl_2(DME)]$ (0.474 g, 2.29 mmol), and the reaction mixture was stirred for 12 h at room temperature. Then the solution was filtered through Celite to separate unreacted $[NiCl_2(DME)]$, and the Celite was washed with CH_2Cl_2 (30 mL). The organic phases were pooled, and the solvent was evaporated. The yellow green solid was dissolved in 20 mL of toluene and precipitated by the addition of hexane (40 mL). The yellow green precipitate was allowed to settle, the supernatant organic phase removed with a cannula, and the solid dried under vacuum yielding a yellow green powder. Yield: 0.911 g, 2.0 mmol, 75%. IR (CH_2Cl_2): 1662 cm^{-1} ($\nu_{C=N}$). Anal. Calcd for $C_{32}H_{60}Cl_4N_4Ni_2O_8$: C, 43.28; H, 6.81; N, 6.31. Found: C, 43.90; H, 6.50; N, 6.20.

Synthesis of [Ni(μ-Cl)$_2$(2-pyridin-2-ylpropan-2-ol)$_2$]Cl$_2$ (12). To a solution of **10** (0.354 g, 2.58 mmol) in CH_2Cl_2 (30 mL) was added 0.5 equiv of $[NiCl_2(DME)]$ (0.274 g, 1.29 mmol), and the reaction mixture was stirred for 12 h at room temperature. Reaction conditions and workup were similar to those for **11**, affording a yellow green powder. Yield: 0.518 g, 0.51 mmol, 79%. Anal. Calcd for $C_{32}H_{44}Cl_4N_4Ni_2O_4$: C, 47.57; H, 5.49; N, 6.93. Found: C, 47.95; H, 5.15; N, 7.00. Single crystals of **12**$\cdot 2CH_2Cl_2$ suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.

Table 5. X-ray Experimental Data for the Dinuclear Complexes **11** and **12**$\cdot 2CH_2Cl_2$

	11	**12**$\cdot 2CH_2Cl_2$
formula	$C_{32}H_{60}Cl_4N_4Ni_2O_8$	$C_{32}H_{44}Cl_4N_4Ni_2O_4 \cdot 2CH_2Cl_2$
M_r	888.1	486.88
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.018(5)	10.203(5)
b (Å)	10.698(5)	11.204(5)
c (Å)	11.480(5)	21.881(5)
V (Å^3)	1061.4	2471.5
Z	1	2
color	yellow	yellow
cryst dimens (mm)	0.15 × 0.12 × 0.10	0.15 × 0.12 × 0.10
D_{calc} (g cm^{-3})	1.389	1.308
F(000)	468	1000
μ (mm^{-1})	1.187	1.229
temp (K)	173(2)	173(2)
wavelength (Å)	0.710 69	0.710 69
radiation	Mo Kα graphite monochromated	
diffractometer	KappaCCD	
scan mode	ϕ scans	
hkl limits	−12, 14/ −14, 15/0, 16	−13, 13/0, 14/ 0, 28
θ limits (deg)	2.36/30.00	2.54/27.44
no. of data measd	6129	5354
no. of data with $I > 2\sigma(I)$	4056	3531
no. of variables	226	228
R	0.0460	0.0746
R_w	0.0963	0.2312
GOF	0.870	1.030
largest peak in final diff (e/Å^3)	0.530	0.947

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. Experiments with **11** and **12** were carried out with 1.05×10^{-2} mmol of Ni complex as catalyst, and the amount of complex needed for 6 catalytic runs was dissolved in 60 mL of toluene. The complex $[NiCl_2(PCy_3)_2]$ was taken for comparative purposes (4×10^{-2} mmol of Ni). For each catalysis, 10 mL of this solution was injected into the reactor. Depending on the amount of cocatalyst added, between 0 and 5 mL of solvent was added so that the total volume of all solutions was 15 mL. This can be summarized by the following equation: 10 mL (Ni solution) + y mL (solvent) + z mL (cocatalyst solution) = 15 mL.

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 gazeous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by addition of ethanol (10 mL), transferred in a Schlenk flask, and separated from the metal complexes by trap-to-trap distillation (120 °C, 20 Torr). All volatiles were evaporated (120 °C, 20 Torr static pressure) and recovered in a second flask previously immersed in liquid nitrogen to avoid any loss of product. For gas chromatographic analyses, 1-heptene was used as internal reference. The catalytic results are presented in Tables 3 and 4.

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(27) Cotton, F. A. *Inorg. Synth.* **1971**, *13*, 160−164.

X-ray Structure Determinations of 11 and 12·2CH$_2$Cl$_2$. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The relevant data are summarized in Table 5. Data were collected using ϕ-scans, the structures were solved by direct methods using the SHELX 97 software,[28,29] 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, $U_{11} = 0.04$), except for the hydrogen atoms of the CH$_2$Cl$_2$ molecules of crystallization in **12**·2CH$_2$Cl$_2$ which were omitted owing to disorder. 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, Nos. CCDC 224691 and 224692. 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: X-ray data for **11** and **12**·2CH$_2$Cl$_2$, in CIF format, and ORTEP plots with complete atom numbering for both structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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

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