

2-Acetyloxymethyl-substituted 5,6,7-trihydroquinolinyl-8-ylideneamine-Ni(II) chlorides and their application in ethylene dimerization/trimerization

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Abstract

Six examples of 2-acetyloxymethyl-substituted 5,6,7-trihydroquinolinyl-8-ylideneamine-nickel(II) chlorides, [2-(CH₂OC(O)Me)-8-{N(Ar)}C₉H₈N]NiCl₂ (Ar = 2,6-Me₂C₆H₃ **Ni1**, 2,6-Et₂C₆H₃ **Ni2**, 2,6-i-Pr₂C₆H₃ **Ni3**, 2,4,6-Me₃C₆H₂ **Ni4**, 2,6-Et₂-4-MeC₆H₂ **Ni5**, 2,4,6-t-Bu₃C₆H₂ **Ni6**), have been prepared by a one-pot template reaction of 2-(hydroxymethyl)-6,7-dihydroquinolin-8(5H)-one with nickel dichloride hexahydrate, the corresponding aniline and acetic acid. All complexes were characterized by elemental analysis and IR spectroscopy, while dinuclear **Ni2** and mononuclear **Ni3**·OH₂ have additionally been the subject of single crystal X-ray diffraction studies; in both structures the acetyloxymethyl group remained uncoordinated. On activation of **Ni1** – **Ni6** with MMAO, hexenes (C₆: ca. 48% 1-hexene) formed the major product of ethylene oligomerization along with minor quantities of butenes (C₄); high overall activities of up to 1.33 × 10⁶ g·mol⁻¹ (Ni) h⁻¹ (for mesityl-containing **Ni4**) were achieved at 30 °C and 10 atm C₂H₄. By comparison with MAO as co-catalyst, **Ni1** – **Ni6** exhibited lower activities but displayed a specificity towards ethylene dimerization (C₄: 64-99% 1-butene). Furthermore, sizable induction periods were a feature of the MAO runs with **Ni1**/MAO reaching peak catalytic activity only after 45 minutes.

Keywords: Nickel precatalyst; ethylene di-/tri-merization; co-catalyst; substituent influence.

Introduction

Linear α -olefins (LAO's) constitute key commodity chemicals and petrochemical intermediates that are widely used, for example, as synthetic lubricant additives, reactants for forming oxo alcohols (to

give detergents) and co-monomers for the production of linear low density polyethylene (LLDPE). Metal-mediated ethylene oligomerization is one of the most important methods for the synthesis of such LAOs with both main group and transition metal catalysts used industrially. In the 1960s, Ziegler discovered that alkyl aluminums can promote oligomerization to give α -olefins ^[1], while almost 20 years later, the Shell Higher Olefin Process (SHOP) made use of a nickel catalyst to mediate the ethylene oligomerization step ^[2]. Due in part to the high selectivity for α -olefins and high activity of this nickel catalyst, many academic groups have in the intervening years been focused on developing new generation late transition metal catalyst systems. In particular, nickel complexes bearing *N,N*-diimine ligands have been shown to display exceptionally high catalytic activities in ethylene oligo-/polymerization. Subsequently, further advancements have seen alternative bidentate ligand frames including *N,N* ^[3], *N,O* ^[4], *P,N* ^[4a,5] and *P,O* ^[6] as well as tridentate-type ligands, *N,P,N* ^[7], *N,N,O* ^[8] and *N,N,N* ^[9]. Elsewhere, a multitude of other studies concerned with nickel complexes as catalysts for ethylene oligomerization have been disclosed.^[10]

< Chart 1 >

Within the *N,N*-bidentate class of Ni(II) complexes, the 2-iminopyridine-nickel halides (**A**, Chart 1) have displayed good activities for both ethylene oligomerization and polymerization ^[3a,3c,11]. In recent years our group has reported routes to nickel precatalysts bearing carbocyclic-fused 2-iminopyridine ligands such as that present in **B** (Chart 1), which have also been shown to exhibit high activity in ethylene oligomerization ^[3e,12]. With a view to developing this fused ligand approach, we have been interested in how a remote ester group positioned at the 2-position in **B** would influence both catalytic performance and oligomer distribution. To this end, we report six examples of *N*-(2-acetyloxymethyl-5,6,7-trihydroquinolin-8-ylidene)arylamino-nickel dichlorides, **C**, in which the steric and electronic properties of the *N*-aryl group have been systematically varied. An in-depth study is then conducted to determine the effects of the precatalyst structure, type and amount of co-catalyst, temperature and run time on the selectivity (and activity) of the ethylene oligomerization. Full synthetic and characterization details are additionally presented for the complexes.

Experimental section

General considerations

All manipulations of air- and/or moisture-sensitive operations were undertaken in a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen immediately prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in n-heptane) were purchased from Albemarle Corp. High-purity ethylene ethylaluminium sesquichloride (EASC, 0.87 M in n-heptane) and high-purity ethylene were obtained from Beijing Yansan Petrochemical Co and used as received. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. Gas chromatographic (GC) analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 mm film thickness). The compound 2-(hydroxymethyl)-6,7-dihydroquinolin-8(5H)-one (**1**) was prepared using the literature procedure^[13]; all anilines were obtained from commercial suppliers.

Synthesis of [2-(CH₂OC(O)Me)-8-{N(Ar)}C₉H₈N]NiCl₂ (**Ni1** – **Ni6**)

(a) Ar = 2,6-Me₂C₆H₃ (**Ni1**). 2-(Hydroxymethyl)-6,7-dihydroquinolin-8(5H)-one (**1**) (354 mg, 2 mmol), 2,6-dimethylaniline (363 mg, 3 mmol) and NiCl₂·6H₂O (451 mg, 1.9 mmol) were added to a one-neck round bottom flask. Acetic acid (30 mL) was then introduced and the mixture stirred at reflux for 8 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was extracted with 2 mL of dichloromethane, and 30 mL of diethyl ether was layered onto the extract and pale yellow solid was slowly precipitated. The solid, compound **Ni1**, was collected by filtration and washed three times with diethyl ether (3 x 20 mL) to afford 640 mg (71%). FT-IR (cm⁻¹): 3496 (m), 3390 (s), 1741 (ν_{C=O}, w), 1663 (m), 1604 (ν_{C=N}, s), 1536 (w), 1477 (w), 1442 (w), 1374 (w), 1301 (w), 1242 (s), 1108 (w), 1059 (w), 766 (m), 721 (w). Anal. Calc. for C₂₀H₂₂Cl₂N₂NiO₂ (452.00): C, 53.14; H, 4.91; N, 6.20. Found: C, 53.52, H, 4.88; N, 6.13%.

(b) Ar = 2,6-Et₂C₆H₃ (**Ni2**). By using a similar procedure as described for **Ni1** but with 2,6-diethylaniline as the amine, **Ni2** was obtained as a yellow powder (632 mg, 66%). FT-IR (cm⁻¹): 3498 (w), 3392 (w), 2964 (w), 1750 (ν_{C=O}, m), 1623 (m), 1598 (ν_{C=N}, m), 1482 (w), 1452 (w), 1372

(w), 1222 (s), 1055 (m), 861 (w), 814 (w), 783 (m), 718 (s). Anal. Calc. for $C_{22}H_{26}Cl_2N_2NiO_2$ (480.05): C, 55.04; H, 5.46; N, 5.84. Found: C, 54.87; H, 5.63; N, 6.20%.

(c) Ar = 2,6-i-Pr₂C₆H₃ (**Ni3**). By using a similar procedure as described for **Ni1** but with 2,6-diisopropylaniline as the amine, **Ni3** was obtained as a yellow powder (613 mg, 60%). FT-IR (cm⁻¹): 3497 (m), 3388 (m), 2963 (w), 1746 (ν_{C=O}, m), 1622 (m), 1596 (ν_{C=N}, m), 1486 (w), 1457 (w), 1375 (m), 1235 (s), 1189 (w), 1147 (w), 1113 (w), 1087 (m), 1044 (m), 916 (w), 875 (w), 828 (w), 781 (m), 730 (m). Anal. Calc. for $C_{24}H_{30}Cl_2N_2NiO_2$ (508.11): C, 56.73; H, 5.95; N, 5.51. Found: C, 56.59; 6.03; N, 5.70%.

(d) Ar = 2,4,6-Me₃C₆H₂ (**Ni4**). By using a similar procedure as described for **Ni1** but with 2,4,6-trimethylaniline as the amine, **Ni4** was obtained as a yellow powder (667 mg, 72%). FT-IR (cm⁻¹): 3310 (m), 1747 (ν_{C=O}, m), 1621 (m), 1596 (ν_{C=N}, m), 1481 (w), 1433 (w), 1378 (w), 1229 (s), 1052 (m), 830 (w), 770 (m). Anal. Calc. for $C_{21}H_{24}Cl_2N_2NiO_2$ (466.03): C, 54.12; H, 5.19; N, 6.01. Found: C, 54.06; H, 5.33; N, 5.87%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**Ni5**). By using a similar procedure as described for **Ni1** but with 2,6-diethyl-4-methylaniline as the amine, **Ni5** was obtained as a yellow powder (577 mg, 58%). FT-IR (cm⁻¹): 3391 (m), 1750 (ν_{C=O}, m), 1623 (m), 1599 (ν_{C=N}, m), 1486 (w), 1457 (w), 1431 (w), 1369 (w), 1230 (s), 1149 (w), 1051 (m), 859 (m), 826 (w), 719 (m). Anal. Calc. for $C_{23}H_{28}Cl_2N_2NiO_2$ (494.08): C, 55.91; H, 5.71; N, 5.67. Found: C, 55.78; H, 5.97; N, 5.54%.

(f) Ar = 2,4,6-t-Bu₃C₆H₂ (**Ni6**). By using a similar procedure as described for **Ni1** but with 2,4,6-tri-*tert*-butylaniline, **Ni6** was obtained as a yellow powder (522 mg, 44%). FT-IR (cm⁻¹): 3492 (m), 3392 (m), 1740 (ν_{C=O}, m), 1664 (m), 1603 (ν_{C=N}, m), 1485 (w), 1414 (w), 1378 (w), 1352 (w), 1238 (s), 1148 (w), 1109 (w), 1057 (m), 904 (w), 873 (w), 823 (w), 717 (m). Anal. Calc. for $C_{30}H_{42}Cl_2N_2NiO_2$ (592.27): C, 60.84; H, 7.15; N, 4.73. Found: C, 60.74; H, 6.99; N, 4.80%.

X-ray crystallographic studies

Single crystals **Ni2** and **Ni3** suitable for the X-ray diffraction studies were grown by slow diffusion of *n*-hexane into a dichloromethane solution of the corresponding complex at room temperature. Cell parameters were obtained by global refinement of the positions of all collected reflections with

graphite-mono-chromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 170 K. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the Olex2 1.2 package and SHELXT (Sheldrick) ^[14]. Details of the X-ray structure determinations and refinements are provided in Table S1.

Typical procedure for ethylene oligomerization

Ethylene polymerization at 5 or 10 atm C₂H₄. The ethylene oligomerizations were carried out in a 250 mL stainless steel autoclave equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. The autoclave was evacuated and refilled with ethylene three times. A solution of the pre-catalyst (**Ni1** – **Ni6**, 4 μmol) in toluene (50 mL), the co-catalyst (MAO or MMAO) and more toluene (50 mL) were then sequentially injected by syringe to the autoclave. When the desired reaction temperature was reached, the ethylene pressure was increased to 10 atm and the stirring commenced. After the designated time at this temperature/pressure, the autoclave was cooled with an ice bath and the pressure slowly released. A small amount of this cooled reaction solution (about 1 mL) was collected and quenched with 5% HCl (1 mL). A sample of this mixture (0.02 μL) was then immediately injected into the GC instrument to determine the distribution of the oligomers. The mass of C₄ and C₆ was calculated based on the ratio of the corresponding peaks to the toluene peak in the gas chromatogram.

Results and discussion

Synthesis and characterization of Ni1-Ni6

The *N*-(2-acetyloxymethyl-5,6,7-trihydro-quinolin-8-ylidene)arylamino-nickel dichlorides, [2-(CH₂OC(O)Me)-8-{N(Ar)}C₉H₈N]NiCl₂ (Ar = 2,6-Me₂C₆H₃ **Ni1**, 2,6-Et₂C₆H₃ **Ni2**, 2,6-*i*-Pr₂C₆H₃ **Ni3**, 2,4,6-Me₃C₆H₂ **Ni4**, 2,6-Et₂-4-MeC₆H₂ **Ni5**, 2,4,6-*t*-Bu₃C₆H₂ **Ni6**), could be readily prepared using a one-pot template reaction of 2-hydroxymethyl-5,6,7-trihydroquinolin-8-one (**1**), the corresponding aniline and NiCl₂·6H₂O with acetic acid as both solvent and reactant (Scheme 1). A three-step route based on sequential condensation, acetoxylation and complexation was unsuccessful due, in the main, to the inability to

remove residual aniline in the first step. All six complexes were characterized by FT-IR spectroscopy and elemental analyses. In addition, crystals of **Ni2** and the aqua adduct **Ni3**·OH₂ have the subject of single crystal X-ray diffraction studies.

< Scheme 1 >

Crystals of **Ni2** and **Ni3**·OH₂ suitable for X-ray determinations were obtained by the slow diffusion of diethyl ether into dichloromethane solutions of the corresponding complex. Perspective views of each complex are shown in Figures 1 and 2; selected bond distances and angles are collected in Table S2. The structure of **Ni2** consists of a NiCl(μ-Cl)₂NiCl core in which two chlorides bridge the metal centers to form a dinickel complex in a manner similar to that reported elsewhere [3e,9e,12a,15]. Each nickel center in this centrosymmetric dimer is bound by an *N,N*-chelating 2-acetyloxymethyl-5,6,7-trihydro-quinolin-8-ylideneamine to complete a geometry that can be best described as distorted square pyramidal. The 2-acetyloxymethyl group remains pendant while the *N*-aryl groups are inclined almost perpendicular to the neighboring imine vectors. The saturated sections of the fused six-membered rings are puckered on account of the three sp³-hybridized carbons atoms, C6, C7 and C8. There are no intermolecular contacts of note.

The structure of **Ni3**·OH₂ is based on a single nickel center that is surrounded by a *N,N*-chelating 2-acetyloxymethyl-5,6,7-trihydro-quinolin-8-ylideneamine, two terminal chloride ligands and a water molecule to form a distorted trigonal bipyramidal geometry at nickel [16]. Related aqua adducts of the general formula (N,N)NiCl₂(OH₂) have been reported elsewhere [7a,12b]. The presence of the water ligands leads to intermolecular OH...Cl hydrogen bonding [O(1)···Cl(2) 3.116 Å] resulting in two molecules of **Ni3**·OH₂ assembling to form a dimer (Figure 3). It is assumed that the molecule of water originates from the crystallization step that were performed in vessels open to the air. As with **Ni2**, the C6-C7-C8 section of the fused six-membered ring is puckered while the 2-acetyloxymethyl group is similarly not involved in coordination to the metal center.

< Figure 1 >

< Figure 2 >

< Figure 3 >

In the IR spectra of **Ni1** – **Ni6**, absorption bands are seen in the range 1596 - 1604 cm⁻¹, which are typical of nickel(II)-bound imines [3e,12a,17]. By contrast, the uncoordinated carbonyl groups belonging to the ester moieties can be seen between 1741 cm⁻¹ and 1750 cm⁻¹. The microanalytical

data for all complexes were in full support of compositions of the type LNiCl_2 or $[\text{LNiCl}_2]_2$.

Catalytic evaluation for ethylene polymerization

(a) *Co-catalyst screen.* To explore the performance of these nickel precatalysts in ethylene oligomerization, **Ni1** was selected as the test precatalyst and initially screened using three different types of co-catalyst, including modified methylaluminoxane (MMAO), methylaluminoxane (MAO) and ethylaluminium sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$, EASC). Typically, these initial runs were performed at 30 °C with the ethylene pressure maintained at 10 atm (Table 1).

On examination of the results, **Ni1**/MMAO was found to be the most effective precatalyst/co-catalyst combination forming hexenes (C_6) as the major product (88.9%) along with butenes (C_4) as the minor one. The second most effective combination involved MAO, which displayed a selectivity for forming 1-butene. On the basis of the level of activities, MMAO and MAO were chosen for more in-depth parallel investigations.

< Table 1 >

(b) *Catalytic evaluation using MMAO.* To determine the optimal performance of these MMAO-promoted ethylene oligomerizations, variations in the molar Al:Ni ratio, reaction temperature and polymerization time were all systematically explored with **Ni1** once again used as the test precatalyst; the results are summarized in Table 2.

< Table 2 >

Firstly with the temperature maintained at 30 °C, the Al:Ni molar ratio was varied from 1000 to 4000 resulting in the highest activity of $1.28 \times 10^6 \text{ g} \cdot \text{mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ achievable at a ratio of 3250; the activity then steadily decreased on further raising the ratio (entries 1 - 9, Table 2). In terms of the oligomer distribution, the preference for C_6 products becomes more evident at higher molar ratios reaching a maximum of 91.9% at a ratio of 4000 (entry 9, Table 2), while the selectivity for 1-hexene remains relatively constant at around 48% for all the Al:Ni ratios.

Secondly, with the Al:Ni molar ratio retained at 3250, the temperature was raised from 20 °C to 50 °C with the catalytic activity initially increasing to a peak level at 30 °C before decreasing and then maintaining a constant level up to 50 °C (entries 10 - 12 vs. entry 6, Table 2). Moreover, the amount of 1-butene gradually decreased as the temperature was increased while the amount of

1-hexene (*ca.* 48%) remained fairly constant; such observations have also been noted with other nickel catalysts [3e,9e,18].

Thirdly, with the temperature and Al:Ni molar ratio fixed at 30 °C and 3250, respectively, the runs using **Ni1**/MMAO were performed over 5, 15, 45 and 60 minutes. The highest activity of $6.44 \times 10^6 \text{ g} \cdot \text{mol}^{-1}(\text{Ni}) \cdot \text{h}^{-1}$ was observed after 5 minutes. On prolonging the reaction time, the activity decreased gradually (entries 13 - 16 *vs.* entry 6, Table 2). Furthermore, the content of C₄ gradually decreased with the amount of C₆ constituting 92.4% of the mixture after 60 minutes; the 1-hexene content, however, remained constant at around 48%. Finally, the effect of ethylene pressure was explored under otherwise identical conditions. On lowering the pressure to 5 atm C₂H₄ only a slight drop in activity for **Ni1**/MMAO was noted. In contrast, the amount of C₆ products was slightly enhanced at lower pressure (entry 17 *vs.* entry 6, Table 2).

From the above findings, the optimal conditions using **Ni1**/MMAO were established as: Al:Ni molar ratio = 3250, P_{C₂H₄} = 10 atm, run temperature = 30 °C and run time = 30 minutes. Using these conditions, the catalytic evaluation of the remaining nickel complexes was then undertaken; the results are also listed in Table 2 (entries 18 - 22). As can be seen, all nickel complexes (**Ni1** - **Ni6**) showed high activities ($1.00 - 1.33 \times 10^6 \text{ g} \cdot \text{mol}^{-1}(\text{Ni}) \text{ h}^{-1}$) which decreased in the order: **Ni4** > **Ni1** > **Ni6** > **Ni3** > **Ni2** > **Ni5**. Although the range in catalytic activities are not significantly different, this order does suggest that the precatalysts incorporating the least sterically encumbered *ortho*-substitutents (**Ni1**, **Ni4**) promoted higher activities. With regard to the C₆ content, **Ni5** possessed the highest value of 98.1% (entry 21, Table 2) while the other catalysts were essentially invariant at around 86%. In terms of the 1-hexene selectivity, little variation was observed between structural types with values falling around 47% for all the complexes in line with comparable rates of isomerization (entries 18 - 22, Table 2).

(c) *Catalytic evaluation using MAO as co-catalyst.* As with the **Ni1** – **Ni6**/MMAO investigation, a similar approach was conducted in the first instance using **Ni1**/MAO; the results are summarized in Table 3.

The effect of the Al:Ni molar ratio was initially explored with the temperature kept at 30 °C, the ethylene pressure at 10 atm and the run time at 30 minutes (entries 1 - 6, Table 3). The results showed that **Ni1**/MAO displayed a peak activity of $1.28 \times 10^5 \text{ g mol}^{-1}(\text{Ni}) \text{ h}^{-1}$ with an Al:Ni molar

ratio of 2500. Either raising or reducing the Al:Ni ratio from 2500 resulted in a decrease in the activity. In all cases C₄ products were exclusively obtained with the selectivity for 1-butene reaching its highest level at lower Al:Ni molar ratios.

With the Al:Ni molar ratio fixed at 2500, the influence of temperature on the performance of **Ni1**/MAO was evaluated. On varying the temperature between 20 °C and 50 °C the highest activity of $1.28 \times 10^5 \text{ g mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ was achieved at 30 °C (entries 4, 7 - 9, Table 3). Once again only C₄ products could be detected with the temperature influencing the isomerization with the lower temperature runs favoring the selectivity of 1-butene.

By varying the run time, it was interesting to note that the activities over short reaction times (5 min and 15 min) were not high as observed in previous reports ^[5a,8b-8d,18a], which is likely due to an induction period necessary with this class of catalyst (entries 10 - 13 vs. entry 4, Table 3). Indeed, the highest catalytic activity using **Ni1**/MAO of $1.54 \times 10^5 \text{ g mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ was observed only after 45 minutes (entry 12, Table 3) which contrasts with the short induction period seen with **Ni1**/MMAO. In addition, the content of 1-butene gradually decreased with prolonging the reaction time, with only 65.3% of 1-butene detectable after 60 minutes. Meanwhile, reducing the ethylene pressure from 10 atm to 5 atm, over 30 a minute run time, saw a dramatic drop in activity from 1.28 to $0.51 \times 10^5 \text{ g mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ (entry 14 vs. entry 4, Table 3).

Using the optimal conditions established for **Ni1**/MAO [Al:Ni molar ratio = 2500, P_{C₂H₄} = 10 atm, run temperature = 30 °C and run time = 30 minutes], the remaining nickel precatalysts, **Ni2** - **Ni6**, were evaluated (entries 15 - 19, Table 3). The results show that the catalyst activity ranges between $0.86 - 2.50 \times 10^5 \text{ g mol}^{-1} (\text{Ni}) \cdot \text{h}^{-1}$, with their relative values falling in the order: **Ni3** > **Ni4** > **Ni1** > **Ni5** > **Ni2** > **Ni6**. By comparison with the MMAO runs, there were some differences in this order with most bulky precatalyst (**Ni6**) now the least active.

In common to both the MAO and MMAO runs, all the catalysts reached their optimum activity at 30 °C. However, the activity of **Ni1-Ni6**/MAO was close to an order of magnitude less than that seen with **Ni1-Ni6**/MMAO. On the other hand, all the MAO runs resulted in the dimerization of ethylene (C₄) with no evidence of any C₆ products^[18b]. Indeed, the selectivity for 1-butenes was in most cases high. By contrast with MMAO, both trimerization and dimerization products were achieved with C₆ products forming the major component. Furthermore, the maximum 1-hexene selectivity was around 48% implying significant isomerization. It is uncertain as to the origin of this

co-catalyst effect on chain length but it may be due to the steric properties of the *iso*-butyl groups in the MMAO influencing the rate at which β -H elimination occurs.

A further key point relates to the role of the acetyloxymethyl group in the oligomerization. The current precatalysts (**C**, Chart 1) have a preference to form short chain oligomers as opposed to longer chain oligomers reported using **B** (Chart 1). It would seem likely that ester oxygen atoms play an active role in the oligomerization by filling vacant sites in the active catalyst thereby inhibiting propagation ^[3c,9b,12,19].

Conclusions

A series of nickel complexes, **Ni1** – **Ni6**, bound by a novel class of bidentate 5,6,7-trihydroquinolinyl-8-ylideneamine ligand that have each been appended with a 2-acetyloxymethyl group, are disclosed. Complex characterization has been made by using a range of techniques including in two cases by single crystal diffraction which reveal the acetyloxymethyl group to remain uncoordinated. On activation with MMAO, all catalysts exhibited good activity at 30 °C in the range $1.00 - 1.33 \times 10^6 \text{ g mol}^{-1}(\text{Ni}) \text{ h}^{-1}$, forming a mixture of C_6 (up to 48% 1-hexene) and C_4 products (up to 99% 1-butene) with a significant bias towards the longer chain hydrocarbon. On the other hand, the activity of **Ni1** – **Ni6**/MAO was notably lower (range: $0.86 - 2.50 \times 10^5 \text{ g mol}^{-1}(\text{Ni}) \text{ h}^{-1}$) but exhibited a specificity for ethylene dimerization (1-butene content: 64-99%). It is worth noting that **Ni1**/MAO displayed a clear induction period with peak activities only evident after longer run times. It has been speculated the acetyloxymethyl group can undergo coordination with the active species leading to rapid β -H elimination; steric effects associated with the *iso*-butyl groups in the MMAO may provide the origin of the switch to mainly C_6 products seen with this co-catalyst.

Supporting Information

Details of the X-ray structure determinations and refinements of compounds **Ni2** and **Ni3** are provided in Table S1 and their selected bond distances and angles are collected in Table S2. CCDC 1947410 and 1947411 contain the supplementary crystallographic data for compounds **Ni2** and **Ni3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing

data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Captions of Tables, Figures, Chart and Scheme

Table 1 Co-catalyst screen using **Ni1** as the precatalyst

Table 2 Ethylene oligomerization using MMAO as co-catalyst

Table 3 Ethylene oligomerization using MAO as co-catalyst

Figure 1 ORTEP representation of **Ni2** with the thermal ellipsoids set at 30% probability level; hydrogen atoms have been omitted for clarity. The atoms labelled with 'i' were generated through symmetry.

Figure 2 ORTEP representation of **Ni3**·OH₂ with the thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Figure 3 Dimeric assembly through OH···Cl intermolecular hydrogen bonding in **Ni3**·OH₂

Chart 1 Structural developments deriving from 2-iminopyridine-nickel(II) halide (**A**)

Scheme 1 One-pot template assembly of **Ni1** – **Ni6** from **1**

Table 1 Co-catalyst screen using **Ni1** as the precatalyst^[a]

Entry	Co-cat.	Al:Ni	<i>t</i> [min]	Activity ^[b]	Oligomer Distribution ^[c] (%)			
					C ₄ /ΣC	α-C ₄	C ₆ /ΣC	α-C ₆
1	MMAO	2000	30	0.9	11.1	73.7	88.9	48.8
2	MAO	2000	30	0.06	100	>99	-	-
3	EASC	500	30	0.04	100	>99	-	-

[a] General conditions: 4 μmol of **Ni1**, 10 atm of C₂H₄, 100 mL of toluene;

[b] 10⁶ g·mol⁻¹ (Ni) h⁻¹;

[c] Determined by GC and ΣC signifies the total amounts of oligomers.

Table 2 Ethylene oligomerization using MMAO as co-catalyst^[a]

Entry	Precat.	<i>T</i> [°C]	Al:Ni	<i>t</i> [min]	Activity ^[b]	Oligomer Distribution ^[c] (%)			
						C ₄ /ΣC	α-C ₄	C ₆ /ΣC	α-C ₆
1	Ni1	30	1000	30	0.36	14.2	69.6	85.8	46.8
2	Ni1	30	1500	30	0.55	14.4	74.1	85.6	47.5
3	Ni1	30	2000	30	0.91	11.0	73.7	88.9	48.8
4	Ni1	30	2500	30	0.99	13.0	80.6	87.0	48.2
5	Ni1	30	3000	30	1.04	16.0	83.0	84.0	48.2
6	Ni1	30	3250	30	1.28	13.3	97.0	86.6	48.5
7	Ni1	30	3500	30	1.25	9.9	86.1	90.1	47.8
8	Ni1	30	3750	30	1.23	8.5	>99	91.5	48.0
9	Ni1	30	4000	30	1.13	8.1	78.9	91.9	48.0
10	Ni1	20	3250	30	1.11	10.0	>99	90.0	49.5
11	Ni1	40	3250	30	1.10	12.0	82.9	88.0	47.6
12	Ni1	50	3250	30	1.00	6.1	73.6	93.9	47.8
13	Ni1	30	3250	5	6.44	14.2	91.6	85.8	48.1
14	Ni1	30	3250	15	2.11	14.0	68.1	86.0	48.3
15	Ni1	30	3250	45	0.71	8.9	81.2	91.1	47.5
16	Ni1	30	3250	60	0.44	7.6	>99	92.4	47.4
17 ^[d]	Ni1	30	3250	30	1.20	10.0	>99	90.0	48.1
18	Ni2	30	3250	30	1.07	15.7	63.7	84.3	46.9
19	Ni3	30	3250	30	1.10	14.5	64.9	85.5	47.9
20	Ni4	30	3250	30	1.33	14.9	77.4	85.1	48.2
21	Ni5	30	3250	30	1.00	1.9	>99	98.1	47.5
22	Ni6	30	3250	30	1.25	14.0	52.9	86.0	48.1

[a] General conditions: 4 μmol of pre-catalyst, 10 atm of C₂H₄, 100 mL of toluene;

[b] 10⁶ g·mol⁻¹ (Ni)·h⁻¹;

[c] Determined by GC and ΣC signifies the total amounts of oligomers;

[d] 5 atm of C₂H₄.

Table 3 Ethylene oligomerization using MAO as co-catalyst^[a]

Entry	Precat.	<i>T</i> [°C]	Al:Ni	<i>t</i> [min]	Activity ^[b]	Oligomer Distribution ^[c] (%)	
						C ₄ /ΣC	α-C ₄
1	Ni1	30	1500	30	0.35	100	>99
2	Ni1	30	2000	30	0.58	100	>99
3	Ni1	30	2250	30	1.17	100	74.9
4	Ni1	30	2500	30	1.28	100	77.6
5	Ni1	30	2750	30	1.11	100	88.3
6	Ni1	30	3000	30	1.09	100	84.2
7	Ni1	20	2500	30	0.77	100	>99
8	Ni1	40	2500	30	1.14	100	73.5
9	Ni1	50	2500	30	0.82	100	67.9
10	Ni1	30	2500	5	0.78	100	>99
11	Ni1	30	2500	15	1.05	100	>99
12	Ni1	30	2500	45	1.54	100	68.4
13	Ni1	30	2500	60	0.49	100	65.3
14 ^[d]	Ni1	30	2500	30	0.51	100	71.4
15	Ni2	30	2500	30	1.11	100	71.2
16	Ni3	30	2500	30	2.50	100	71.6
17	Ni4	30	2500	30	1.92	100	73.0
18	Ni5	30	2500	30	1.26	100	71.6
19	Ni6	30	2500	30	0.86	100	64.3

[a] General conditions: 4 μmol of pre-catalyst, 10 atm of C₂H₄, 100 mL of toluene;

[b] 10⁵ g mol⁻¹ (Ni) h⁻¹;

[c] Determined by GC and ΣC signifies the total amounts of oligomers;

[d] 5 atm of C₂H₄.