Synthesis of nickel complexes with bidentate N,O-type ligands and application in the catalytic oligomerization of ethylene†‡§¶

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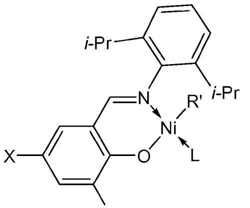
The dinuclear complexes [Ni(μ-Cl){(4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol}]$_2$Cl$_2$ **14** and [Ni(μ-Cl){(pyridin-2-yl)methanol}]$_2$Cl$_2$ **16** have been synthesized in high yields by reaction of NiCl$_2$ with 2 mol. equiv. of the ligands 4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol **13** or (pyridin-2-yl)methanol **15**, respectively. The reaction of NiCl$_2$ with 3 mol. equiv. of **15** afforded in high yield the mononuclear, octahedral *mer*-[Ni{(pyridin-2-yl)methanol}$_3$Cl$_2$] complex **18**. The reaction of **16** with NaH led to the deprotonation of one of the pyridine alcohol ligands to form [Ni{(pyridin-2-yl)methanol}{(pyridin-2-yl)methanolate}Cl] **21** in which the metal is coordinated by one pyridine alcohol and one pyridine alcoholate ligand. The crystal structures of the dinuclear, chloride-bridged octahedral complexes in **14**·C_6H_{12} and in **16**·3CH_2Cl_2 and of the mononuclear, octahedral complex **18** in **18**·CH_2Cl_2 have been determined by X-ray diffraction. In the latter case, intermolecular OH · · · Cl bonding interactions generate a centrosymmetric pseudo-dimer. Complexes **14**, **16** and **21** have been tested in ethylene oligomerization with AlEtCl$_2$ (Al/Ni ratios of 2, 4 or 6) or MAO (50, 100 or 200 equiv.) as co-catalysts under 10 bar of ethylene and yielded mostly dimers and trimers. Complex **16** in the presence of 6 equiv. of AlEtCl$_2$ proved to be the most active system with a turnover frequency (TOF) up to 187 500 C_2H_4 (mol Ni h)$^{-1}$. Complex **16** with 200 equiv. of MAO was also the most active, with TOF up to 104 300 C_2H_4 (mol Ni h)$^{-1}$ under 30 bar of ethylene.

Introduction

Olefin polymerization catalyzed by late transition metal complexes has been intensively developed for the production of low-density polyethylene (LDPE) and high-density polyethylene (HDPE).[1–5] However, the discovery of the 'nickel effect" in catalytic olefin chemistry highlighted the oligomerizing character of nickel catalysts which favour chain transfer over chain growth.[6,7] The high industrial demand for linear α-olefins (LAO), particularly in the C_4–C_{20} range, has emphasized the key role of nickel complexes as catalysts.[8–10] The use of heteroditopic ligands, including bidentate P,O,[11,12] P,N[13] and N,O[14,15] -type ligands, allows a fine tuning of the catalytic properties of their Ni(II) complexes in olefin oligomerization.

The high activity and selectivity in LAO of the SHOP process[16–18] has generated a considerable interest for nickel complexes with a P,O-type ligands in catalytic ethylene oligomerization.[11,19–24] Based on a neutral phenyl nickel complex, it produces a Schulz–Flory mass distribution of the α-olefins and has inspired the synthesis of numerous nickel catalysts with P,N[25–27] and N,O[28] -type ligands. Neutral nickel catalysts with N,O-type ligands proved to be active for ethylene polymerization without cocatalyst and these include complexes described by the groups of Grubbs (type **1**),[14,15,29] Mecking[30–32] (type **2**) and others[33–37] with salicylaldimine ligands or by Brookhart and co-workers with anilinotropone ligands (type **3**) or anilinoperinaphthenone ligands (type **4**).[38–40]



R = I, H, *t*-Bu, Ph,...
R' = Ph, Me
X = I, H, OMe, NO_2
L = PPh_3, Py, MeCN

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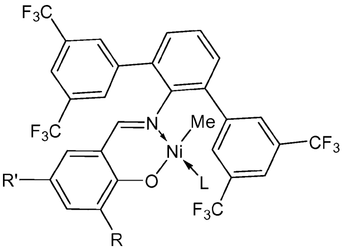

R = I, 9-anthryl
R' = I, H
L = Py, TPPTS, TPPDS, H_2N-PEG

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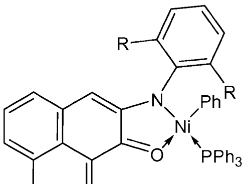

R = Me, *i*-Pr

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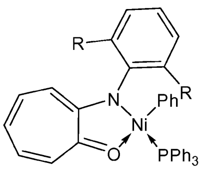

R = Me, *i*-Pr, *t*-Bu, Ph, F, Br, CF_3

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† Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

‡ The HTML version of this article has been enhanced with colour images.

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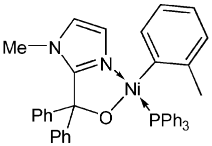
¶ Electronic supplementary information (ESI) available: Selected hydrogen bonding interactions in the structures of **14**·C_6H_{12}, **16**·3CH_2Cl_2 and **18**·CH_2Cl_2 (Tables S1–S3). See DOI: 10.1039/b716111e

Other neutral nickel complexes with anionic N,O⁻ ligands, such as the imidazole-alcoholate complexes **5**,[41] iminocarboxamide complexes **6**[42] and 2-(alkylideamino)benzoate complexes **7**,[43] form active catalysts for the oligomerization or polymerization of ethylene without any cocatalyst. In these cases, ethylene insertion in the Ni–aryl or Ni–alkyl bond represents the first step of the reaction and is followed by β-H migration, leading to olefin elimination and formation of a nickel–hydride complex, which is the active species.



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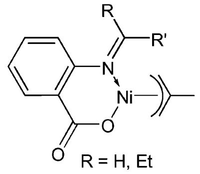
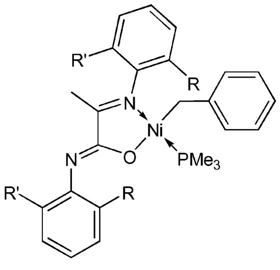


R = H, Et
R' = Et, *t*-Bu

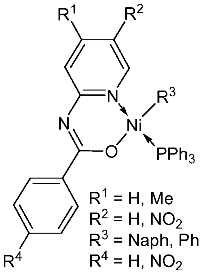
7



R = R' = Me, Et, *i*-Pr

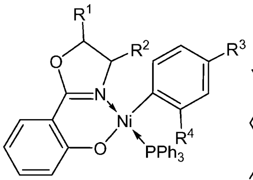
6

However, many nickel precatalysts with N,O-type ligands have to be activated with a co-catalyst, such as alkylaluminiums or $B(C_6F_5)_3$. This is the case with the ligands salicylaldimines,[44–49] *N*-(2-pyridyl)benzamides (in **8**),[50] 2-oxazolinylphenolates (in **9**),[51,52] or β-ketiminates (in **10**).



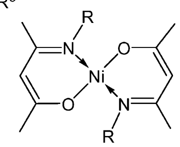
R¹ = H, Me
R² = H, NO₂
R³ = Naph, Ph
R⁴ = H, NO₂

8



R¹ = H, Me
R² = H, Ph
R³ = H, Me
R⁴ = H, Me

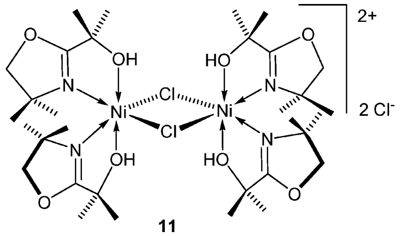
9



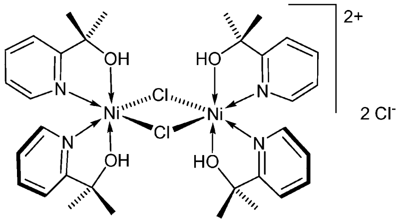
R = Ph, 2-Me-Ph, *t*-Bu

10

We reported recently the synthesis of Ni(II) precatalysts with zwitterionic N,O-benzoquinonemonoimine-type ligands which presented good activities for ethylene oligomerization with $AlEtCl_2$ or MAO as a co-catalyst. They favoured the dimerization and trimerization of ethylene and the formation of the C_6 olefins resulted from chain growth and/or reinsertion of 1-butene or 2-butene.[53] We have also used oxazoline alcohols and pyridine alcohols to synthesise the Ni(II) complexes **11** and **12**, respectively, of which the dinuclear structures were established by X-ray diffraction.[54]



11

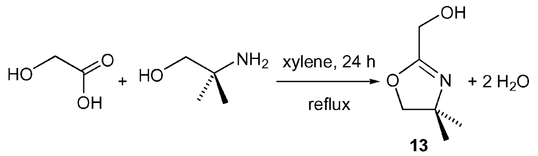


12

Even in the presence of small amounts of $AlEtCl_2$ or MAO as a co-catalyst, these complexes showed high activities in ethylene oligomerization (turnover frequencies (TOF) up to 174 300 mol C_2H_4 (mol Ni h)$^{-1}$ for **11** with only 6 equiv. of $AlEtCl_2$), giving mostly C_4 olefins and 1-butene. Since relatively small changes in the substitution pattern of the chelating ligand may have significant consequences on the structure and the catalytic properties of their Ni(II) complexes,[13] we wished to evaluate the possible influence of the *gem*-dimethyl substituents of the alcohol ligands and prepared the new Ni(II) complexes **14** and **16** to evaluate them for the catalytic oligomerization of ethylene, with MAO or $AlEtCl_2$ as co-catalyst.

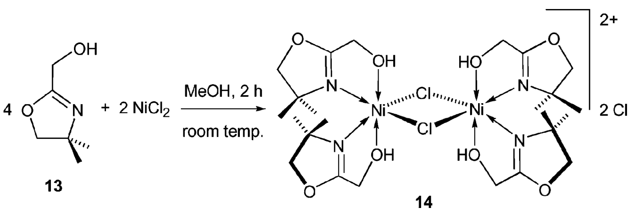
Results and discussion

The (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol ligand **13** was prepared according to the literature[55] by double condensation of glycolic acid with 2-amino-2-methyl-1-propanol in xylene at reflux during 24 h [eqn (1)]. Additional characterizations by ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy are reported in the Experimental section.

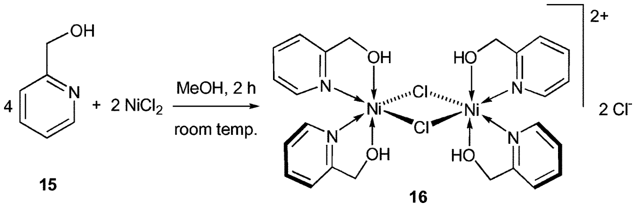


(1)

Complexes **14** and **16** were synthesized at room temperature by reaction of a methanol solution of $NiCl_2$ with 2 mol. equiv. of ligand **13** or of (pyridin-2-yl)methanol **15**, respectively, and after work-up, they were isolated as green powders in almost quantitative yields [eqn (2) and (3)].



(2)



(3)

These two dicationic complexes are paramagnetic and have been characterized by IR spectroscopy, elemental analysis and X-ray diffraction. The dinuclear centrosymmetric structures of **14**·C_6H_{12} and **16**·$3CH_2Cl_2$ are shown in Fig. 1 and 2 and selected bond distances and bond angles are given in Table 1.

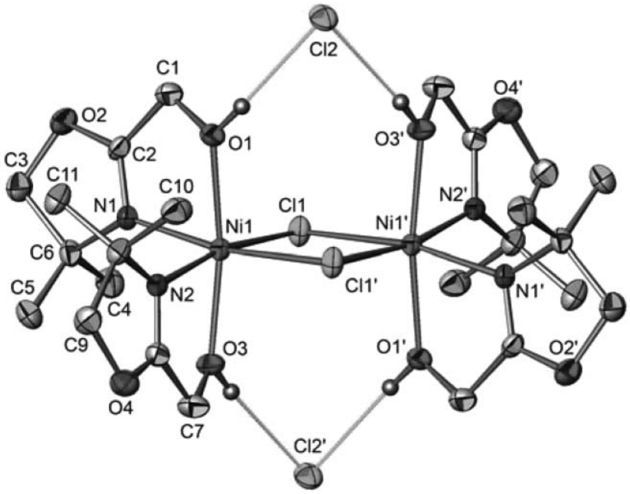


Fig. 1 ORTEP view of the structure of the oxazoline alcohol complex **14** in **14**·C_6H_{12} with thermal ellipsoids drawn at the 50% probability level, symmetry operation generating equivalent atoms: −*x*, −*y*, −*z* + 1.

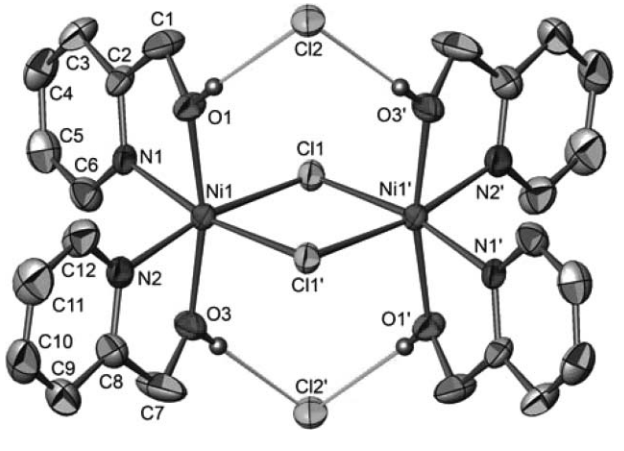


Fig. 2 ORTEP view of the structure of the pyridine alcohol complex **16** in **16**·$3CH_2Cl_2$ with thermal ellipsoids drawn at the 50% probability level, symmetry operation generating equivalent atoms: −*x*, −*y* + 1, −*z*.

Table 1 Selected bond lengths (Å) and angles (°) in **14**·C_6H_{12}[a] and **16**·$3CH_2Cl_2$[b]

	14·C_6H_{12}	**16**·$3CH_2Cl_2$
Ni1–Cl1′	2.397(2)	2.409(2)
Ni1–Cl1	2.404(2)	2.419(2)
Ni1–O1	2.108(4)	2.063(4)
Ni1–O3	2.117(4)	2.059(4)
Ni1–N1	2.062(4)	2.062(5)
Ni1–N2	2.063(4)	2.064(5)
O1–C1	1.420(6)	1.432(8)
C1–C2	1.489(7)	1.507(9)
C2–O2	1.337(6)	—
C2–N1	1.271(6)	1.330(8)
O3–C7	1.421(6)	1.433(9)
C7–C8	1.486(7)	1.50(1)
C8–O4	1.339(6)	—
C8–N2	1.269(6)	1.333(9)
Ni1 · · · Cl2	4.713(3)	4.535(2)
Ni1 · · · Cl2′	4.702(3)	4.552(2)
O1–Ni1–N1	77.5(2)	77.8(2)
O1–Ni1–Cl1′	93.8(1)	95.4(2)
O1–Ni1–Cl1	92.5(1)	93.4(2)
O1–Ni1–O3	171.5(2)	167.6(2)
O1–Ni1–N2	96.5(2)	94.1(2)
N1–Ni1–Cl1′	91.5(2)	88.5(2)
N1–Ni1–Cl1	169.8(1)	168.8(2)
N1–Ni1–N2	92.9(2)	98.0(2)
N1–Ni1–O3	96.6(2)	93.8(2)
N2–Ni1–Cl1′	169.4(1)	89.3(2)
N2–Ni1–Cl1	90.5(2)	169.4(2)
O3–Ni1–Cl1′	92.6(2)	93.4(2)
O3–Ni1–Cl1	93.5(2)	95.9(2)
Cl1–Ni1–Cl1′	86.84(8)	85.48(5)
Ni1–Cl1–Ni1′	93.16(8)	93.52(5)
N2–Ni1–O3	77.4(2)	77.9(2)
O1–C1–C2	106.3(4)	109.2(5)
C1–C2–N1	123.1(4)	116.7(5)
C2–N1–Ni1	114.0(3)	115.8(4)
Ni1–O3–C7	113.8(4)	113.7(4)
O3–C7–C8	106.4(4)	109.7(6)
C7–C8–N2	123.3(5)	115.9(6)
C8–N2–Ni1	113.7(3)	116.2(4)

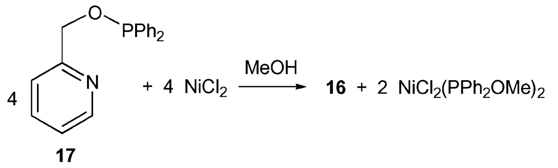
[a] Symmetry operation generating equivalent atoms: −*x*, −*y*, −*z* + 1. [b] Symmetry operation generating equivalent atoms: −*x*, −*y* + 1, −*z*.

The dications in **14**·C_6H_{12} and in **16**·$3CH_2Cl_2$ form centrosymmetric dimers and their Ni(II) centres adopt a distorted octahedral coordination geometry, very similar to those of **11** and **12** which contained *gem*-dimethyl substituents in α-position to the OH donor.[54] Each Ni(II) is surrounded by two N,O chelates, whose N and OH donor groups are *cis* and *trans* to each other, respectively, and by two bridging chlorides which are *trans* to the nitrogen atoms. The unit cell **16**·$3CH_2Cl_2$ contains two independent but almost identical molecules. In both **14** and **16**, the two chloride counter anions do not interact with the metal centres and are at 4.702(3) and 4.713(3) Å for **14** and 4.535(2) and 4.552(2) Å for **16** from a Ni(II) centre. However, interactions between the chloride counter-anions and the hydrogen atoms of the OH functions are observed, with O1–H1 · · · Cl2 and O3′–H3′ · · · Cl2 distances of 2.984(4) and 2.994(4) Å (ESI, Table S1¶), for **14** and 2.993(4) and 2.972(5) Å (ESI, Table S2¶), for **16**, respectively (calculated O1–H1 · · · Cl2 and O3′–H3′ · · · Cl2 angles of 158 and 158° for **14** (ESI, Table S1¶) and 157 and 162°, for **16**, respectively (ESI, Table S2¶). As shown by the O1–Ni–O3 angle of 171.5(2)° for **14**·C_6H_{12} against 168.2(2)° for **11**, the metal centre in **14**·C_6H_{12} has a coordination geometry less distorted than in **11**. The Ni–N and Ni–Cl distances are slightly shorter in **14**·C_6H_{12} than in **11**.

Complex **16** has similar structural characteristics to **12** and these will therefore not be discussed in detail. The O1–C1–C2 angles in

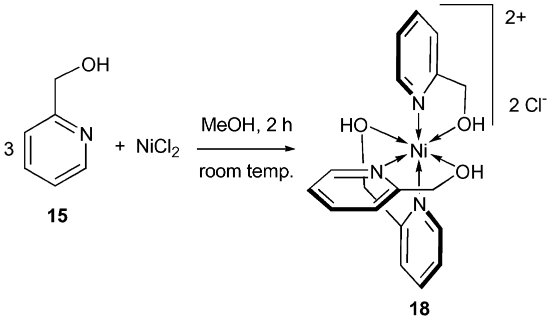
14 and **16** are *ca.* 3° larger than the corresponding O–CMe$_2$–C angles in **11** and **12**, which is consistent with the *gem*-effect in the latter complexes. The structure of a nickel complex coordinated by two (pyridin-2-yl)methanol ligands has been described recently but the coordination of two water molecules led instead to a mononuclear structure with an octahedral nickel centre.[56]

Complex **16** has been obtained recently in a less convenient way by reaction of the phosphinitopyridine ligand **17** with NiCl$_2$ in MeOH. This reaction led to the cleavage of the P–O bond and formation of **16** and [NiCl$_2$(PPh$_2$OMe)$_2$] [eqn (4)].[57]



(4)

When NiCl$_2$ was reacted with more than 3 mol. equiv. of (pyridin-2-yl)methanol **15**, the octahedral nickel complex **18** was formed quantitatively and isolated as a blue powder. The reaction of complex **16** with **15** in methanol in a 1 : 2 ratio also led to the formation of this complex, as indicated by a colour change of the solution from green to blue [eqn (5)].



(5)

The crystal structure of **18**·CH$_2$Cl$_2$ has been determined by X-ray diffraction. An ORTEP view of the molecular structure is shown in Fig. 3 and selected bond distances and bond angles are given in Table 2.

In the crystals of **18**·CH$_2$Cl$_2$, three molecules of (pyridin-2-yl)methanol **15** chelate the metal centre in a distorted octahedral geometry (Table 2) and form a mononuclear asymmetric molecule with a meridional coordination of the three nitrogen atoms and of the three oxygens. The Ni1–N2 and Ni1–N3 bonds are in *trans* position and of similar length (2.083(2) and 2.075(2) Å, respectively). The *trans* influence of the nitrogen N1 *trans* to oxygen O2 makes the Ni1–O2 distance slightly longer (2.078(2) Å) than Ni1–O1 and Ni1–O3 (2.043(2) and 2.044(2) Å, respectively). The Ni1–Cl1 (4.488(1) Å) and Ni1–Cl2 (4.328(1) Å) distances are too long to represent any significant bonding interaction. The counter anions Cl1 and Cl2 form hydrogen bonds with the hydrogen atoms H1 and H3, respectively (Fig. 3), as indicated by the O1–H1···Cl1 and O3–H3···Cl2 distances of 2.922(3) and 2.934(3) Å, respectively (calculated distances H1···Cl1 and H3···Cl2: 2.08 and 2.10 Å and calculated angles O1–H1···Cl1 and O3–H3···Cl2: 176 and 169°, respectively, ESI,¶ Table S3). Interestingly, the atom Cl2 connects two cations by hydrogen bonding, as depicted in Fig. 3 (O2′–H2′···Cl2 distance: 2.986(2) Å, calculated O2′–H2′···Cl2 angle: 172°, ESI,¶Table S3).

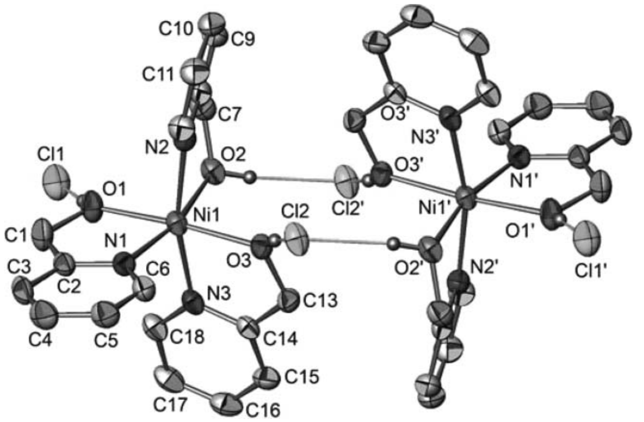


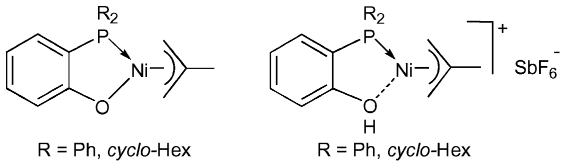
Fig. 3 ORTEP view of the structure of the oxazoline alcohol complex **18** in **18**·CH$_2$Cl$_2$ with thermal ellipsoids drawn at the 50% probability level, symmetry operation generating equivalent atoms (′): $-x + 1, -y + 2, -z + 1$.

Table 2 Selected bond lengths (Å) and angles (°) in **18**·CH$_2$Cl$_2$[a]

Ni–O1	2.043(2)	O1–C1	1.421(3)
Ni–O2	2.078(2)	O2–C7	1.434(3)
Ni–O3	2.044(2)	O3–C13	1.423(3)
Ni–N1	2.055(2)	N1–C2	1.340(4)
Ni–N2	2.083(2)	N2–C8	1.339(3)
Ni–N3	2.075(2)	N3–C14	1.433(4)
Ni···Cl1	4.488(1)	C1–C2	1.499(4)
Ni···Cl2	4.328(1)	C7–C8	1.510(4)
		C13–C14	1.495(4)
O1–Ni–O2	89.03(8)	O3–Ni–N1	100.53(8)
O1–Ni–O3	175.07(8)	O3–Ni–N2	89.99(9)
O1–Ni–N1	79.17(8)	O3–Ni–N3	78.45(8)
O1–Ni–N2	94.93(9)	N1–Ni–N2	96.41(8)
O1–Ni–N3	96.66(9)	N1–Ni–N3	95.63(8)
O2–Ni–O3	91.63(8)	N2–Ni–N3	164.7(1)
O2–Ni–N1	167.31(8)	O2–Ni–N3	90.31(8)
O2–Ni–N2	79.85(9)		

[a] Symmetry operation generating equivalent atoms: $-x + 1, -y + 2, -z + 1$.

We also considered converting the neutral donor ligand of complex **16** (dative HO→Ni bond) into a anionic ligand by deprotonation of at least one of the pyridine alcohol ligands with NaH, in order to study the catalytic properties of the resulting complex. Heinicke *et al.* have shown that whereas the neutral methallylnickel(II) phosphanylphenolate complexes **19** catalyze the polymerization of ethylene, the corresponding, protonated cationic methallylnickel phosphinophenol complexes **20** catalyze its oligomerization.[20,58]



19 **20**

The reaction of complex **16** with NaH in THF formed **21** which has been characterized by elemental analysis and IR spectroscopy [eqn (6)].

$$\mathbf{16} + 2\,\mathrm{NaH} \xrightarrow[\text{room temp.}]{\text{THF, 24 h}} 2\ [\mathrm{Ni(PyCH_2O)(PyCH_2OH)Cl}] \qquad (6)$$

21

Table 3 Comparative catalytic data for complexes **14**, **16** and **21** in the oligomerization of ethylene with $AlEtCl_2$ as co-catalyst[a]

Complex	Amount/ 10^{-5} mol	Al/Ni ratio	t/min	Selectivity[b] (%) C_4	C_6	C_8	Productivity/g C_2H_4 (g Ni h)$^{-1}$	TOF/mol C_2H_4 (mol Ni h)$^{-1}$	1-Butene (% mol)[c]	k_α[d]
14	1.05	2	35	92	8	0	9900	20700	62	<0.10
14	1.05	4	35	63	31	6	46400	97400	20	0.33
14	1.05	6	35	64	29	7	73900	155000	16	0.30
14	4	2	35	97	3	<1	<500	<1000	79	<0.10
16	4	4	35	68	30	2	16700	35200	11	0.29
16	4	6	35	69	27	4	24900	52300	6	0.27
16	1.05	2	35	95	5	<1	<1000	<1000	87	<0.10
16	1.05	4	35	81	17	2	20500	42900	39	0.14
16	1.05	6	35	70	25	5	89400	187500	10	0.23
21	4	2	35	78	21	1	9900	20700	16	0.18
21	4	4	35	68	29	3	16100	33700	9	0.29
21	4	6	35	69	28	3	19300	40500	6	0.27
21	1.05	2	35	77	19	4	12100	25300	43	0.19
21	1.05	4	35	72	23	5	35900	75300	32	0.21
21	1.05	6	35	62	32	6	47600	99800	29	0.34
ref[d]	4	2	35	83	15	2	4000	8400	13	0.12
ref	4	4	35	60	35	5	35300	74100	3	0.39
ref	4	6	35	61	34	5	35000	73600	3	0.37

[a] *Conditions*: $T = 25–30$ °C, 10 bar C_2H_4, reaction time 35 min. [b] No C_{10} oligomers were detected. [c] Selectivity within the C_4 fraction. [d] k_α = Hexenes [mol]/butenes [mol]. [e] **ref**: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

Complex **21** proved to be paramagnetic in solution and its magnetic moment, determined by the Evans method in CD_2Cl_2,[59–62] was 2.7 μ_B. This value is similar to those recently reported for other Ni(II) complexes with P,N-type ligands and suggests a distorted tetrahedral geometry in solution.[63,64]

Catalytic oligomerization of ethylene

The complexes **14**, **16** and **21** have been evaluated in the catalytic oligomerization of ethylene with different amounts of $AlEtCl_2$ or MAO as co-catalyst and the complex $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$ was used as a reference catalyst (**ref**). This is convenient since it is easier to check its purity by NMR techniques, in contrast to the case of paramagnetic $[NiCl_2(PCy_3)_2]$. Furthermore, $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$ has well-established catalytic properties for this reaction.[65] A comparison of the catalytic results between **14** and **16** will show the influence of the basicity of the nitrogen and that between **16** and **21** the impact of an anionic ligand *vs.* a neutral ligand on the oligomerization of ethylene. In order to study the influence of the concentration of the precatalysts and to compare the data with previous results obtained with Ni(II) complexes coordinated by P,N-type ligands,[13] we used 1.05×10^{-2} or 4×10^{-2} mmol of precatalyst dissolved in a total volume of 15 mL of chlorobenzene and toluene.

Use of $AlEtCl_2$ as co-catalyst

The precatalysts **14**, **16** and **21** were evaluated with 2, 4 or 6 equiv. of $AlEtCl_2$ as co-catalyst (Al/Ni ratios of 2, 4 or 6, respectively) (Table 3, Fig. 4). The low solubility of **16** in chlorobenzene could explain its very low activity with 2 equiv. of co-catalyst (less than 1000 mol C_2H_4 (mol Ni h)$^{-1}$). Indeed, more than 2 equiv. of $AlEtCl_2$ are needed to form sufficiently soluble, active species in the catalytic solution and with 6 equiv. of $AlEtCl_2$ **16** afforded the highest turnover frequencies: 52 300 and 187 500 mol C_2H_4 (mol Ni h)$^{-1}$ with 4×10^{-2} mmol and 1.05×10^{-2} of precatalyst, respectively.

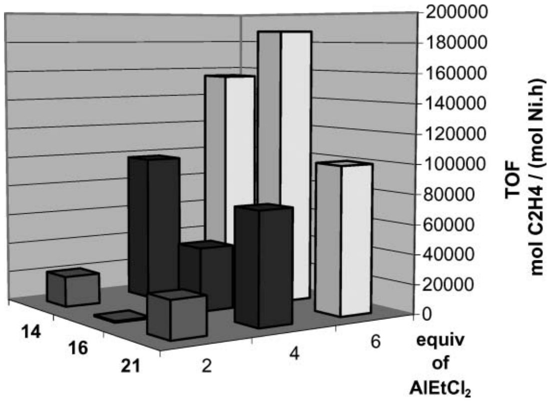


Fig. 4 Catalytic activities of the complexes **14**, **16**, and **21** (quantity of complex: 1.05×10^{-2} mmol) in the oligomerization of ethylene using $AlEtCl_2$ as co-catalyst.

In contrast to **16**, complexes **14** and **21** were soluble in chlorobenzene and showed high activities with 2, 4 or 6 equiv. of $AlEtCl_2$ (Table 3). The highest activities were always observed with 1.05×10^{-2} mmol of precatalyst and 6 equiv. of $AlEtCl_2$: 155 000, 187 500 and 99 800 mol C_2H_4 (mol Ni h)$^{-1}$ for **14**, **16** and **21**, respectively. The selectivities for C_4 olefins and 1-butene with complexes **14**, **16** and **21** decreased with increasing catalytic activity (Table 3). Complex **16** presented selectivities for C_4 olefins up to 95% and for 1-butene up to 87% with 2 equiv. of $AlEtCl_2$ (Fig. 5). The isomerization of 1-butene to 2-butene became more important with increasing activities. However, a decrease of the concentration of catalyst from 4×10^{-2} to 1.05×10^{-2} mmol had a beneficial impact on the selectivity for 1-butene, as shown with **21** where the selectivity increased from 6 to 29% when 6 equiv. of $AlEtCl_2$ were used.

Table 4 Catalytic data and distribution of the C_6 oligomers for complexes **14**, **16** and **21** in the oligomerization of ethylene with $AlEtCl_2$ as co-catalyst[a]

Complex	Amount/ 10^{-5} mol	Al/Ni ratio	Selectivity (mass%) 1-Hexene	2- and 3-Hexene[b]	C_6[c] from 1-butene	C_6[d] from 2-butene
14	1.05	2	16	76	<1	7
14	1.05	4	3	54	12	31
14	1.05	6	3	44	3	50
16	4	4	2	43	7	48
16	4	6	<1	32	4	63
16	1.05	4	8	63	9	20
16	1.05	6	3	50	2	45
21	4	2	3	48	8	41
21	4	4	<1	33	5	61
21	4	6	1	40	6	53
21	1.05	2	14	74	2	10
21	1.05	4	3	53	11	33
21	1.05	6	3	44	5	48

[a] *Conditions*: $T = 25$–30 °C, 10 bar C_2H_4, reaction time 35 min. [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.

Table 5 Comparative catalytic data for complexes **14**, **16** and **21** in the oligomerization of ethylene with MAO as co-catalyst[a]

Complex	Amount/ 10^{-5} mol	MAO (equiv.)	Selectivity C_4	C_6	C_8	$>C_8$	Productivity/g C_2H_4 (g Ni h)$^{-1}$	TOF/mol C_2H_4 (mol Ni h)$^{-1}$	1-Butene (% mol)[b]	k_α[c]
14	1.05	50	85	11	3	0	5300	11100	57	<0.10
14	1.05	100	70	24	5	<1	12900	27000	36	0.23
14	1.05	200	75	20	4	1	17300	36300	35	0.18
14[d]	1.05	200	92	7	1	0	26400	55300	61	<0.10
16	4	50	94	6	<1	0	1000	2200	64	<0.10
16	4	100	74	22	4	<1	4700	9800	28	0.20
16	4	200	66	29	5	<1	6700	14100	23	0.29
16	1.05	50	91	8	1	0	5700	12000	61	<0.10
16	1.05	100	79	18	3	0	11600	24200	40	0.15
16	1.05	200	75	20	4	<1	17700	37100	34	0.18
16[d]	1.05	200	85	13	2	<1	49700	104300	51	0.11
21	1.05	50	92	7	1	0	2800	5900	61	<0.10
21	1.05	100	81	17	2	0	9900	20700	45	0.14
21	1.05	200	80	17	3	<1	11000	23000	42	0.14
ref[e]	4	50	43	46	8	3	18600	40000	3	0.72
ref	4	100	25	54	14	7	19200	41300	3	1.47
ref	4	200	26	52	16	6	17600	36900	3	1.31
ref	4	400	41	45	10	4	18900	39600	4	0.72

[a] *Conditions*: $T = 25$–30 °C, 10 bar C_2H_4, reaction time 35 min. [b] Selectivity within the C_4 fraction. [c] k_α = Hexenes [mol]/butenes [mol]. [d] Pressure: 30 bar. [e] **ref**: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

The low selectivity for C_4 olefins with very active catalytic systems could be explained by the competing reinsertion of 1-butene to form 2-hexene, 3-hexene and 2-ethyl-1-butene and the reinsertion of 2-butene, although more difficult, to form 3-methyl-1-pentene and 3-methyl-2-pentene.[53] Table 3 shows that with 1.05×10^{-2} mmol of precatalyst, less branched oligomers are formed than with 4×10^{-2} mmol of precatalyst, suggesting that a lower catalyst concentration disfavored the re-insertion of olefins. Accordingly, increasing the amount of co-catalyst favored the re-insertion of olefins and resulted in an increase of the C_6 fraction (Table 4), in particular of the C_6 oligomers formed from 2-butene (Table 4).

Use of MAO as co-catalyst

The precatalysts **14**, **16** and **21** (1.05×10^{-2} mmol) have been evaluated in the presence of MAO (50, 100 or 200 equiv.) and all the complexes were active (Tables 5 and 6, Fig. 6–8). Complexes **14** and **16** have similar activities, between 11 100 and 12 000 mol C_2H_4 (mol Ni h)$^{-1}$ with 50 equiv. of MAO, between 24 200 and 27 000 mol C_2H_4 (mol Ni h)$^{-1}$ with 100 equiv. and between 36 300 and 37 100 mol C_2H_4 (mol Ni h)$^{-1}$ with 200 equiv. MAO. These complexes presented similar selectivities for C_4 olefins (up to 91%) and for 1-butene (up to 61%) (Fig. 7). Complex **21** was less active than **14** and **16** (Fig. 8) with 200 equiv. of MAO but it was more selective for C_4 oligomers (up to 92%) and for 1-butene (up to 61%). A pressure increase from 10 to 30 bar led to a very high increase of catalytic activity for complexes **14** and **16** (Table 5). Whereas **16** displayed the highest activity of 104 300 mol C_2H_4 (mol Ni h)$^{-1}$, **14** presented the best selectivities for C_4 olefins (92%) and for 1-butene (61%). A pressure increase had a beneficial but modest impact on the selectivity for 1-hexene, which increased from 7 to 11% with **14** and from 6 to 9% with **16** in the presence of 200 equiv. of MAO (Table 6).

Table 6 Catalytic data and distribution of the C_6 oligomers for complexes **14**, **16** and **21** in the oligomerization of ethylene with MAO as co-catalyst[a]

			Selectivity (mass%)			
Complex	Amount/10^{-5} mol	MAO (equiv.)	1-Hexene	2- and 3-Hexene[c]	C_6 from 1-butene[d]	C_6 from 2-butene[e]
14	1.05	50	13	60	12	15
14	1.05	100	7	56	12	25
14	1.05	200	7	54	12	27
14[e]	1.05	200	11	63	13	14
16	4	50	15	59	13	13
16	4	100	5	53	12	30
16	4	200	4	53	12	31
16	1.05	50	16	59	13	12
16	1.05	100	8	58	12	22
16	1.05	200	6	54	12	28
16[e]	1.05	200	9	58	12	21
21	1.05	50	17	58	12	13
21	1.05	100	10	58	12	20
21	1.05	200	8	60	12	20

[a] *Conditions*: $T = 25$–30 °C, 10 bar C_2H_4, 35 min. [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] Pressure 30 bar.

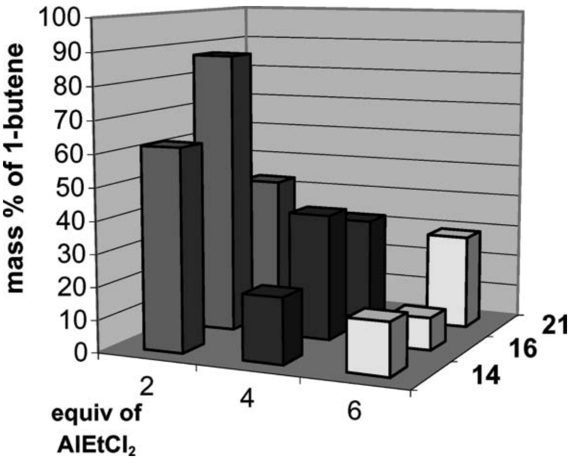


Fig. 5 Selectivity for 1-butene in the C_4 fraction for the complexes **14**, **16**, and **21** (quantity of complex: 1.05×10^{-2} mmol) in the oligomerization of ethylene using $AlEtCl_2$ as co-catalyst.

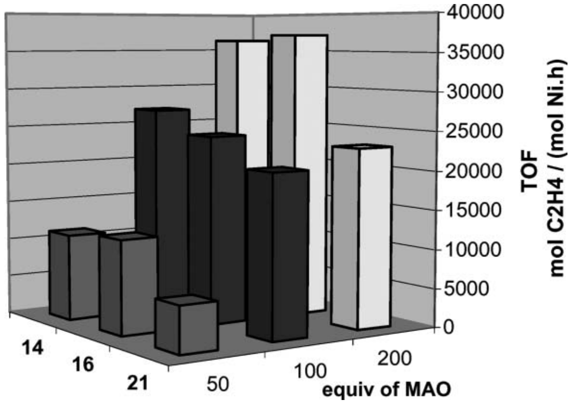


Fig. 6 Catalytic activities of the complexes **14**, **16** and **21** (quantity of complex: 1.05×10^{-2} mmol) in the oligomerization of ethylene using MAO as co-catalyst.

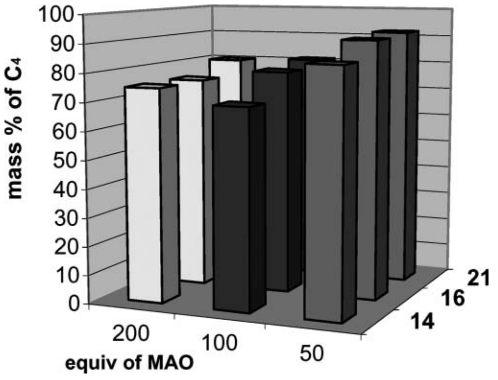


Fig. 7 Selectivity in C_4 olefins for the complexes **14**, **16** and **21** (quantity of complex: 1.05×10^{-2} mmol) in the oligomerization of ethylene using MAO as co-catalyst.

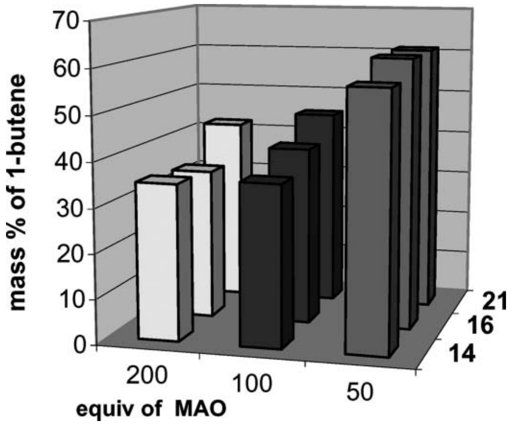


Fig. 8 Selectivity for 1-butene in the C_4 fraction with complexes **14**, **16** and **21** (quantity of complex: 1.05×10^{-2} mmol) in the oligomerization of ethylene using MAO as co-catalyst.

Two different concentrations were used for precatalyst **16** (1.05×10^{-2} and 4×10^{-2} mmol in a total volume of 10 mL of solution). Higher activities and better selectivities for 1-butene (40% with 100 equiv. of MAO and 34% with 200 equiv.) were obtained with 1.05×10^{-2} mmol of precatalyst (Table 5).

Conclusion

The high yield reaction of $NiCl_2$ with 2 mol. equiv. of the oxazoline alcohol **13** or of (pyridin-2-yl)methanol **15** yielded the corresponding dinuclear complexes **14** or **16** with octahedral metal coordination. They are very similar to the dinuclear complexes **11** and **12** with oxazoline alcohol or pyridine alcohol ligands bearing *gem*-dimethyl substituents in α position to the donor oxygen atom.[54] The reaction of $NiCl_2$ with 3 mol equiv. of **15** led to the octahedral, mononuclear complex **18** which can also be formed by reaction of **16** with the pyridine alcohol in a 1 : 2 ratio. Deprotonation of one of the two pyridine alcohol ligands of **16** with NaH afforded complex **21**.

The complexes **14**, **16** and **21** have been evaluated in the catalytic oligomerization of ethylene with 50, 100 and 200 equiv. of MAO or with 2, 4 and 6 equiv. of $AlEtCl_2$ as co-catalyst. When 1.05×10^{-2} mmol of complex was used, **16** presented the best activities, up to 187 500 mol C_2H_4 (mol Ni h)$^{-1}$ with only 6 equiv. of $AlEtCl_2$ and the best selectivities for C_4 olefins (up to 95%) and for 1-butene (up to 87%) with 2 equiv. of $AlEtCl_2$. A comparison between precatalysts containing the pyridine alcohol or the oxazoline alcohol ligands shows that it remains difficult to generalise the observations made with one system.[54] When 4×10^{-2} mmol of precatalysts was used in the presence of $AlEtCl_2$, **16** and **21** showed similar activities compared to those obtained with Ni(II) complexes bearing P,N type ligands.[13]

With MAO, precatalysts **14**, **16** and **21** were very active and **16** presented the highest activities up to 37100 mol C_2H_4 (mol Ni h)$^{-1}$ with 200 equiv. of MAO and selectivities for C_4 olefins (up to 94%) and 1-butene (up to 64%) with 50 equiv. of MAO. Precatalysts **14**, **16** and **21** in the presence of MAO showed higher activities than **11** and **12** (with 1.05×10^{-2} mmol of complex) and Ni(II) complexes bearing P,N type ligands (with 4×10^{-2} mmol of complex). The increase of the ethylene pressure to 30 bar resulted in more active complexes **14** and **16** (the TOF of **16** increased to 104 300 mol C_2H_4 (mol Ni h)$^{-1}$) and more selective for C_4 olefins (selectivity increase for **14** from 75 to 92%) and for 1-butene (selectivity increase for **14** from 35 to 61%). The fact that the catalytic properties of **14** and **16** are rather similar to those of **11** and **12** may be related to their structural similarities. If the *gem*-Me_2 groups in **11** and **12** makes the donor OH function in α-position more electron-rich and a better donor, the variation in the C–CH_2–O *vs.* C–CMe_2–O angles is limited.

Experimental

The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 and 75.5 MHz on a Bruker AC300 instrument. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". IR spectra in the range of 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^{-1}). Commercial $NiCl_2 \cdot 6H_2O$ was dried by heating at 160 °C overnight under vacuum to give anhydrous $NiCl_2$. Magnetic moments were determined by the Evans method in CD_2Cl_2 using a solution of CH_3NO_2 in CD_2Cl_2 (20 : 80, v/v) as reference.[59–62] The commercial (pyridin-2-yl)methanol (**15**) was distilled at 115 °C. 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).

Synthesis of (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol (13)

To a solution of glycolic acid (4.08 g, 53.7 mmol) in 100 mL of xylene, was added 5 mL of 2-amino-2-methyl-1-propanol (53.7 mmol) and the mixture was stirred at reflux for 24 h. After evaporation of the solvent under reduced pressure, the resulting yellow oil was distilled under reduced pressure (160 °C, 0.8 mbar) and **13** was obtained as a white powder by placing the oil in a refrigerator (mp of **13** is around 15 °C). Yield: 4.24 g (62%). ^1H NMR ($CDCl_3$): δ 1.30 (s, 6H, CH_3), 4.05 (s, 2H, CH_2), 4.26 (s, 2H, CH_2OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.2 (s, CH_3), 56.9 (s, CH_2OH), 66.6 (s, $\mathit{C}CH_3$), 79.7 (s, CH_2), 166.9 (s, NCO).

Synthesis of [Ni(μ-Cl){(4,5-dihydro-4,4-dimethyloxazol-2-yl)-methanol}]$_2$Cl$_2$ (14)

A solution of 2 mol. equiv. of (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol (**13**) (1.22 g, 9.6 mmol) in 20 mL of methanol was added to a solution of anhydrous $NiCl_2$ (0.61 g, 4.8 mmol) in 50 mL of methanol and the reaction mixture was stirred for 2 h at room temperature. After reaction, the methanol was removed under reduced pressure, the residue was washed with diethylether, dried under reduced pressure and **14** was isolated as a green powder. Yield: 1.65 g (90%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **14**. Anal. Calc. for $C_{24}H_{44}Cl_4N_4Ni_2O_8$: C, 37.15; H, 5.72; N, 7.22. Found: C, 36.97; H, 6.13; N, 6.68%. IR (KBr): 1674 (s), 1637 (vs), 1508 (w), 1467 (m), 1450 (m sh), 1406 (m), 1371 (m), 1281 (s), 1209 (m), 1185 (w sh), 1063 (vs), 952 (s), 843 (w) cm^{-1}.

Synthesis of [Ni(μ-Cl){(pyridin-2-yl)methanol}]$_2$Cl$_2$ (16)

Complex **16** was prepared by reaction of $NiCl_2$ (0.86 g, 6.6 mmol) and (pyridin-2-yl)methanol (**15**) (1.44 g, 13.2 mmol) by following the same procedure described for **14** and it was isolated as a green powder. Yield: 2.18 g (95%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **16**. Anal. Calc. for $C_{24}H_{28}Cl_4N_4Ni_2O_4$: C, 41.43; H, 4.06; N, 8.05. Found: C, 41.25; H, 4.48; N, 7.61%. HRMS: Mass Calcd for $C_{12}H_{14}ClN_2NiO_2$: 311.0092. Found: 311.0099 $(Ni(N,O)_2Cl)^+$. IR (KBr): 1608 (vs), 1571 (s), 1483 (s), 1444 (s), 1440 (s sh), 1349 (w), 1286 (s), 1237 (m), 1156 (s), 1065 (s sh), 1050 (s sh), 1033 (vs), 778 (s sh), 765 (s), 727 (m), 648 (m), 626 (w) cm^{-1}.

Synthesis of [Ni{(pyridin-2-yl)methanol}$_3$Cl$_2$] (18)

To a solution of $NiCl_2$ (0.70 g, 5.4 mmol) in 30 mL of methanol was added a solution of 4 equiv. of (pyridin-2-yl)methanol (2.00 g, 21.6 mmol) in 5 mL of methanol and the reaction mixture was stirred for 2 h at room temperature. At the end of the reaction, the methanol was removed under reduced pressure and the residue was washed with diethyl ether (3 × 20 mL) to eliminate unreacted (pyridin-2-yl)methanol and dried under reduced pressure. The product was isolated as a blue powder. Yield: 2.05 g (93%). Single crystals of **18**·CH_2Cl_2 suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. Anal. Calc.

for $C_{18}H_{21}Cl_2N_3NiO_3$: C, 47.31; H, 4.63; N, 9.20. Found: C, 47.10; H, 4.96; N, 8.51%. IR (KBr): 1608 (vs), 1571 (s), 1483 (s), 1444 (s), 1440 (s sh), 1349 (w), 1286 (s), 1237 (m), 1156 (s), 1065 (s sh), 1050 (s sh), 1033 (vs), 778 (s sh), 765 (s), 727 (m), 648 (m), 626 (w) cm^{-1}.

Synthesis of [Ni{(pyridin-2-yl)methanol}{(pyridin-2-yl)-methanolate}Cl] (21)

To a suspension of **16** (1.50 g, 4.3 mmol) in THF was added excess NaH (1.00 g, 41.7 mmol) and the mixture was stirred for 24 h at room temperature. At the end of the reaction, the solvent was removed under reduced pressure and 20 mL of CH_2Cl_2 was added. The green solution obtained was filtered to eliminate unreacted NaH and **16**. After removing the solvent under reduced pressure, **21** was washed with diethylether, dried under vacuum and isolated as a dark green powder. Yield: 0.97 g (72%). Anal. Calc. for $C_{12}H_{13}ClN_2NiO_2$: C, 46.29; H, 4.21; N, 9.00. Found: C, 45.92; H, 4.57; N, 8.64%. IR (KBr): 1632 (vs), 1597 (vs), 1569 (s sh), 1479 (w), 1438 (s), 1371 (vs), 1282 (m), 1244 (w), 1153 (w), 1077 (s), 1049 (s), 848 (m), 761 (vs), 729 (w), 704 (m), 643 (w) 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 catalytic solution of the precatalyst is dependent on the nature and the amount of the co-catalyst.

With $AlEtCl_2$, 4 × 10^{-2} mmol of Ni complex were dissolved in 14, 13 or 12 mL of chlorobenzene depending on the amount of the co-catalyst and injected into the reactor under an ethylene flux. Then 1, 2 or 3 mL of a co-catalyst solution, corresponding to 2, 4 or 6 equiv. respectively, is added to form a total volume of 15 mL with the precatalyst solution. When 1.05 × 10^{-2} mmol of precatalyst was used, a solution of the complex in 14 mL of chlorobenzene was injected into the reactor, followed by 0.26, 0.52 or 0.75 mL of a solution of the co-catalyst corresponding to 2, 4 or 6 equiv. of $AlEtCl_2$, respectively.

With MAO, 1.05 × 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 2, 4 or 8 mL (for a complex amount of 4 × 10^{-2} mmol) or 0.51, 1.05 or 2.10 mL (for a complex amount of 1.05 × 10^{-2} mmol) of a co-catalyst solution, corresponding to 50, 100 or 200 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 co-catalyst 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 min) a dry-ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool down 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 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,

Table 7 Crystallographic details and data collection

	14·C_6H_{12}	**16**·$3CH_2Cl_2$	**18**·CH_2Cl_2
Formula	$C_{24}H_{50}Cl_4N_4Ni_2O_8 \cdot C_6H_{12}$	$C_{24}H_{28}Cl_4N_4Ni_2O_4 \cdot 3CH_2Cl_2$	$C_{18}H_{21}Cl_2N_3NiO_3 \cdot CH_2Cl_2$
M_r	860.01	950.50	541.91
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T/K	173(2)	173(2)	173(2)
a/Å	9.519(2)	10.2260(2)	10.9430(4)
b/Å	10.696(2)	11.5260(2)	11.3560(4)
c/Å	10.759(3)	17.0800(5)	12.321(5)
α/°	79.71(5)	89.150(1)	91.790(1)
β/°	66.07(5)	77.950(1)	113.320(2)
γ/°	72.39(5)	74.300(1)	118.250(2)
V/Å^3	952.4(4)	1893.47(7)	1192.48(8)
Z	1	2	2
D_c/g cm^{-3}	1.499	1.667	1.509
F(000)	452	964	556
Radiation type	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	1.32	1.74	1.29
Crystal shape, colour	Prism, green	Prism, green	Prism, blue
Crystal size/mm	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10
Measd reflect.	14833	25759	15347
Indep. reflect.	5561	10998	6929
Obsd reflect.	4446	6976	4133
Criter. obs. refl.	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.051	0.064	0.056
θ_{max}/°	30.1	30.0	30.0
$R\,[F^2 > 2\sigma(F^2)]$	0.071	0.086	0.049
$wR(F^2)$, S	0.201, 1.07	0.230, 0.93	0.145, 0.96
No. param.	217	424	271

0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product.

Crystal structure determinations

Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) (Table 7). Data were collected using phi-scans and the structures were solved by direct methods (SIR97) using the SHELX97 software,[66,67] 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 ($d_{\text{C–H}} = 0.95$ Å, $U_{11} = 0.04$). All non-hydrogen atoms were refined anisotropically.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716111e

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