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Neutral Ni(II) Catalysts based on Maple-Lactone Derived [N,O] Ligands for the Polymerization of Ethylene

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Abstract

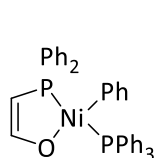
This paper describes the synthesis of neutral nickel(II) catalysts for the polymerization of ethylene. A series of 2-(arylamino)-5-methylcyclopent-2-en-1-one (aryl = 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, 3,5-dimethylphenyl and 4-methylphenyl) proligands, derived from the condensation of aryl amines with maple lactone, were synthesised as their keto-enamine tautomers. Deprotonation with NaH gave their respective sodium imino-enolate salts, which underwent salt metathesis with Ni(II) precursors to give square planar [Ni(Ar)(κ²-imino-enolate)(PPh₃)] (Ar = Ph, *ortho*-tolyl) complexes containing 5-membered [N,O] chelates. Precatalysts with N-Dipp (Dipp = 2,6-diisopropylphenyl) substituents were found to exhibit moderate activity in the polymerization of ethylene when using B(C₆F₅)₃ or [Ni(cod)₂] (cod = 1,4-cyclooctadiene) as co-activators, producing polymers with a high molecular weight, as determined by GPC. The reaction was found to be highly dependent on temperature, with the catalysts most active at 80 °C. Differences in polymer structure were also found when using B(C₆F₅)₃ or [Ni(cod)₂] as the cocatalyst, with [Ni(cod)₂] producing a more highly branched polymer. Reducing the steric bulk at the N substituent of the ligand led to inactive species.

Introduction

Olefin polymerization is of great interest to both industry and academia with significant, on-going research being carried out by many groups across the world.¹ Commercially, polyethylene can be

produced using heterogeneous catalysts based on titanium with aluminium co-catalysts (Ziegler-Natta systems),² or with chromium systems that don't require an activator.³ Homogeneous catalysts based on group 4 metallocenes, that use methylaluminoxane (MAO) as a co-catalyst, were subsequently discovered that offered access to improved polymer properties.^{4, 5} Building on these advances, the discovery of 'post-metallocene' catalysts for alkene polymerization has shown that catalysts based on Fe, Co, Ni and Pd can all be developed for applications in ethylene polymerization.⁶⁻⁹ This has been of particular interest for facilitating copolymerization reactions with functionalised olefins that contain polar substituents due to their rapidly expanding range of desirable properties.¹⁰⁻¹³ Commercially important examples include polyketone copolymers, formed from ethylene and carbon monoxide, which are of interest due to their photodegradability and their use in engineering plastics.¹⁴

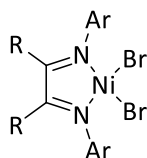
Although oxophilic metals such as titanium and zirconium show excellent activity in the polymerization of olefins, when polar co-monomers are present, these can irreversibly bind to the metal and poison the catalyst. In contrast, late transition metals, such as nickel or palladium, exhibit lower oxophilicity.¹⁵ As a result, polar substrates are more weakly bound to the metal centre, therefore substitution at the active site is more facile, ultimately resulting in successful copolymerization.¹³ The use of nickel catalysts is well established in olefin oligomerization, most notably in the Shell Higher Olefin Process (SHOP) which was developed from 1968 onwards.¹⁶ Catalysts of the form **A (Chart 1)** with [P,O]-donor anionic ligands produce mainly short chain oligomers rather than polymers. However, upon addition of a phosphine scavenger (such as [Ni(cod)₂] or [Rh(acac)(C₂H₄)₂]), these oligomerization catalysts can be transformed into polymerization catalysts that are tolerant to polar impurities in homopolymerization reactions and polar monomers in copolymerization reactions.¹⁷⁻¹⁹



A¹⁶

1968

Oligomers



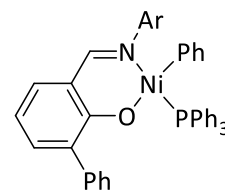
B²⁰

1995

Mw: 280,000 gmol⁻¹

Activity = 892

Temp = 0 °C



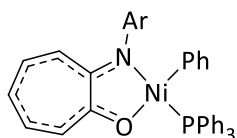
C²⁶

1998

Mw: 242,000 gmol⁻¹

Activity = 28

Temp = 0 °C



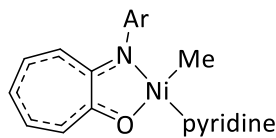
D³¹

2003

Mw: 62,500 gmol⁻¹

Activity = 120

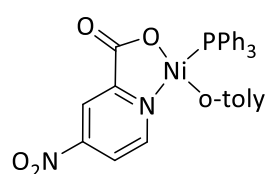
Temp = 80 °C



E⁵²

2009

scCO₂, only trace
amounts of polymer



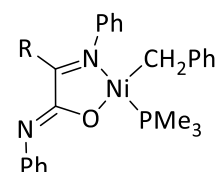
F³³

1997

Mw not stated

Activity = 0.03

Temp = 80 °C



G⁵³

2008

Mw: 182,000 gmol⁻¹

Activity = 77

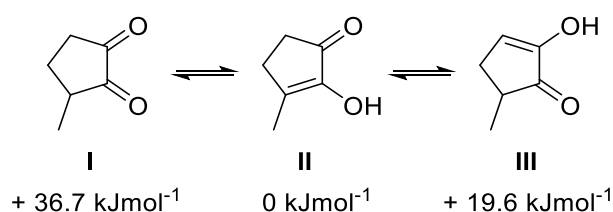
Temp = 20 °C

Chart 1. Selected historical developments in Ni catalysis applied to the oligomerization/polymerization of ethylene, with dates of development, polymerization temperature and activity (g mmol⁻¹ h⁻¹ bar⁻¹). Ar = bulky aryl group. Activity reported for Ar = Dipp (2,6-*i*-Pr₂C₆H₃).

Seminal work by Brookhart and co-workers in the 1990s demonstrated that cationic Ni catalysts bearing α -diimine ligands could generate low density polyethylene with high molecular weights (**B**, **Chart 1**).²⁰ However, early catalysts of this type experienced a short lifetime when polymerization was carried out above 60 °C, having a significant impact on the total turnover numbers achieved.²¹ This is problematic for industrial applications where polymerisations are normally carried out between 90 °C and 110 °C for HDPE.²² This family of catalysts has subsequently been extensively studied, which has helped address this problem.^{15, 23, 24, 25} Grubbs and co-workers further developed the use of nickel in polymerization catalysis by using anionic [N,O]-type ligands (**C**, **Chart 1**), which yielded very active neutral Ni catalysts generating polymers with high Mw.²⁶ Furthermore, with judicious choice of ligand substituents, the need for co-activators could also be removed.²⁷ However, despite these advances, our understanding of neutral Ni(II) [N,O] catalysts still lags behind [N,N]-type catalysts for the polymerization of ethylene.²⁸⁻³⁰ In addition to well established steric effects, the bite angle of the ligand has a possible role in influencing the rate of polymerization, with Brookhart and co-workers

finding in 2001 that a 5-membered chelate ring can have a higher activity compared to similar catalysts with a 6-membered chelate ring.³¹ Other neutral Ni complexes with 5-membered [N,O] chelates have also proven useful in the polymerization of ethylene.³²⁻³⁵ Ni catalysts based on 2-anilinoperinaphthenones gave active but short-lived catalysts³⁶ and α -iminocarboxamidato Ni catalysts have been extensively studied,^{37, 38} with only the [N,O]-bound Ni centres being catalytically active.³⁹ Expanding to other donor atoms, neutral Ni catalysts with 5-membered [N,N]⁴⁰ and [P,O]^{41, 42} chelates have been explored recently, and NHC-containing chelates have given Ni catalysts with very high thermal stabilities,⁴³ demonstrating that a wide variety of ligands can deliver catalytically active Ni centres.

We became interested in understanding what ligand properties are required to generate active, neutral Ni catalysts, particularly with the potential importance of small bite-angles^{44, 45} and chelate ring-size. In particular, we noted Brookhart's work in the development of very active catalysts with a 5-membered chelating ligand (**D**),^{31, 46, 47} and wanted to investigate: i) if the bite angle could be changed by altering the carbacyclic ligand backbone and what the effect would be, and ii) to see whether conjugation between the N and O donors, as found in anilitropone ligands, was vital. We noted that maple lactone is a cheap, bio-sourced molecule that with simple modification would generate a range of 5-membered chelating [N,O] ligands with potentially interesting properties. Although maple lactone is listed commercially under the diketone description, maple lactone has several tautomeric forms (**Scheme 1**). Computationally, the keto-enol tautomer **II** has been predicted to be more stable than the diketone tautomer (**I**) due to π -delocalisation in the α,β -enone system,⁴⁸ and also more stable than **III** due to the eclipsing steric interaction between the methyl group and a C-H in the 5-membered ring.⁴⁹ We set out to utilise this molecule as the building block for a set of novel [N,O] proligands for complexation to nickel(II). These complexes were then examined for catalytic activity towards ethylene polymerization in order to investigate the potential influence of bite angle and conjugation including the donor atoms.

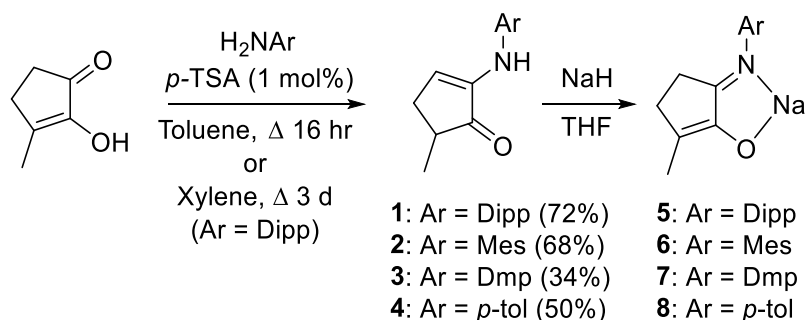


Scheme 1. Computed relative energies of the three major isomers of maple lactone.^{48, 49}

Results and Discussion

Synthesis of proligands

To confirm the identity of the preferred tautomer of maple lactone, single crystals were grown from ethyl acetate / petroleum ether (40-60). Single crystal X-ray diffraction experiments confirmed the presence of tautomer **II** (**Scheme 1**), with C-O bond lengths of 1.231(2) Å and 1.359(2) Å identifying the ketone and alcohol functionality respectively, as well as a C-C bond length of 1.345(2) Å indicative of a carbon-carbon double bond (see ESI for SCXRD data). The proligands were synthesised by the condensation of maple lactone with substituted anilines in the presence of catalytic quantities of *p*-toluenesulfonic acid (**Scheme 1**), with single substitution occurring selectively at the ketone position. Interestingly, the resulting compounds underwent tautomerization forming the keto-enamine; a similar result was observed in the synthetic pathway to imino-enamido ligands that have been used in group 4 complexes for the production of polyethylene.^{21, 49} The keto-enamine tautomer was confirmed through multinuclear NMR spectroscopy, infrared spectroscopy and single crystal X-ray diffraction experiments. Using ¹H NMR spectroscopy, the resonance corresponding to the methyl group was observed as a singlet in maple lactone, but a doublet in **1 – 4**. Additionally, there was also a pseudo-triplet at δ 5.5 ppm relating to the olefinic C-H present in **1 – 4**. Through single crystal diffraction data (**Figure 1** for **1**), a decrease in bond length of C2-C3 was observed, from 1.509(3) Å in maple lactone to 1.345(3) Å in **1**, indicative of the change from a single to a double bond. Likewise, an increase of bond length is seen for C1-C5 from 1.344(2) Å to 1.522(3) Å along with a shortening of the C-O bond from 1.359(2) Å to 1.219(2) Å, again confirming that the keto-enamine has formed. Similar bond lengths were observed for **2 – 4** (see ESI for SCXRD data). Additional characterization was achieved using mass spectrometry and elemental analysis.



Scheme 2. Proligand synthesis and subsequent deprotonation (isolated yields not recorded).

Dipp = 2,6-*i*-Pr₂C₆H₃; Mes = 2,4,6-Me₃C₆H₂; Dmp = 3,5-Me₂C₆H₃; *p*-tol = 4-MeC₆H₄.

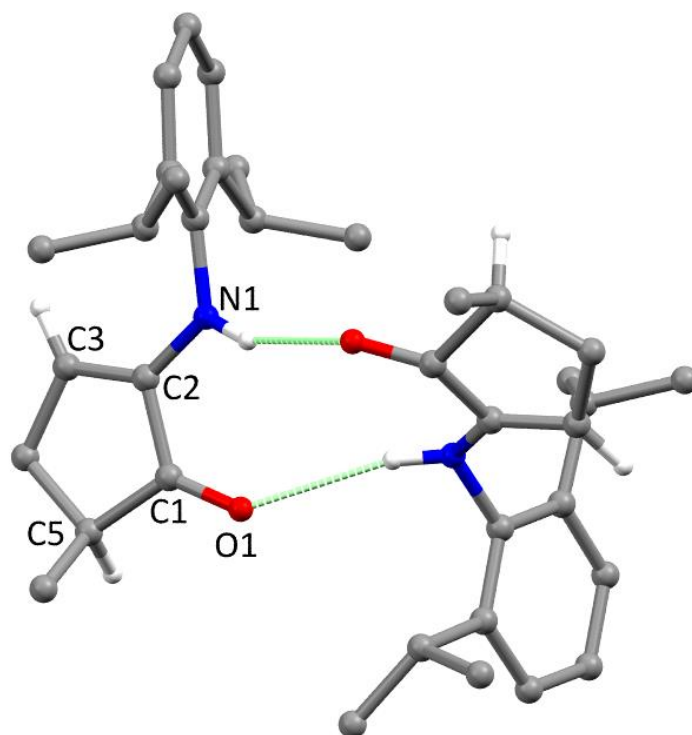


Figure 1. Molecular structure of **1**, existing as a H-bonded dimer, with only selected H atoms shown. Selected bond distances (Å): C1-C2 1.471(3), C2-C3 1.345 (3), C1-C5 1.522 (3), C2-N1 1.365(2), C1-O1 1.219 (2), O1-H 2.303, (N1)H-O 2.073.

Compounds **1** – **4** were deprotonated using excess NaH forming solids after concentration of the filtrate (**Scheme 2**). These salts can be reacted directly with Ni precursors without further purification, but to better understand the nature of these species single crystals of **5** were grown and analysed by X-ray diffraction in order to determine its solid-state structure. A single crystal X-ray diffraction study showed **5** to exist as a hexameric species with a hexagonal prismatic arrangement of Na and O atoms with each O atom triply bridging the four-coordinate Na atoms. Interestingly, the ligand is chelating the Na atoms in its imino-enolate form (**Figure 2**), with bonds lengths indicative of a C=N double bond [1.286(5) Å] and an enolate functionality [C=C: 1.369(5) Å]. Clearly, there is an interplay between various tautomers in all these different species with different tautomers preferred for maple lactone, the proligands and **5**.

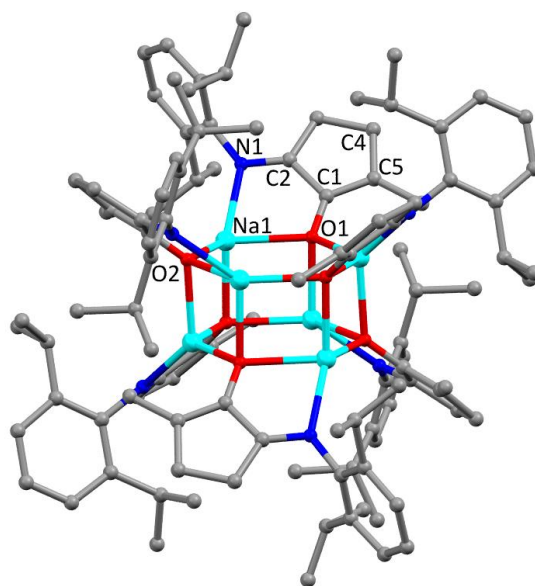
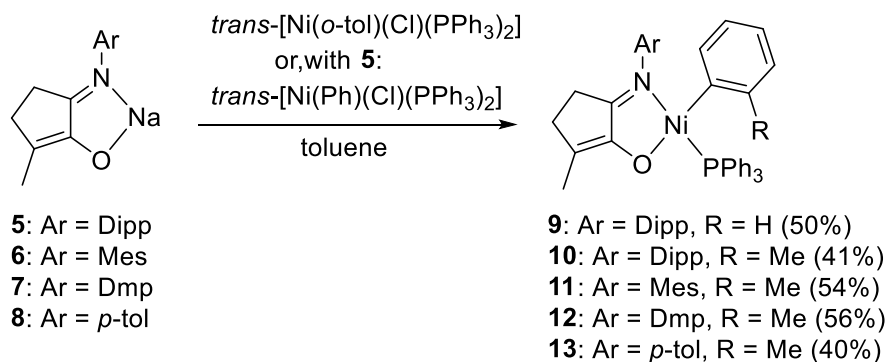


Figure 2. Molecular structure of **5**, with H atoms omitted for clarity (Na = turquoise, O = red, N = blue, C = grey). Selected bond distances (Å) and angles (°): Na1-O1 2.290(3), Na1-O2 2.265(3), Na1-O3 2.288(3), Na1-N1 2.356(3), O1-C1 1.318(4), N1-C2 1.286(5), C1-C2 1.475(6), C1-C5 1.369(5), C4-C5 1.503(6), O1-Na1-N1 76.5(1).

Synthesis and characterisation of Ni complexes

Neutral Ni(II) precatalysts for ethylene polymerization require a hydrocarbyl Ni-substituent to initiate the reaction as well as a neutral ligand that can dissociate in order to create a vacant site. Ni-Ar complexes of proligands **1** – **4** with PPh₃ co-ligands were therefore prepared using metathesis from the sodium salts **5** – **8** (Scheme 3). They were characterised using multinuclear NMR spectroscopy, X-ray crystallography and high-resolution mass spectrometry. From **5**, Ni complexes containing either a Ph or *ortho*-tolyl substituent were synthesized via salt metathesis, from the appropriate Ni precursor,⁵⁰ in order to determine the effect of initiating group on activity and stability. We noted that the *ortho*-tolyl precursor *trans*-[Ni(*o*-tol)(Cl)(PPh₃)₂] is relatively air and moisture stable, a useful feature for a precatalyst, in contrast to the Ph precursor *trans*-[Ni(Ph)(Cl)(PPh₃)₂] which degrades in solution to form biphenyl via disproportionation when there is no excess PPh₃ present.⁵¹



Scheme 3. Synthesis of Ni complexes.

Complexes **9** – **13** were prepared in similar yields of 40 – 56% and displayed a single $^{31}\text{P}\{^1\text{H}\}$ NMR resonance between δ 21 and 27 ppm. The ^1H NMR spectrum of **10** showed evidence for slow rotation about the Ni-Ar bond as four distinct doublets and two septet resonances were observed for the diisopropyl groups, unlike the two doublets visible in the proligand. This slow rotation is also evident in **11**, with singlet resonances for each Mes methyl group visible. Single crystal X-ray diffraction revealed similar molecular structures for **9** (Figure 3) and **10** (see ESI) with the imine donor *trans* to PPh_3 , similar to other [N,O]-type ligands with Ni (Chart 1). Comparing **9** and **10**, bite angles of the [N,O] ligand were almost identical at $85.59(5)$ (**9**) and $85.75(9)^\circ$ (**10**), which is slightly larger, but still similar, to other 5-membered chelate ligands in literature, which are in the region of $82.5^\circ - 84.0^\circ$.^{31-33, 52, 53} For **9** and **10**, the Ni-C bond lengths are identical within error [Ni1-C19 $1.890(3)$ Å], while the other bond lengths to Ni have some minor variations; the Ni-N bond is shorter in **9** but the Ni-O bond length is shorter in **10** [Ni-N: $1.955(1)$ (**9**) and $1.978(2)$ (**10**); Ni-O: $1.945(1)$ (**9**) and $1.918(2)$ Å (**10**)]. Both complexes feature distorted square planar Ni centres; for **9** the Ph ligand lies out of the Ni square plane ($\text{O-Ni-C} = 166.2^\circ$), whereas for **10** the PPh_3 ligand is further out of the square plane ($\text{N-Ni-P} = 162.6^\circ$). Compared to other Ni precatalysts, the Ni-P bond lengths are similar, with reported values of between 2.14 Å and 2.18 Å, and the Ni-N bonds are slightly longer than average at $1.955(1)$ and $1.978(2)$ Å, with other bond lengths recorded between 1.89 Å – 1.98 Å.^{26, 31, 33, 52, 53} The imino-enolate tautomer was confirmed with C-O bond lengths of $1.321(2)$ (**9**) and $1.326(3)$ Å (**10**) and C=N bond lengths of $1.294(2)$ (**9**) and $1.302(4)$ Å (**10**).

Changing the N-substituents leads to only relatively small structural changes. The Ni-P bond lengths for **11** [$2.1408(5)$ Å] and **12** [$2.1461(7)$ Å] are shorter than for **9** [$2.1503(4)$] and **10** [$2.1613(8)$ Å], while the Ni-N and Ni-O bond lengths for **11** and **12** [Ni-N $1.955(2)$ and $1.957(2)$; Ni-O $1.941(1)$ $1.937(2)$ Å respectively] resemble those seen in **9** [Ni-N $1.955(1)$; Ni-O $1.945(1)$ Å] more than those seen in **10** [Ni-N $1.978(2)$ and Ni-O $1.918(2)$ Å]. However, the bite angles are very similar across all complexes at $85.4(1) - 85.8(1)^\circ$. The shorter Ni-O bonds and longer Ni-N bonds in **10** are ascribed to the increased

steric bulk of the Dipp and *o*-tol groups causing an increase in distance for the Ni-N bond, and subsequent shortening of the Ni-O bond, and there is also a lengthening of the Ni-P bond in **10** compared to the other precatalysts.

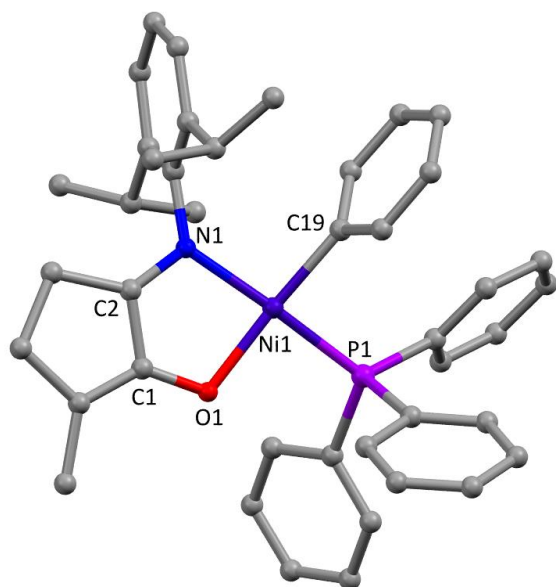


Figure 3. Molecular structure of **9**, with selected H atoms removed for clarity. Selected bond distances (Å) and angles (°): Ni1-C19 1.890(2), Ni1-P1 2.1503(4), Ni1-O1 1.945(1), Ni1-N1 1.955(1), O1-C1 1.321(2), C2-N1 1.294(2), C1-C5 1.358(2), C2-C3 1.497(2), O1-Ni1-N1 85.59(5).

Ethylene polymerization results

Initial catalytic screening of **9** and **10** with [Ni(cod)₂] as a phosphine scavenger was conducted at 60 °C under 40 barg of ethylene using a preheated autoclave equipped with gas-entraining stirrer to identify the best initiating aryl group for the production of polyethylene. Comparing runs for **9** and **10** showed that the *o*-tolyl group increased the activity of the catalyst, to 6.28 g (mmol h bar)⁻¹ from 3.95 g (mmol h bar)⁻¹ for **9** (Table 1, Runs 1,2). As the aryl group acts as an initiator, it seems likely that this reflects the lower stability of the Ni-Ph compound at elevated temperatures, as revealed by ¹H NMR spectroscopy. Hence, **10** was found to be more active, possibly as a result of its enhanced thermal stability, which was also demonstrated by ¹H NMR spectroscopy. This led us to focus on complexes with *o*-tolyl initiating groups.

Run	Catalyst	Catalyst loading (mmol)	Temperature (°C)	Ethylene pressure (barg)	Mass (g)	Activity (g (mmol h bar) ⁻¹)
1	9	0.030	60	40	5.920	3.95
2	10	0.022	60	40	6.904	6.28

Table 1 Initial catalytic screening of initiating groups for ethylene polymerization using 3 eq. [Ni(cod)₂] as cocatalyst, 100 mL toluene and the precatalyst that were premixed in a Schlenk flask before transfer to a pre-warmed autoclave.

The effect of steric bulk present near the metal centre was investigated through variation of the imine substituent. Altering the steric properties of the aryl imine group strongly influenced the catalytic activity. An activity of 4.25 g (mmol h bar)⁻¹ was achieved at 60 °C with 10 barg of ethylene for catalyst **10**, which reduced to 0.23 g (mmol h bar)⁻¹ for the Mes-substituted precatalyst **11** due to decreased steric bulk at the *ortho* position of the aryl imine group. This trend is continued with **12** and **13**, which showed a dramatic drop in polymerization activity to 0.08 g (mmol h bar)⁻¹ (**Table 2, Runs 3-6**) as the steric bulk was decreased further with the methyl groups moved to the *meta* and *para* positions. Similar trends have been observed by other groups in the literature.^{26,37}

Run	Catalyst	Catalyst loading (mmol)	Temperature (°C)	Ethylene pressure (barg)	Mass ^a (g)	Activity (g (mmol h bar) ⁻¹)
3	10	0.005	60	10	0.106	4.25
4	11	0.005	60	10	0.006	0.23
5	12	0.005	60	10	0.002	0.08
6	13	0.005	60	10	0.002	0.07

Table 2 Initial catalytic screening for ethylene polymerization using 600 rpm stirring, 4 eq. B(C₆F₅)₃ as initiator, 30 mL toluene and catalyst added to autoclave in glovebox before autoclave warmed and pressurised. ^a Measured after 1 day drying at 80 °C in a vacuum oven.

Having found the optimal catalyst from the synthesised library, **10** was then screened to identify the limits of the catalytic activity. At low pressure (0.5 barg ethylene) and at room temperature with a variety of activators, no activity was observed. The pressure was then increased to 10 barg ethylene, still at room temperature, and various activators were trialled, which showed polymerization of ethylene when B(C₆F₅)₃ was added to remove PPh₃. (Table 2, Run 7-9). The effect of polymerization temperature was then explored (**Table 3, Runs 3, 10-15**). This showed an increase in the activity, peaking at 80 °C (**Table 3, Run 14**) before dropping off. This drop off above 80 °C could be due to either

poor gas dissolution into the reaction solvent, or deactivation of the active species in solution at high temperatures. This decrease in catalytic activity at elevated temperatures is common in this family of catalysts, with decreases of activity observed in previous work above 60 °C.^{54,55} For the anilintropone catalyst **D**, activity also peaked at 80°C.³⁶

Increased catalytic loading was also trialled (**Runs 16 and 17**), which showed an increase in polymer yield, but a decrease in the activity and productivity of the catalyst. The polymerization at 80 °C shows an activity of 33.5 g (mmol h bar)⁻¹, displaying moderate activity as defined by Britovsek *et al.*⁶ This level of activity is defined across all classes of polymerization catalyst, however, and for [N,O]-type catalysts, this activity is within the expected range. Work by Grubbs and coworkers showed activities in the magnitude of 5 to 56 g (mmol h bar)⁻¹ with increasing bulk of the phenoxyimine ligand backbone (**C, Chart 1**) from H substituents, to phenyl through to anthracene.²⁶ Other work in the field has shown activities in similar conditions between 3-33 g (mmol h bar)⁻¹.⁵⁶⁻⁵⁸ This activity is still low compared to previous activities shown by Brookhart and co-workers for **D (Chart 1, Ar = Dipp)** of ca. 120 g (mmol h bar)⁻¹, however, this catalyst was short lived at 80°C. High activities could be potentially due to beneficial conjugation between the donor atoms in the anilintropone ligand as all other aspects of this ligand are similar to **1**.

Run	Catalyst	Catalyst loading (mmol)	Temperature (°C)	Ethylene pressure (barg)	Mass ^a (g)	Activity (g (mmol h bar) ⁻¹)
7	10	0.005	60	1	0	0
8	10	0.005	60	15	0.187	4.99
9	10	0.005	60	20	0.211	4.22
10	10	0.005	r.t	10	0.013	0.52
11	10	0.005	40	10	0.063	2.51
12	10	0.005	50	10	0.112	4.48
13	10	0.005	70	10	0.318	12.7
14	10	0.005	80	10	0.837	33.5
15	10	0.005	90	10	0.505	20.2
16	10	0.020	r.t	10	0.032	0.32
17	10	0.020	60	10	0.387	3.87

Table 3 Catalytic activity for ethylene polymerization over a range of conditions. Standard conditions = 600 rpm stirring, 4 eq. $B(C_6F_5)_3$ as initiator, 30 mL toluene and **10** added to autoclave in glovebox before autoclave warmed and pressurised. ^a Measured after 1 day drying at 80 °C in a vacuum oven.

Polymer characterization

The polymers were characterized using differential scanning calorimetry (DSC), NMR spectroscopy and gel permeation chromatography (see ESI). NMR spectroscopic analysis was hampered for all the polymers formed using $B(C_6F_5)_3$ due to low solubility in C_6D_5Br at room temperature. The melting point of the polymers formed under standard conditions using $B(C_6F_5)_3$ as the cocatalyst were similar at 117(±4) °C, which equates to a relatively low percentage of Me branching.²¹ The polymer formed at 40 barg ethylene with $[Ni(cod)_2]$ as the cocatalyst exhibited a much lower melting point (51 °C) as well as a glass transition point at -1.5 °C (**Table 4, Run 2**) typical of a highly-branched polymer, as also deduced from ¹H NMR spectroscopy (ca. 83 branches per 1000 C atoms).^{21, 59} Further studies into the effect of the cocatalyst were carried out using $[Ni(cod)_2]$ at 10 barg and 60°C demonstrating the formation of a viscous polymer, different to that formed when $B(C_6F_5)_3$ was used as the cocatalyst. This polymer was soluble in $CDCl_3$, unlike runs 2 – 17, and showed a high percentage of branching with 157 Me groups per 1000 carbons; ethyl, propyl and butyl branches were also observed. Shan *et al.* have also observed differences in the polymer upon changing the cocatalyst, but the effect was based on altering the stability of the metal centre, affecting the activity and M_w of the polymers formed, rather than the extent of branching.⁶⁰ The effect of changing the Ni-hydrocarbyl initiating group has also been probed in a Ni [P,O] system, with differences upon the addition of $B(C_6F_5)_3$ or $[Ni(cod)_2]$ noted.⁶¹ For the anilinetropone catalyst **D** (Ar = Dipp), no change was observed upon the addition of different phosphine scavengers ($B(C_6F_5)_3$, BPh_3 and $[Ni(cod)_2]$), but then this catalyst is active without a cocatalyst.³⁶ For a Ni phenoxyimine catalyst (type **C**), no difference was observed for polymers formed from using either $B(C_6F_5)_3$ or $[Ni(cod)_2]$ as a cocatalyst.²⁶

For the polymer with the narrowest PDI (run 2 using $[Ni(cod)_2]$), values of $M_n = 38,000$, PDI = 2.3, 83 Me branches per 1000 carbon atoms and $T_m = 51^\circ C$ were found. In comparison, Dipp-substituted precatalyst **B** (Chart 1, R = H) + MMAO gave polyethylene with $M_n = 100,000$, PDI = 2.7, 7 Me branches per 1000 carbon atoms and $T_m = 129^\circ C$.²⁰ A related complex with a bis(Dipp)acenaphthenequinonediimine ligand gave polyethylene with $M_n = 170,000$, PDI = 2.3, 74 Me branches per 1000 carbon atoms and $T_m = 97^\circ C$.²⁰ Catalyst **D** (Ar = Dipp) gave polyethylene with varying degrees of Me branches, from 8 to 113 per 1000 C atoms, with M_n of 204,000 and 6,700 respectively (PDI = 2.81 and 2.03) upon changing temperature and pressure.³¹

Run	Temperature (°C)	Mw ^a (g mol ⁻¹)	Tm (°C)
2	60	79,100	51
12	50	63,500	118
3	60	46,100	113
13	70	101,000	114
14	80	24,000	121
15	90	51,000	118

Table 4 Polyethylene properties. ^a Determined by GPC in 1,2,4-trichlorobenzene at 150 °C vs. linear polystyrene standards, and corrected by calibration. Main peak in the GPC data, shoulders present in some of the data. Run 2: [Ni(cod)₂] cocatalyst and 40 barg ethylene. B(C₆F₅)₃ and 10 barg ethylene used for all others.

Conclusions

In conclusion, a series of Ni(II) complexes with 5-membered chelating [N,O] ligands derived from maple lactone were synthesised and characterised. They were screened towards the polymerization of ethylene and were found to exhibit moderate activity, producing polymers with a high molecular weight, as determined by GPC, when using B(C₆F₅)₃ or [Ni(cod)₂] as an activator. However, poorly soluble polyethylene with a relatively high melting point (117(±4) °C) was produced when B(C₆F₅)₃ was used as a cocatalyst, compared to more highly branched polymers with lower melting points when [Ni(cod)₂] was used as a cocatalyst. It was found that steric bulk played an important role in producing an active catalyst, with only the diisopropylphenyl-substituted catalyst displaying high activities. It was also demonstrated that this catalyst was still active at elevated temperatures, with the optimum temperature found to be 80 °C. Higher pressures of ethylene was found to increase the catalytic turnover and frequency. The Dipp-substituted complex was not as active as previous Ni-anilintropone catalysts despite the similar N-substitution and chelate size, suggesting that other factors may be responsible for increased activity. The utilisation of these nickel(II) complexes as catalysts for the co-polymerization of ethylene with polar monomers is currently ongoing.

Experimental

Reactions were either performed under an oxygen-free (H_2O , $\text{O}_2 < 0.5$ ppm) nitrogen atmosphere using standard Schlenk line techniques and an MBRAUN UNIlab Plus glovebox or in the open laboratory, as indicated. Anhydrous toluene, anhydrous DCM and anhydrous THF were obtained from an MBRAUN SPS-800 and petroleum ether 40-60 was distilled from sodium wire; benzene and benzene- d^6 were dried over molten potassium and distilled. All anhydrous solvents were degassed before use and stored over activated molecular sieves.

The following compounds were prepared according to literature methods: $[\text{Ni}(\text{Ph})\text{Cl}(\text{PPh}_3)_2]$,⁶² $[\text{Ni}(o\text{-tolyl})\text{Cl}(\text{PPh}_3)_2]$.⁵⁰ The following were purchased from commercial suppliers and used without further purification: maple lactone, 3,5-dimethylaniline, *p*-toluidine, *p*-toluenesulfonic acid, sodium hydride (95%), nickel chloride, nickel chloride hexahydrate, zinc dust, triphenylphosphine, *o*-tolylmagnesium chloride, chlorobenzene. 2,6-Diisopropylaniline and 2,4,6-trimethylaniline were distilled under reduced pressure before use. Air sensitive samples for NMR spectroscopy were prepared in NMR tubes equipped with a J. Young tap. NMR spectra were recorded on Bruker AV300 (300 MHz), AVI400 (400 MHz), AVIII400 (400 MHz) or AVHDIII (400 MHz) spectrometers at 25 °C unless specified. Chemical shifts δ are noted in parts per million (ppm). ^1H and ^{13}C spectra were calibrated to the residual proton resonances of the deuterated solvent. ^{31}P NMR spectra were referenced to external samples of 85% H_3PO_4 at 0 ppm. X-ray diffraction experiments were performed on single crystals of the samples covered in inert oil and placed under the cold stream (100 K) of a Bruker X8 APEX-II four-circle diffractometer (Heriot-Watt University), except for **9**, which was collected in the cold stream (150 K) of a Bruker APEX-II diffractometer (LIKAT), **1**, which was collected at the UK EPSRC National Crystallography Service at the University of Southampton, and **5** which was collected at the Advanced Light Source (ALS), Berkley. Exposures were collected using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å), except for the sample analysed at the ALS synchrotron. Indexing, data collection and absorption corrections were performed, and structures were solved using direct methods (SHELXT)⁶³ and refined by full-matrix least-squares (SHELXL) interfaced with the programme OLEX2.^{64, 65}

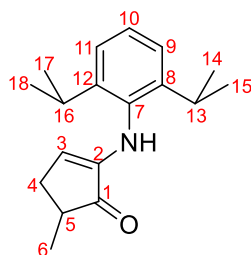
CCDC deposition numbers: 1973377-1973387.

Polymerization reactions were run either using a Parr autoclave equipped with a gas entraining stirrer, electric heating mantle and automatic temperature control (LIKAT) or a magnetically stirred Parr 9010 0.45 L autoclave (Heriot-Watt University). Polymer analysis was carried out using NMR spectroscopy, differential scanning calorimetry (DSC) and GPC analysis (University of Warwick). NMR analysis was carried out on spectrometers listed above in deuterated bromobenzene. DSC measurements were carried out on a TA Instruments DSC 2010 and GPC analysis was carried out at Warwick Scientific services using an Agilent PL-GPC 220 high temperature system. Elemental analyses were performed

by Dr Brian Hutton at Heriot-Watt University using an Exeter CE440 elemental analyser or by Mr Stephen Boyer at London Metropolitan University. Mass spectrometry analysis was performed at the EPSRC UK National Mass Spectrometry Facility at Swansea University, using an Atmospheric Solids Analysis Probe interfaced to a Water Xevo G2-S instrument.

2-((2,6-diisopropylphenyl)amino)-5-methylcyclopent-2-en-1-one (1)

Maple lactone (3.58 g, 31.9 mmol), 2,6-diisopropylaniline (6.0 mL, 31.9 mmol), *p*-toluenesulfonic acid monohydrate (22.0 mg, 0.116 mmol) and xylene (100 mL) was added to a 250 mL round bottomed flask. This mixture was then heated to reflux (140 °C) with a Dean-Stark apparatus for three days. Solvent was then removed through rotary evaporation, and the resultant oil was purified using column chromatography (10% ethyl acetate, 90% petroleum ether 40-60) yielding a red/brown solid. 6.23 g, 23.0 mmol, 72% yield.

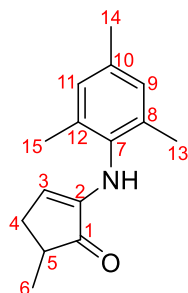


^1H NMR (CDCl_3 , 300 MHz): δ 7.26-7.15 (3H, m, $\text{H}_{9,10,11}$), 5.56 (1H, t, $J = 3.22$ Hz, H_3), 5.41 (1H, br s, NH), 3.11 (2H, sept, $J = 6.94$ Hz, $\text{H}_{13,16}$), 2.71 (1H, ddd, $J = 17.58, 6.32, 3.22$ Hz, H_4'), 2.48 (1H, m, H_5), 2.02 (1H, ddd, $J = 17.76, 3.22, 1.96$ Hz, H_4''), 1.23 (3H, d, $J = 7.41$ Hz, H_6), 1.20-1.15 (12H, 2xd, $J = 6.94$ Hz, $\text{H}_{14,15,17,18}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 206.88 (C, C_1), 146.44 (C, $\text{C}_{8,12}$), 144.96 (C, C_2), 135.53 (C, C_7), 127.07 (CH, C_{10}), 123.65 (CH, $\text{C}_{9,11}$), 121.71 (CH, C_3), 39.26 (CH, C_5), 32.66 (CH_2 , C_4), 28.25 (CH, $\text{C}_{13,16}$), 24.14/23.96 ($2\times\text{CH}_3$, $\text{C}_{14,15,16,17}$), 16.67 (CH_3 , C_6). HRMS (EI): Calcd. for $\text{C}_{18}\text{H}_{26}\text{NO}^+$: 272.2009, $[\text{M}+\text{H}]^+$, Found: 272.2010 m/z. Elemental analysis calcd. (%) for $\text{C}_{18}\text{H}_{25}\text{NO}$: C; 79.66, H; 9.28, N; 5.16; found: C; 79.52, H; 9.35, N; 5.21.

2-(mesitylamino)-5-methylcyclopent-2-en-1-one (2)

Maple lactone (3.58 g, 31.9 mmol), 2,4,6-trimethylaniline (4.5 mL, 31.9 mmol), *p*-toluenesulfonic acid monohydrate (11.0 mg, 0.058 mmol) and toluene (100 mL) was added to a 250 mL round bottomed flask. This mixture was then heated under reflux (110 °C) using a Dean-Stark apparatus for 16 hr. The solvent was then removed through rotary evaporation, and the resultant oil was purified using

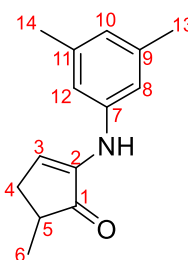
gradient column chromatography (10% ethyl acetate, 90% hexane increasing to 15% ethyl acetate) yielding a dark brown solid. 4.97 g, 21.7 mmol, 68% yield.



^1H NMR (CDCl_3 , 300 MHz): δ 6.89 (2H, s, $\text{H}_{9,11}$), 5.54 (1H, t, $J = 3.25$ Hz, H_3), 5.27 (1H, br s, NH), 2.74 (1H, ddd, $J = 17.77, 6.39, 3.25$ Hz, $\text{H}_{4'}$), 2.49 (1H, m, H_5), 2.28 (3H, s, H_{14}), 2.15 (6H, s, $\text{H}_{13,15}$), 2.06 (1H, ddd, $J = 17.77, 3.25, 1.95$ Hz, $\text{H}_{4''}$), 1.24 (3H, d, $J = 7.47$ Hz, H_6). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 298K): δ 207.20 (C, C_1), 142.88 (C, C_2), 135.82 (C), 135.31 (C), 134.50 (C, $\text{C}_{8,12}$), 129.22 (CH, $\text{C}_{9,11}$), 122.00 (CH, C_3), 39.35 (CH, C_5), 32.80 (CH_2 , C_4), 20.95 (CH_3 , C_{14}), 18.19 (CH_3 , $\text{C}_{13,15}$), 16.75 (CH_3 , C_6). HRMS (EI): Calcd. for $\text{C}_{15}\text{H}_{20}\text{NO}^+$: 230.1539, $[\text{M}+\text{H}]^+$, Found: 230.1529 m/z. Elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{19}\text{NO}$: C; 78.56, H; 8.35, N; 6.11. Found: C; 78.61, H; 8.43, N; 6.20.

2-((3,5-dimethylphenyl)amino)-5-methylcyclopent-2-en-1-one (3)

Maple lactone (3.00 g, 26.8 mmol), 3,5-dimethylaniline (3.24 g, 26.8 mmol), *p*-toluenesulfonic acid (25.4 mg, 0.134 mmol) and toluene (150 mL) were added to a 250 mL round bottomed flask. This mixture was then heated under reflux (110 °C) using Dean-Stark apparatus overnight (16 hr). The solvent was then removed under rotary evaporation. The crude oil was then purified through column chromatography (10% ethyl acetate, 90% hexane). The fractions containing product was then collected and recrystallised from hot/cold pet. ether 40-60, yielding a red/brown solid. 2.59 g, 12.03 mmol, 45% yield.



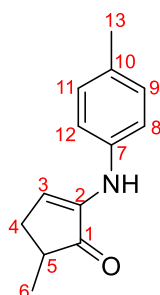
^1H NMR (CDCl_3 , 300 MHz): δ 6.67 (2H, s, $\text{H}_{8,12}$), 6.65 (1H, t, $J = 3.33$ Hz, H_3), 6.58 (1H, s, H_{10}), 6.11 (1H, br s, NH), 2.90 (1H, ddd, $J = 18.00, 6.59, 3.41$ Hz, $\text{H}_{4'}$), 2.46 (1H, m, H_5), 2.29 (6H, s, $\text{H}_{13,14}$), 2.26-2.18

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(1H, ddd, $J = 18.00, 3.41, 2.06$ Hz, $H_{4''}$), 1.23 (3H, d, $J = 7.19$ Hz, H_6). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 207.49 (C, C_1), 141.88 (C, C_2), 139.24 (C), 139.18 (C), 123.09 (CH, C_{10}), 122.88 (CH, C_3), 114.66 (CH, $C_{8,12}$), 38.07 (CH, C_5), 33.42 (CH_2 , C_4), 21.59 (CH_3 , $C_{13,14}$), 16.57 (CH_3 , C_6). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NO}^+$: 216.1383, $[\text{M}+\text{H}]^+$, Found: 216.1383; Elemental analysis calcd (%) for $\text{C}_{14}\text{H}_{17}\text{NO}$: C; 78.10, H; 7.96, N; 6.51; found: C; 78.12, H; 8.00, N; 6.57.

5-methyl-2-(*p*-tolylamino)cyclopent-2-en-1-one (4)

Maple lactone (3.00 g, 26.8 mmol), *p*-toluidine (2.79 mL, 26.8 mmol), *p*-toluenesulfonic acid (25.4 mg, 0.134 mmol) and toluene (150 mL) were added to a 250 mL round bottomed flask. This mixture was then heated under reflux (110 °C) using Dean-Stark apparatus overnight (16 hr). The solvent was then removed under vacuum and crude oil was then purified through column chromatography (10% ethyl acetate, 90% hexane) yielding a brown solid (2.69 g, 13.38 mmol, 50% yield).



^1H NMR (CDCl_3 , 300 MHz): δ 7.10 (2H, m, H_{Ar}), 6.95 (2H, m, H_{Ar}), 6.60 (1H, t, $J = 3.10$ Hz, H_3), 6.10 (1H, br s, NH), 2.89 (1H, ddd, $J = 17.74, 6.54, 3.27$ Hz, $H_{4'}$), 2.46 (1H, m, H_5), 2.29 (3H, s, H_{13}), 2.21 (1H, ddd, $J = 17.74, 3.27, 2.09$ Hz, $H_{4''}$), 1.24 (3H, d, $J = 7.58$ Hz, H_6). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 207.44 (C, C_1), 139.48 (C), 139.44 (C), 130.45 (C), 129.94 (CH, $C_{9,11}$), 122.47 (CH, C_3), 117.00 (CH, $C_{8,12}$), 38.14 (CH, C_5), 33.38 (CH_2 , C_4), 20.74 (CH_3 , C_{13}), 16.55 (CH_3 , C_6). HRMS (ESI-MS) m/z calc for $\text{C}_{13}\text{H}_{16}\text{NO}^+$: 202.1226 $[\text{M}+\text{H}]^+$, Found: 202.1225. Elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{15}\text{NO}$: C; 77.58, H; 7.51, N; 6.96. Found: C; 77.10, H; 7.55, N 6.80.

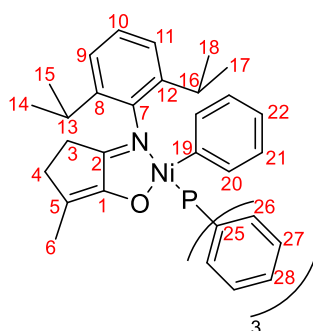
General synthesis of 5 – 8

A typical reaction is described as follows. Sodium hydride (0.442 g, 18.4 mmol, 5 eq.) was added to a Schlenk flask together with dry THF (10 mL). 2-((2,6 diisopropylphenyl)amino)-5-methylcyclopent-2-en-1-one (1.000 g, 3.685 mmol) dissolved in dry THF (20 mL) was then added at 0 °C with stirring and

left to stir overnight at room temperature. The solvent was then removed under high vacuum and the resulting solid washed with petroleum ether (40-60). The solid was then dissolved in toluene (40 mL) and filtered. The filtrate was then reduced in volume under high vacuum and the product reacted as formed.

Synthesis of 9

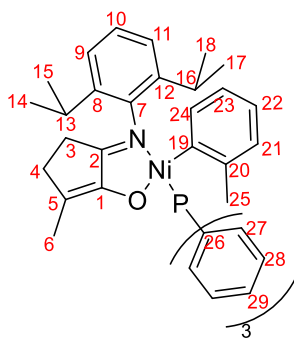
1 (205 mg, 0.74 mmol, 1 equiv.) and NaH (88 mg, 3.7 mmol, 5 equiv.) were combined in a Schlenk tube and THF (30 mL) was added. The mixture was stirred for 3 days, then left to settle and the clear pale orange solution was filtered. All volatiles were removed under reduced pressure giving an off-white residue. [Ni(Ph)Cl(PPh₃)₂] (513 mg, 0.74 mmol, 1 equiv.) and toluene (25 mL) were added and the mixture stirred for 16 hours producing a dark orange solution. The solution was filtered, the solvent was removed and the residue extracted with hexane (30 mL) giving a red solution that was filtered. This was concentrated under reduced pressure and the product crystallised at 5 °C as red crystals in two crops (245 mg, 0.366 mmol, 50%).



¹H NMR (300 MHz, Benzene-*d*₆, 25 °C): δ 7.91 – 7.58 (m, 6H, H₂₆), 7.10 (m, 2H, H₂₀), 7.07 – 6.79 (m, 12H, overlapping H_{9, 10, 11, 27, 28}), 6.52 – 6.27 (m, 3H, H_{21, 22}), 3.82 (septet, *J* = 6.8 Hz, 2H, H_{13, 16}), 2.35 – 2.13 (m, 2H, H₄), 2.07 – 1.93 (m, 2H, H₃), 1.71 (s, 3H, H₆), 1.28 (d, *J* = 6.8 Hz, 6H, H_{14, 17}), 1.13 (d, *J* = 6.8 Hz, 6H, H_{15, 18}); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 193.87 (d, *J* = 2 Hz, C, C₂), 166.05 (d, *J* = 2 Hz, C, C₁), 146.73 (d, *J* = 45.7 Hz, C, C₁₉), 143.13 (C, C₇), 140.70 (C, C_{8,12}), 137.91 (d, *J* = 2.7 Hz, CH, C₂₁), 134.54 (d, *J* = 10.5 Hz, CH, C₂₆), 132.05 (d, *J* = 44.2 Hz, C, C₂₅), 129.41 (d, *J* = 2.5 Hz, CH, C₂₇), 127.18 (C, C₅), 127.57 (C, C₂₈), 125.86 (CH, C₁₀), 125.11 (d, *J* = 1.8 Hz, CH, C₂₀), 123.06 (CH, C₁₁), 121.40 (CH, C₂₂), 33.52 (CH₂, C₄), 28.30 (CH, C₁₃, C₁₆), 25.51 (CH₂, C₃), 25.02 (CH₃, C_{15,18}), 23.82 (CH₃, C_{14,17}), 13.40 (CH₃, C₆). ³¹P{¹H} NMR (122 MHz, C₆D₆): δ 25.20. HRMS (ASAP): *m/z* calcd for C₄₂H₄₅NNiOP⁺: 668.2592 [M+H]⁺, Found: 668.2602.

Synthesis of 10

trans-[Ni(*o*-tolyl)Cl(PPh₃)₂] (0.9600 g, 1.36 mmol) and sodium 5-((2,6-diisopropylphenyl)imino)-2-methylcyclopent-1-en-1-olate (**5**) (0.4000 g, 1.36 mmol) were dissolved in a Schenk flask with toluene (20 mL). This was then heated to 50 °C and stirred over the weekend. The solvent was then removed and the complex was then washed with cold petroleum ether (40-60) (20 mL), and the product extracted by repeated washings with hot petroleum ether (40-60) yielding a red/orange solid (0.3799 g, 0.56 mmol, 41%).

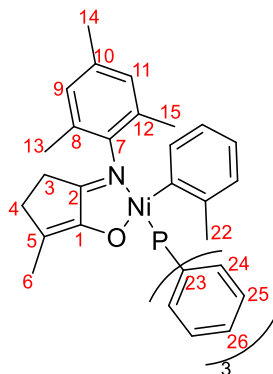


¹H (400 Hz, C₆D₆): δ 7.81 (6H, tm, H₂₇), 7.06 (m, 11H, overlapping Ar and PPh₃), 6.77 (1H, dd, J = 7.63, 1.47 Hz, H_{Ni-o-tolyl}), 6.75 (1H, dm, J = 7.63, H_{Ni-o-tolyl}), 6.44 (1H, br t, J = 7.19 Hz, H_{Ar}), 6.35 (1H, dd, J = 7.34, 0.88 Hz, H_{Ni-o-tolyl}), 6.24 (1H, td, J = 7.34, 1.17, H_{Ni-o-tolyl}), 4.49 (1H, sept, J = 6.75 Hz, H_{iPr}), 3.23 (1H, sept, J = 6.75 Hz, H_{iPr}), 3.16 (3H, s, H₂₅), 2.23 (bs, 2H, H₄), 2.00 (bs, 2H, H₃), 1.65 (s, 3H, H₆), 1.64 (3H, d, J = 6.75 Hz, H_{iPr}), 1.32 (3H, d, J = 6.75 Hz, H_{iPr}), 1.07 (3H, d, J = 6.75 Hz, H_{iPr}), 0.87 ppm (3H, d, J = 6.75 Hz, H_{iPr}). ¹³C{¹H} (100.6 Hz, C₆D₆): δ 193.96 (C), 165.94 (C), 165.86 (C), 143.77 (C), 143.74 (C), 141.11 (C), 137.28 (CH), 134.77 (CH), 134.66 (CH), 132.07 (C), 131.64 (C), 129.51 (CH), 128.37 (CH), 128.12 (CH), 128.00 (CH), 127.87 (CH), 127.76 (CH), 127.63 (CH), 127.55 (CH), 127.25 (CH), 125.93 (CH), 123.41 (CH), 123.01 (CH), 122.54 (CH), 122.51 (CH), 122.12 (CH), 33.52 (CH₂), 28.73 (CH), 27.74 (CH), 26.21 (CH₃), 26.19 (CH₂), 25.76 (CH₃), 25.47 (CH₃), 25.18 (CH₃), 24.41 (CH₃), 23.69 (CH₃), 13.50 ppm (CH₃). ³¹P{¹H} (162 Hz, C₆D₆): δ 21.46 ppm. HRMS (ASAP) m/z calcd for C₄₃H₄₇NNiOP⁺: 682.2749 [M+H]⁺, Found: 682.2755.

Synthesis of 11

trans-[Ni(*o*-tolyl)Cl(PPh₃)₂] (0.9416 g, 1.33 mmol) and sodium 5-(mesitylimino)-2-methylcyclopent-1-en-1-olate (**6**) (0.4000 g, 1.59 mmol) were dissolved in a Schenk flask with toluene (20 mL). This was then heated to 50 °C and stirred over the weekend. The solvent was then removed and the complex

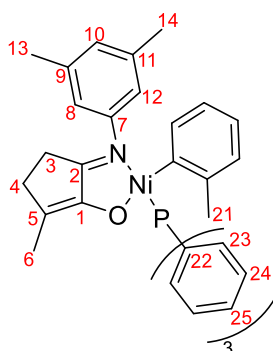
was then washed with petroleum ether (40-60) (20 mL), and the product recrystallized from toluene/petroleum ether (40-60) yielding a yellow solid (0.4600 g, 0.72 mmol, 54%).



^1H (400 Hz, C_6D_6): δ 7.75 (6H, m, H_{24}), 7.39 (1H, m), 7.09 (1H, m), 7.01 (m, 9H), 6.62 (1H, bs), 6.47 (1H, m), 6.31 (2H, tm, $J = 6.60$ Hz, $\text{H}_{\text{Ni-}o\text{-tolyl}}$), 2.94 (3H, s, H_{22}), 2.55 (3H, s, H_{Mes}), 2.21 (2H, bs, H_4), 2.17 (3H, s, H_{Mes}), 1.97 (3H, s, H_{Mes}), 1.75 (2H, bs, H_3), 1.71 (3H, s, H_6). $^{13}\text{C}\{^1\text{H}\}$ (100.6 Hz, C_6D_6): δ 193.61 (C), 156.72 (C), 143.67 (C), 138.36 (C), 137.23 (C), 135.01 (CH), 134.90 (CH), 134.31 (CH), 134.11 (CH), 132.51 (CH), 132.42 (CH), 131.65 (CH), 129.74 (C), 129.07 (C), 128.88 (CH), 128.84 (CH), 128.52 (CH), 126.54 (C), 125.39 (C), 122.30 (C), 114.33 (C), 34.02 (CH_2), 29.08 (CH_2), 27.14 (CH_2), 26.47 (CH_3), 24.96 (CH_3), 22.79 (CH_3), 20.82 (CH_3), 19.08 (CH_3), 18.31 (CH_3), 18.16 (CH_3), 16.70 (CH_3), 13.67 (CH_3), 13.61 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ (162 Hz, C_6D_6): δ 25.05 ppm. HRMS (ASAP) m/z calcd for $\text{C}_{40}\text{H}_{41}\text{NNiOP}^+$: 640.2274 [$\text{M}+\text{H}$] $^+$, Found: 640.2293.

Synthesis of 12

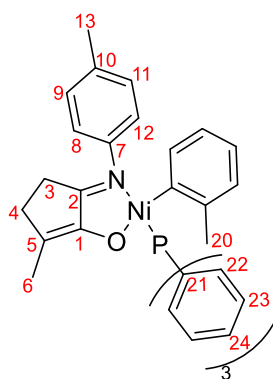
trans-Ni(*o*-tolyl)Cl(PPh_3) $_2$ (0.9938 g, 1.40 mmol) and sodium 5-((3,5-dimethylphenyl)imino)-2-methylcyclopent-1-en-1-olate (**7**) (0.4000 g, 1.69 mmol) were dissolved in a Schenk flask with toluene (20 mL). This was then heated to 50 °C and stirred over the weekend. The solvent was then removed under vacuum. The complex was then washed with petroleum ether (40-60) (2x20 mL) and the product recrystallized using toluene/petroleum ether 40-60 yielding a bright yellow solid (0.4820 g, 0.769 mmol, 56%).



^1H (400 Hz, C_6D_6): δ 7.90 (6H, tm), 7.61 (d, $J = 6.32$ Hz, 1H) 7.11 (m, 9H), 6.57 (t, $J = 6.04$ Hz, 2H), 6.49 (s, 1H), 6.40 (bs, 3H), 2.82 (s, 3H), 2.30 (bs, 2H), 2.19 (m, 1H), 2.09 (s, 6H), 1.92 (m, 1H), 1.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (100.6 Hz, C_6D_6): δ 192.33 (C), 166.35 (C), 166.28 (C), 147.74 (C), 143.52 (C), 137.07 (C), 136.87 (C), 134.86 (C), 134.75 (CH), 134.12 (CH), 133.93 (CH), 132.50 (C), 132.06 (C), 129.58 (CH), 126.11 (CH), 122.09 (CH), 121.42 (CH), 33.86 (CH_2), 26.21 (CH_3), 25.59 (CH_2), 24.22 (CH_3), 20.87 (CH_3), 13.41 ppm (CH_3). $^{31}\text{P}\{^1\text{H}\}$ (162 Hz, C_6D_6): δ 27.24 ppm. HRMS (ASAP) m/z calcd for $\text{C}_{39}\text{H}_{39}\text{NNiOP}^+$: 626.2123 [$\text{M}+\text{H}$] $^+$, Found: 626.2132.

Synthesis of 13

trans-[Ni(*o*-tolyl)Cl(PPh₃)₂] (0.5299 g, 0.747 mmol) and sodium 2-methyl-5-(*p*-tolylimino)cyclopent-1-en-1-olate (**8**) (0.2000 g, 0.896 mmol) were dissolved in a Schenk flask with toluene (20 mL). This was then heated to 50 °C and stirred over the weekend. This was then filtered, the solvent removed and the complex washed with petroleum ether (40-60) (20 mL), before the product was recrystallized from toluene/petroleum ether (40-60) yielding red/orange solid (0.1830 g, 0.299 mmol, 40%).



^1H (400 Hz, C_6D_6): δ 7.78 (6H, bs), 7.52 (bd, $J = 5.36$ Hz, 1H) 7.01 (bs, 9H), 6.62 (m, 4H), 6.50 (m, 2H), 6.27 (bs, 1H), 2.73 (s, 3H), 2.17 (bs, 2H), 2.00 (m, 1H), 1.90 (s, 3H), 1.78 (m, 1H), 1.72 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (100.6 Hz, C_6D_6): δ 193.14 (C), 166.48 (C), 166.41 (C), 152.02 (C), 151.57 (C), 145.86 (C), 143.63 (C), 137.28 (CH), 135.03 (CH), 134.82 (CH), 133.71 (C), 132.63 (C), 132.17 (C), 129.76 (CH), 128.61 (CH), 123.42 (CH), 122.62 (CH), 122.26 (CH), 34.02 (CH_2), 25.87 (CH_3), 25.45 (CH_2), 20.83 (CH_3), 13.61 (CH_3). $^{31}\text{P}\{^1\text{H}\}$ (162 Hz, C_6D_6): δ 27.31 ppm. HRMS (ASAP) m/z calcd for $\text{C}_{38}\text{H}_{37}\text{NNiOP}^+$: 612.1966 [$\text{M}+\text{H}$] $^+$, Found: 612.1972.

A typical polymerization is as follows: A 100 mL beaker was charged with 5×10^{-6} mol [Ni], 2×10^{-5} mol $\text{B}(\text{C}_6\text{F}_5)_3$, and toluene (30 mL) in a glove box and placed in a 450 mL stainless steel reactor. This was

then sealed, removed from the glove box and placed in a pre-heated oil bath and stirred at 600 rpm. The ethylene gas pipe was then purged before being connected to the reactor and the polymerization was then carried out under a fixed pressure. After 30 mins, the ethylene line was then sealed and the reactor release valve opened. Acidified methanol (10 mL) was then added to the solution and this was briefly stirred before being added to acetone (ca. 100 mL) which induced the precipitation of polymer. This polymer was then filtered and dried before weighing and subsequent analysis.

Supporting Information:

NMR and mass spectra for proligands and Ni complexes; X-ray crystal structures, including figures and data, for maple lactone, maple lactone co-crystallised with $[\text{H}_2\text{NiPr}][[\text{OAc}]$, and compounds 2 – 4, 10 – 12; GPC, DSC and NMR spectroscopic data for polyethylene samples.

Author contributions:

M.A., P.M.D.A.E., M.C.H. and M.R. synthesized and characterized the proligands. M.A. synthesised and characterised the sodium and nickel complexes and performed the polymerization studies. P.K. and B.H.M. helped with the ethylene polymerisation studies at higher pressure. M.A., S.M.M. and R.M. undertook the analysis of the results. M.A., S.M.M. and R.M. contributed to writing the paper.

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Notes:

The authors declare no competing financial interests.

References

1. Sturzel, M.; Mihan, S.; Mulhaupt, R., From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2016**, *116*, 1398-1433.
2. Cecchin, G.; Morini, G.; Piemontesi, F., Ziegler-Natta Catalysts. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 2003; Vol. 26, pp 502-554.
3. Theopold, K. H., Homogeneous Chromium Catalysts for Olefin Polymerization. *Eur. J. Inorg. Chem.* **1998**, *1998*, 15-24.
4. Kaminsky, W., Highly active metallocene catalysts for olefin polymerization. *J. Chem. Soc., Dalton Trans.* **1998**, 1413-1418.
5. Coates, G. W., Precise Control of Polyolefin Stereochemistry Using Single-Site Metal Catalysts. *Chem. Rev.* **2000**, *100*, 1223-1252.
6. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F., The Search for New-Generation Olefin Polymerization Catalysts: Life beyond Metallocenes. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428-447.
7. Ittel, S. D.; Johnson, L. K.; Brookhart, M., Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **2000**, *100*, 1169-1204.
8. Small, B. L., Discovery and Development of Pyridine-bis(imine) and Related Catalysts for Olefin Polymerization and Oligomerization. *Acc. Chem. Res.* **2015**, *48*, 2599-2611.
9. Wang, J.; Wang, L.; Yu, H.; Ullah, R. S.; Haroon, M.; Zain-ul-Abdin; Xia, X.; Khan, R. U., Recent Progress in Ethylene Polymerization Catalyzed by Ni and Pd Catalysts. *Eur. J. Inorg. Chem.* **2018**, 1450-1468.
10. Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B., Synthesis of functional 'polyolefins': state of the art and remaining challenges. *Chem. Soc. Rev.* **2013**, *42*, 5809-5832.
11. Dai, S.; Chen, C., Direct Synthesis of Functionalized High-Molecular-Weight Polyethylene by Copolymerization of Ethylene with Polar Monomers. *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 13281-13285.
12. Boffa, L. S.; Novak, B. M., Copolymerization of polar monomers with olefins using transition-metal complexes. *Chem. Rev.* **2000**, *100*, 1479-1493.
13. Nakamura, A.; Ito, S.; Nozaki, K., Coordination-Insertion Copolymerization of Fundamental Polar Monomers. *Chem. Rev.* **2009**, *109*, 5215-5244.
14. Sen, A., Mechanistic Aspects Of Metal-Catalyzed Alternating Copolymerization Of Olefins With Carbon-Monoxide. *Acc. Chem. Res.* **1993**, *26*, 303-310.
15. Mitchell, N. E.; Long, B. K., Recent advances in thermally robust, late transition metal-catalyzed olefin polymerization. *Polym. Int.* **2019**, *68*, 14-26.
16. Keim, W., Oligomerization of Ethylene to alpha-Olefins: Discovery and Development of the Shell Higher Olefin Process (SHOP). *Angew. Chem. Int. Ed.* **2013**, *52*, 12492-12496.
17. Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D., Ethylene Homopolymerization With P,O-Chelated Nickel-Catalysts. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1989-2003.
18. Klabunde, U.; Ittel, S. D., Nickel Catalysis For Ethylene Homopolymerization And Copolymerization. *J. Mol. Catal.* **1987**, *41*, 123-134.
19. Starzewski, K. A. O.; Witte, J., Highly Active Ylide-Nickel Catalysts for the Polymerization of Ethylene. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599-601.
20. Johnson, L. K.; Killian, C. M.; Brookhart, M., New Pd(II)-Based And Ni(II)-Based Catalysts For Polymerization Of Ethylene And Alpha-Olefins. *J. Am. Chem. Soc.* **1995**, *117*, 6414-6415.

21. Gates, D. P.; Svejda, S. K.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M., Synthesis of branched polyethylene using (alpha-diimine)nickel(II) catalysts: Influence of temperature, ethylene pressure, and ligand structure on polymer properties. *Macromolecules* **2000**, *33*, 2320-2334.
22. Xie, T. Y.; McAuley, K. B.; Hsu, J. C. C.; Bacon, D. W., Gas-Phase Ethylene Polymerization - Production Processes, Polymer Properties, And Reactor Modeling. *Ind. Eng. Chem. Res.* **1994**, *33*, 449-479.
23. Wang, F. Z.; Chen, C. L., A continuing legend: the Brookhart-type alpha-diimine nickel and palladium catalysts. *Polymer Chemistry* **2019**, *10*, 2354-2369.
24. Soshnikov, I. E.; Bryliakov, K. P.; Antonov, A. A.; Sun, W.-H.; Talsi, E. P., Ethylene polymerization of nickel catalysts with α -diimine ligands: factors controlling the structure of active species and polymer properties. *Dalton Trans.* **2019**, *48*, 7974-7984.
25. Dai, S. Y.; Sui, X. L.; Chen, C. L., Highly Robust Palladium(II) alpha-Diimine Catalysts for Slow-Chain-Walking Polymerization of Ethylene and Copolymerization with Methyl Acrylate. *Angew. Chem. Int. Ed.* **2015**, *54*, 9948-9953.
26. Wang, C. M.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W., Neutral nickel(II)-based catalysts for ethylene polymerization. *Organometallics* **1998**, *17*, 3149-3151.
27. Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A., Neutral, Single-Component Nickel (II) Polyolefin Catalysts That Tolerate Heteroatoms. *Science* **2000**, *287*, 460-462.
28. Guo, L. H.; Liu, W. J.; Chen, C. L., Late transition metal catalyzed alpha-olefin polymerization and copolymerization with polar monomers. *Mater. Chem. Front.* **2017**, *1*, 2487-2494.
29. Mu, H.; Pan, L.; Song, D.; Li, Y., Neutral Nickel Catalysts for Olefin Homo- and Copolymerization: Relationships between Catalyst Structures and Catalytic Properties. *Chem. Rev.* **2015**, *115*, 12091-12137.
30. Heyndrickx, W.; Occhipinti, G.; Jensen, V. R., Neutral Nickel Ethylene Oligo- and Polymerization Catalysts: Towards Computational Catalyst Prediction and Design. *Chem.-Eur. J.* **2014**, *20*, 7962-7978.
31. Hicks, F. A.; Brookhart, M., A highly active anilinetropone-based neutral nickel(II) catalyst for ethylene polymerization. *Organometallics* **2001**, *20*, 3217-3219.
32. Batten, M. P.; Canty, A. J.; Cavell, K. J.; Ruther, T.; Skelton, B. W.; White, A. H., Synthesis of nickel(II) complexes containing neutral N,N- and anionic N,O- bidentate ligands, and their behaviour as chain-growth catalysts; structural characterisation of complexes containing (mim)(2)CO, mimCO(2)(-), and mimCPh(2)O(-) (mim=1-methylimidazol-2-yl). *Inorg. Chim. Acta* **2006**, *359*, 1710-1724.
33. Desjardins, S. Y.; Cavell, K. J.; Hoare, J. L.; Skelton, B. W.; Sobolev, A. N.; White, A. H.; Keim, W., Single component N-O chelated arylnickel(II) complexes as ethene polymerisation and CO/ethene copolymerisation catalysts. Examples of ligand induced changes to the reaction pathway. *J. Organomet. Chem.* **1997**, *544*, 163-174.
34. Desjardins, S. Y.; Cavell, K. J.; Jin, H.; Skelton, B. W.; White, A. H., Insertion into the nickel-carbon bond of N-O chelated arylnickel(II) complexes. The development of single component catalysts for the oligomerisation of ethylene. *J. Organomet. Chem.* **1996**, *515*, 233-243.
35. Okada, M.; Nakayama, Y.; Shiono, T., Synthesis of anilinonaphthoquinone-based nickel complexes and their application for olefin polymerization. *J. Organomet. Chem.* **2007**, *692*, 5183-5189.
36. Jenkins, J. C.; Brookhart, M., A Highly Active Anilinoperinaphthenone-Based Neutral Nickel(II) Catalyst for Ethylene Polymerization. *Organometallics* **2003**, *22*, 250-256.
37. Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X., α -Iminocarboxamidato-Nickel(II) Ethylene Polymerization Catalysts. *J. Am. Chem. Soc.* **2001**, *123*, 5352-5353.
38. Boardman, B. M.; Bazan, G. C., α -Iminocarboxamidato Nickel Complexes. *Acc. Chem. Res.* **2009**, *42*, 1597-1606.
39. Rojas, R. S.; Wasilke, J.-C.; Wu, G.; Ziller, J. W.; Bazan, G. C., α -Iminocarboxamide Nickel Complexes: Synthesis and Uses in Ethylene Polymerization. *Organometallics* **2005**, *24*, 5644-5653.

40. Figueira, C. A.; Lopes, P. S.; Gomes, C. S. B.; Gomes, J. C. S.; Lemos, F.; Gomes, P. T., New phenyl–nickel complexes of bulky 2-iminopyrrolyl chelates: synthesis, characterisation and application as aluminium-free catalysts for the production of hyperbranched polyethylene. *Dalton Trans.* **2018**, *47*, 15857-15872.
41. Zhang, Y.; Mu, H.; Pan, L.; Wang, X.; Li, Y., Robust Bulky [P,O] Neutral Nickel Catalysts for Copolymerization of Ethylene with Polar Vinyl Monomers. *ACS Catalysis* **2018**, *8*, 5963-5976.
42. Zhang, Y.; Mu, H.; Wang, X.; Pan, L.; Li, Y., Elaborate Tuning in Ligand Makes a Big Difference in Catalytic Performance: Bulky Nickel Catalysts for (Co)polymerization of Ethylene with Promising Vinyl Polar Monomers. *ChemCatChem* **2019**, *11*, 2329-2340.
43. Tao, W.-j.; Nakano, R.; Ito, S.; Nozaki, K., Copolymerization of Ethylene and Polar Monomers by Using Ni/IzQO Catalysts. *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 2835-2839.
44. Mansell, S. M., Catalytic applications of small bite-angle diphosphorus ligands with single-atom linkers. *Dalton Trans.* **2017**, *46*, 15157-15174.
45. Newland, R. J.; Smith, A.; Smith, D. M.; Fey, N.; Hanton, M. J.; Mansell, S. M., Accessing Alkyl- and Alkenylcyclopentanes from Cr-Catalyzed Ethylene Oligomerization Using 2-Phosphinophosphinine Ligands. *Organometallics* **2018**, *37*, 1062-1073.
46. Hicks, F. A.; Jenkins, J. C.; Brookhart, M., Synthesis and ethylene polymerization activity of a series of 2-anilino-tropone-based neutral nickel(II) catalysts. *Organometallics* **2003**, *22*, 3533-3545.
47. Jenkins, J. C.; Brookhart, M., A Mechanistic Investigation of the Polymerization of Ethylene Catalyzed by Neutral Ni(II) Complexes Derived from Bulky Anilino-tropone Ligands. *J. Am. Chem. Soc.* **2004**, *126*, 5827-5842.
48. Zborowski, K. K.; Grybos, R.; Weselucha-Birczynska, A.; Kim, Y.; Proniewicz, L. M., Quantum mechanical study of the tautomerism and molecular spectra of 2-hydroxy-3-methyl-2-cyclopenten-1-one. *Mol. Phys.* **2012**, *110*, 343-351.
49. Figueroa, R.; Froese, R. D.; He, Y. Y.; Klosin, J.; Theriault, C. N.; Abboud, K. A., Synthesis of Imino-Enamido Hafnium and Zirconium Complexes: A New Family of Olefin Polymerization Catalysts with Ultrahigh-Molecular-Weight Capabilities. *Organometallics* **2011**, *30*, 1695-1709.
50. Standley, E. A.; Smith, S. J.; Muller, P.; Jamison, T. F., A Broadly Applicable Strategy for Entry into Homogeneous Nickel(0) Catalysts from Air-Stable Nickel(II) Complexes. *Organometallics* **2014**, *33*, 2012-2018.
51. Manzoor, A.; Wienefeld, P.; Baird, M. C.; Budzelaar, P. H. M., Catalysis of Cross-Coupling and Homocoupling Reactions of Aryl Halides Utilizing Ni(0), Ni(I), and Ni(II) Precursors; Ni(0) Compounds as the Probable Catalytic Species but Ni(I) Compounds as Intermediates and Products. *Organometallics* **2017**, *36*, 3508-3519.
52. Guironnet, D.; Gottker-Schnetmann, I.; Mecking, S., Catalytic Polymerization in Dense CO₂ to Controlled Microstructure Polyethylenes. *Macromolecules* **2009**, *42*, 8157-8164.
53. Azoulay, J. D.; Itigaki, K.; Wu, G.; Bazan, G. C., Influence of steric and electronic perturbations on the polymerization activities of alpha-iminocarboxamide nickel complexes. *Organometallics* **2008**, *27*, 2273-2280.
54. Chen, Z.; Mesgar, M.; White, P. S.; Daugulis, O.; Brookhart, M., Synthesis of Branched Ultrahigh-Molecular-Weight Polyethylene Using Highly Active Neutral, Single-Component Ni(II) Catalysts. *Acs Catalysis* **2015**, *5*, 631-636.
55. Wiedemann, T.; Voit, G.; Tchernook, A.; Roesle, P.; Gottker-Schnetmann, I.; Mecking, S., Monofunctional Hyperbranched Ethylene Oligomers. *Journal of the American Chemical Society* **2014**, *136*, 2078-2085.
56. Ji, P. J.; Guo, L. H.; Hu, X. H.; Li, W. M., Ethylene polymerization by salicylaldimine Nickel(II) complexes derived from aryl-naphthylamine. *Journal of Polymer Research* **2017**, *24*, 9.
57. Li, W. W.; Mu, H. L.; Liu, J. Y.; Li, Y. S., 9,9-Dimethylxanthene-based binuclear phenoxy-imine neutral nickel(II) catalysts for ethylene homo- and copolymerization. *Journal of Organometallic Chemistry* **2017**, *836-837*, 34-43.

58. Song, D. P.; Shi, X. C.; Wang, Y. X.; Yang, J. X.; Li, Y. S., Ligand Steric and Electronic Effects on beta-Ketiminato Neutral Nickel(II) Olefin Polymerization Catalysts. *Organometallics* **2012**, *31*, 966-975.
59. Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F., C-13 NMR determination of the composition of linear low-density polyethylene obtained with eta(3)-methallyl-nickel-diimine PF6 complex. *Macromolecules* **1999**, *32*, 1620-1625.
60. Shan, Y. H.; Sun, J. Q.; Xu, Y. J.; Cui, Y. G.; Lin, F., Ethylene polymerization and copolymerization with polar monomers by a neutral nickel catalyst combined with co-catalyst of Ni(COD)(2) or Al(i-Bu)(3). *Chinese Journal of Polymer Science* **2005**, *23*, 301-310.
61. Zhang, Y.; Zhang, Y.; Chi, Y.; Jian, Z., Influence of initiating groups on phosphino-phenolate nickel catalyzed ethylene (co)polymerization. *Dalton Trans.* **2020**, *49*, 2636-2644.
62. Zeller, A.; Herdtweck, E.; Strassner, T., Structural characterization and a new one-pot synthesis of trans-chloro(phenyl)bis(triphenylphosphane)nickel(II). *Eur. J. Inorg. Chem.* **2003**, 1802-1806.
63. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3-8.
64. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
65. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2015**, *71*, 59-75.