



Binding modes of a dimethyliminopentanone ligand on nickel pre-catalysts toward olefin polymerization

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ABSTRACT

Nickel complexes prepared using a 4-(2,6-diisopropylphenylimino)-3,3-dimethylpentan-2-one ligand framework are shown. The potassium salt of the ligand is obtained by deprotonation with KH in diethyl ether. Potassium 4-(2,6-diisopropylphenylimino)-3,3-dimethylpent-2-en-2-olate can then be reacted with Ni(PMe₃)₂(η¹-CH₂Ph)Cl to yield 4-(2,6-diisopropylphenylimino)-3,3-dimethylpent-2-en-2-olato-κ¹O](η¹-CH₂Ph)(PMe₃)₂Ni (**1**). The potassium salt of the ligand can also be reacted with Ni(PMe₃)(η³-CH₂Ph)Cl to yield bis(4-(2,6-diisopropylphenylimino)-3,3-dimethylpent-2-en-2-olato-κ²N,O](η¹-CH₂Ph)₂Ni₂ (**2**) or 4-(2,6-diisopropylphenylimino)-3,3-dimethylpent-2-en-2-olato-κ²N,O](η¹-CH₂Ph)(PMe₃)Ni (**3**), depending on the reaction conditions. The addition of five equivalents of B(C₆F₅)₃ to **1**, **2**, or **3** yields catalytically active species for the homopolymerization of ethylene. The polymer products are described by a single molecular weight distribution, consistent with the presence of a single active site.

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1. Introduction

Nickel-based olefin oligomerization and polymerization pre-catalysts continue to be of interest in industrial and academic laboratories [1]. These late metal systems remain relevant due to their ability to tolerate functional groups, which can facilitate the synthesis of new materials with previously unattained structures and properties [2]. Neutral species, although less active than the cationic counterparts, are under investigation because of this high tolerance toward functionalities [3]. Zwitterionic complexes, where a partial positive charge formally resides at the metal center, constitute a smaller class of pre-catalysts with an intermediate range of reactivities [4].

Lewis acids are in some cases used to activate the metal center upon coordination to a basic functionality on the ligand framework at a site removed from the metal center [5]. This type of activation places the Lewis acid away from the trajectory of monomer insertion. Previous reports have shown that several ligand frameworks are suitable for this type of remote Lewis acid activation [6]. However, until recently most of these systems, lacking substantial aryl bulk yield low molecular weight products. We recently reported the synthesis of 3-(2,6-diisopropylphenylimino)-but-1-en-2-olato-κ²N,O](η¹-CH₂Ph)(trimethylphosphine)nickel, which upon

addition of B(C₆F₅)₃ yields 2-tris(pentafluorophenyl)borate-3-(2,6-diisopropylphenylimino)-but-1-ene(η³-CH₂Ph)nickel (Fig. 1) [7].

Borane coordination to the oxygen stimulates rearrangement of the ligand and binding of the olefin unit to nickel. This previously unexplored type of complex led to the formation of high molecular weight polymer despite the absence of obvious steric bulk around the coordination sphere of the metal.

Here we report on 4-(2,6-diisopropylphenylimino)-3,3-dimethylpentan-2-one, which is a relatively small ligand framework and has remote activation capabilities. The synthesis of 4-(2,6-diisopropylphenylimino)-3,3-dimethylpentan-2-one (Scheme 1) gives rise to a ligand framework, which is not only capable of remote activation but also of mono, bi, and tridentate binding to the nickel center. This variety of binding modes allows for several structures to be isolated and characterized. In the presence of a Lewis acid such as B(C₆F₅)₃, all three pre-catalyst complexes have the potential to form the previously observed N/η²-C=C coordination complex. Preliminary studies show the formation of high molecular weight polymer, which poses a monomodal molecular weight distribution, consistent with the formation of a single active site.

2. Results and discussion

The synthesis of 4-(2,6-diisopropylphenylimino)-3,3-dimethylpentan-2-one (**L-H**) is shown in Scheme 1. 2,6-Diisopropyl aniline was added to a mixture of 3,3-dimethyl-2,5-pentanedione,

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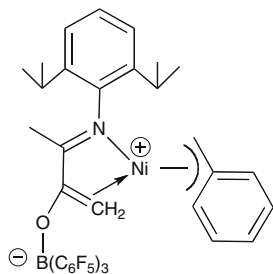
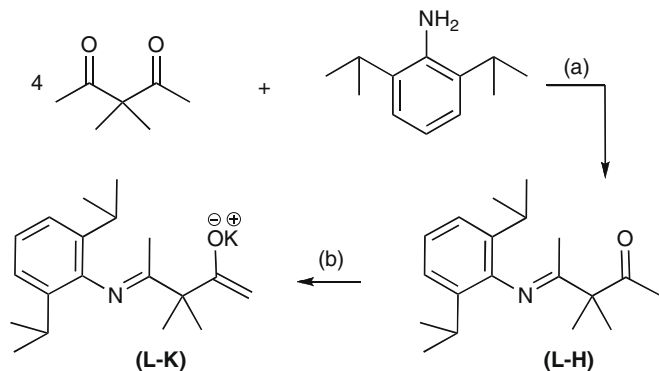


Fig. 1. 2-Tris(pentafluorophenyl)borate-3-(2,6-diisopropylphenylimino)-but-1-ene(η^3 -CH₂Ph)nickel; illustration N/η^2 -C=C coordination.

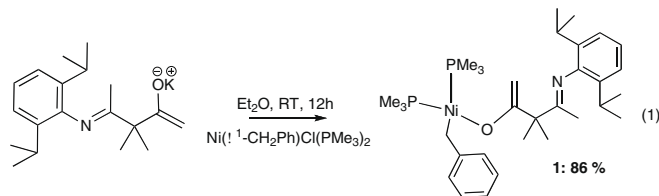


Scheme 1. Ligand synthesis. (a) Catalytic tosic acid, MgSO₄, toluene, reflux 72 h. (b) 1.3 eq. KH, Et₂O, room temperature, 12 h.

tosic acid and MgSO₄ in toluene. The reaction was allowed to heat at reflux for three days to afford crude **L-H** in 82% yield. The crude material was purified first by distillation, to remove excess pentanedione, followed by crystallization from hexanes. ¹H NMR spectroscopy confirmed the formation of the desired ligand.

The potassium salt of ligand is obtained by deprotonation of **L-H** with excess KH in diethyl ether. The resulting suspension was filtered and excess solvent was removed to provide potassium 4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-2-en-2-olate (**L-K**) as a white powder in 95% yield.

Previous reactions with α -iminocarboxamide, aminobutanone and related conjugated ligand frameworks have formed N,N or N,O bidentate structures when reacted with Ni(η^1 -CH₂Ph)Cl(PMe₃)₂ [8]. However when **L-K** was reacted with Ni(η^1 -CH₂Ph)Cl(PMe₃)₂, the ligand coordinated to the metal in a monodentate fashion, as shown in Equation 1. The ¹H NMR spectrum is consistent with the formation of a single isomer containing a nickel center ligated by 4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-1-en-2-olato, κ^1 -CH₂Ph and two PMe₃ ligands. Diagnostic ¹H NMR peaks for the ligand backbone and a single peak in the ³¹P NMR spectrum at $\delta = -21.5$ ppm are consistent with the formation of 4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-1-en-2-olato- κ^1O (η^1 -CH₂Ph)(PMe₃)₂ nickel (**1**) (Equation 1).



Single crystals of **1** suitable for X-ray diffraction were obtained by crystallization from pentane at room temperature. The resulting

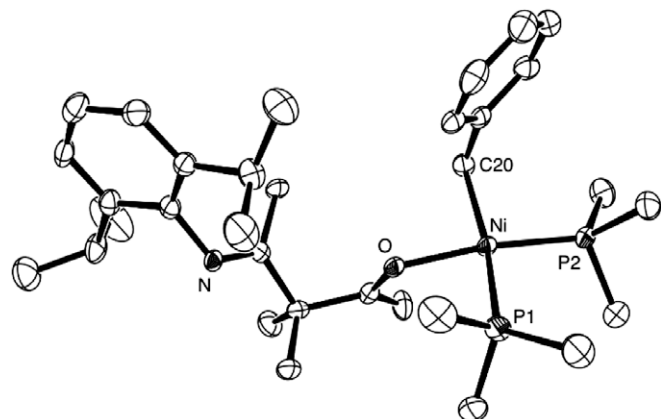
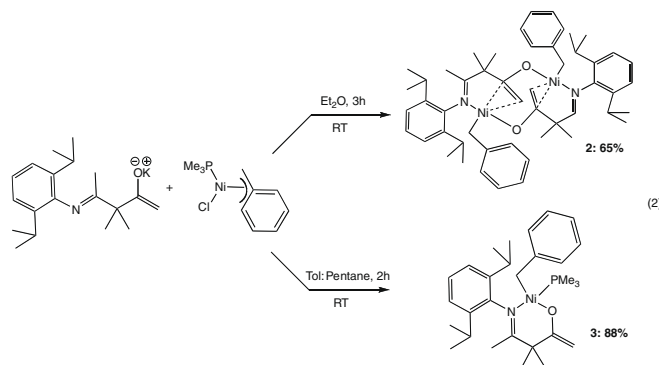


Fig. 2. ORTEP drawing of **1** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

structure, shown in Fig. 2, confirms the monodentate O -binding mode of the 4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-1-en-2-olato fragment and that the two coordinating phosphines are in a *cis*-orientation relative to each other. The square-planar geometry around nickel is slightly distorted. For example, the O-Ni-P(2) and C(20)-Ni-P(1) angles project 13.5° and 17.5°, out of the plane, respectively in opposite directions. The benzyl ligand is located *cis* to the oxygen with an O-Ni-C(20) angle of 90.06(14)°. The Ni-P(1), Ni-P(2), Ni-O(1) and Ni-C(20) bond distances are 2.2348(12) Å, 2.1374(12) Å, 1.946(3) Å and 1.978(4) Å, respectively.

In an attempt to isolate an N,O -bound bidentate complex, we used the monophosphine species Ni(η^3 -CH₂Ph)Cl(PMe₃) [8] as a starting material. The reaction of potassium,4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-2-en-2-olate with Ni(η^3 -CH₂Ph)Cl(PMe₃) was run under two different reaction conditions. At -35 °C in diethyl ether, a dark red precipitate was isolated in 65% yield (Equation 2). The precipitate was insoluble in deuterated solvents such as benzene or toluene and decomposed readily in tetrahydrofuran and dichloromethane, making structural identification by NMR spectroscopy inconclusive.



Crystals of the isolated product suitable for X-ray analysis were obtained from the slow evaporation of a dilute diethyl ether solution. The resulting molecular structure, shown in Fig. 3, reveals a dimeric structure, in which the 4-(2,6-diisopropylphenylimino)-3,3-dimethyl-pent-1-en-2-olato ligand is coordinated to one metal center in a N/η^2 -C=C fashion and to the other metal center via the oxygen. The η^1 -CH₂Ph is bound *cis* to the imine nitrogen. Note that no PMe₃ is observed. The square planar geometry around nickel is slightly distorted with the N-Ni-O(2) and C(1)-Ni-C(8) angles projecting 5.99° and 6.56° out of the plane, respectively in opposite directions.

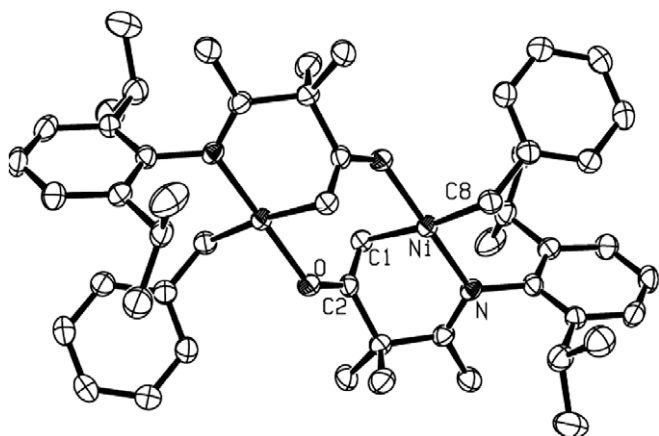


Fig. 3. ORTEP drawing of **2** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

The Ni–C(1) and Ni–C(2) bond distances 2.12(3) Å and 2.29(3) Å, respectively and the double bond character of the C(1)–C(2) bond distance (1.37(4) Å) indicates the presence of olefin coordination. We propose therefore, that the product obtained is bis(4-(2,6-diisopropylphenylimino)-3,3-dimethyl pent-2-en-2-olato- κ^2N,O)(η^1 -CH₂Ph)₂Ni₂ (**2**), as shown in Equation 2.

If the reaction of **L-K** with Ni(η^3 -CH₂Ph)Cl(PMe₃) is run at room temperature using a toluene-pentane mixture (1.5:1), no precipitate is observed and the deep orange solution remains clear over the course of the reaction (Equation 2). The ¹H NMR spectrum of the isolated orange crystals is consistent with the formation of a single isomer containing a nickel center ligated by 4-(2,6-diisopropylphenylimino)-3,3-dimethyl-pent-1-en-2-olato, κ^1 -CH₂Ph and a PMe₃ ligand. The ³¹P NMR spectrum reveals a single peak at $\delta = -21.2$ ppm. Further elucidation of the structure was accomplished by X-ray diffraction studies of a single crystal obtained from pentane at -35 °C. The resulting structure is shown in Fig. 4. Therefore, as shown in Equation 2, the product is 4-(2,6-diisopropylphenylimino)-3,3-dimethyl pent-2-en-2-olato- κ^2N,O -(η^1 -CH₂Ph)(PMe₃)Ni (**3**).

The molecular structure of **3** confirms the *N,O* bidentate binding mode of the 4-(2,6-diisopropylphenylimino)-3,3-dimethyl-pent-1-en-2-olato fragment, and the presence of η^1 -CH₂Ph and PMe₃ li-

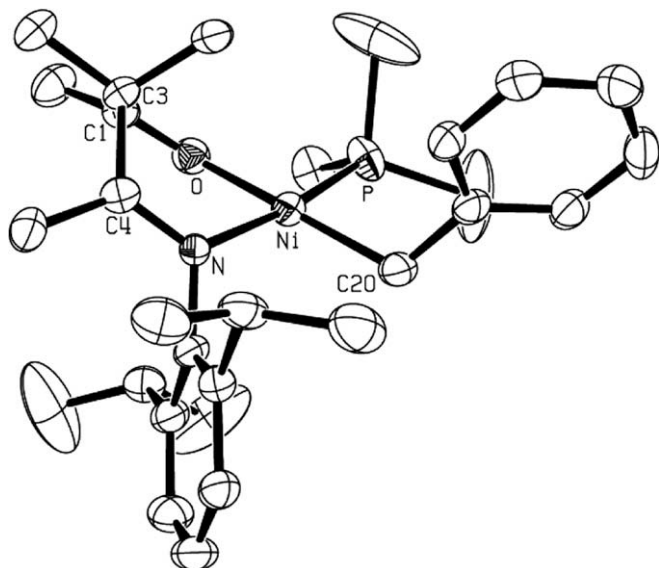


Fig. 4. ORTEP drawing of **3** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

gands. The square-planar geometry around nickel is slightly distorted: the O–Ni–C(20) and N–Ni–P angles project 4.3° and 8.1°, out of the plane, respectively in opposite directions. The PMe₃ is located *trans* to the imine nitrogen and the six membered chelate adopts a boat conformation. For example, the O–C(1)–C(3), N–C(4)–C(3), C(4)–N–Ni, and C(1)–O–Ni bond angles are 115.4°, 117.7°, 120.7°, and 123.9° respectively. The benzyl group is located *cis* to the imine nitrogen with a N–Ni–C(20) angle of 95.06(17)°. The Ni–P, Ni–O, Ni–N and Ni–C(20) bond distances are 2.2348(12) Å, 2.1374(12) Å, 1.946(3) Å and 1.978(4) Å, respectively.

A ¹H NMR study of the reaction of B(C₆F₅)₃ with **1**, **2**, and **3** was performed in an attempt to observe the active species of the nickel complex. In all cases, the formation of an η^3 species is observed with an up field shift of the aromatic protons. However, the formation of a single species is not observed indicating that the active species is not very stable. Due to this instability, isolation of the active species has not been accomplished. Therefore a preliminary survey of polymerizations were run with the *in situ* generation of the active species by adding 5 equivalents of B(C₆F₅)₃ to **1**, **2**, or **3**. Employing this type of activation, all three pre-catalysts were active toward the homopolymerization of ethylene with activities ranging from 230–650 kg/mol^{*} h depending on the reaction conditions. In all cases, the resulting polymers had an *M_n* ranging from 240,000 to 294,000, PDI's ranging from 1.59 to 1.92, and low melting temperatures ranging from 77 to 87 °C. These low melting transitions suggest that the isolated polymer is highly branched. While NMR studies have shown that the active species is unstable and therefore difficult to isolate, the similarities of the polymer products suggest that **1**, **2**, and **3** all form the same active species in the presence of B(C₆F₅)₃.

3. Conclusions

Three new organometallic complexes have been isolated and characterized containing nickel and the 4-(2,6-diisopropylphenylimino)-3,3-dimethylpentan-2-one ligand. The first from the reaction of **L-K** and Ni(η^1 -CH₂Ph)Cl(PMe₃)₂ to yield **1** and the other from the reaction of **L-K** and Ni(η^3 -CH₂Ph)Cl(PMe₃) to yield **2** or **3**, depending on the reaction conditions. The addition of excess B(C₆F₅)₃ to all three structures yields active catalysts for ethylene homopolymerization. The resulting polymers are described by monomodal molecular weight distributions, consistent with the presence of a single active metal site. Due to instability, the active species was not isolated, however the mono, bi, and tridentate binding capabilities of this new ligand system allows for new possibilities in the design of zwitterionic pre-catalysts for ethylene polymerization.

4. Experimental

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. All reagents were used as received from Aldrich unless otherwise specified. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure) and was further purified by passage through an oxygen/moisture trap (Matheson model 6427-4S). Toluene, THF, hexanes, and pentane were distilled from sodium benzophenone ketal. All polymerization reactions were carried out in a Parr autoclave reactor as described below. Toluene for polymerization was distilled from sodium/potassium alloy. NMR spectra were obtained using Varian Unity 400 and 500 spectrometers. Polymers were dried overnight under vacuum and the polymerization activities were calculated from the mass of product obtained. These values were within 5% of the calculated mass by measuring the ethylene

consumed by use of a mass flow controller. The polymers were characterized by Gel Permutation Chromatography (GPC) analysis at 135 °C in *o*-dichlorobenzene (in a Polymers Laboratories, High Temperature Chromatograph, PL-GPC 200) relative to polystyrene standards. Thermal analysis was performed on a Differential Scanning Calorimeter (DSC) TA-Q20 with a scan rate of 10 °C/min. Elemental analysis was performed on a Leeman Labs Inc. CE440 Elemental Analyzer and a Control Equipment Corporation 440 Elemental Analyzer.

4.1. 4-(2,6-Diisopropylphenylimino)-3,3-dimethylpentan-2-one

To a solution of 3,3-dimethylpentane-2,4-dione (15.0 g, 0.117 mol) and catalytic tosic acid, in toluene, 2,6-diisopropylaniline (5.18 g, 0.029 mol) was added. MgSO₄ was then added and the reaction mixture was allowed to stir at reflux for three days. The reaction was monitored by GC-MS. After three days of reflux the aniline had been converted to the desired product (97%) and the diimine structure (3%). Excess pentanedione was removed using vacuum distillation. The product mixture was then purified via recrystallization from hexanes at –20 °C. Colorless crystals were obtained in 60% yield after purification.

¹H NMR (399.95 MHz, [d₆]-benzene, 298 K): δ = 7.19–7.13 (m, 3H, phenyl), 2.81 (sept, 2H, J = 4.0 Hz, *i*Pr–CH), 1.99 (s, 3H, CH₃C=O), 1.38 (s, 3H, CH₃C=N), 1.32 (s, 6H, 2CH₃), 1.19 (d, 6H, J = 7.2 Hz, 2-*i*Pr–CH₃), 1.17 (d, 6H, J = 7.2 Hz, 2-*i*Pr–CH₃). ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 208.42 (imine), 172.39 (C=O), 146.86, 136.49, 124.56, 123.95 (ph-C), 58.93 (C–(CH₃)₂), 28.87 (*i*Pr–CH), 26.38 (CH₃CO), 23.93 (CH₃C=N), 23.52 (*i*Pr–CH₃), 23.30 (*i*Pr–CH₃), 17.43 (C(CH₃)₂). Elemental Anal. Calc.: C 79.39, H, 10.17, N 4.87; found C 79.48, H 10.18, N 4.95%.

4.2. Potassium 4-(2,6-diisopropylphenylimino)-3,3-dimethyl-pent-2-en-2-olate

A suspension of KH (90.5 mg, 2.26 mmol) in diethyl ether was added to a stirring solution of 4-(2,6-diisopropylphenylimino)-3,3-dimethylpentan-2-one (0.500 g, 1.74 mmol) in diethyl ether at room temperature. Slow evolution of H₂ was observed and the reaction was allowed to stir overnight at room temperature. After stirring overnight, the originally cloudy reaction mixture had become clear. The reaction mixture was filtered over celite and excess diethyl ether was removed. Pentane was added several times to wash the isolated solid. The potassium salt was isolated as a pale yellow powder in 98% yield.

¹H NMR (399.95 MHz, [d₆]-benzene, 298 K): δ = 7.18–7.05 (m, 3H, phenyl), 3.47 (s, 1H, CH₂), 3.05 (sept, 2H, J = 6.8 Hz, *i*Pr–CH), 2.73 (s, 1H, CH₂), 1.76 (s, 3H, CH₃C=N), 1.44 (s, 6H, C(CH₃)₂), 1.26 (d, 6H, J = 6.8 Hz, *i*Pr–CH₃), 1.24 (d, 6H, J = 6.8 Hz, *i*Pr–CH₃).

Elemental Anal. Calc.: C 70.10, H 8.67, N 4.30; found C 70.19, H 8.07, N 4.04%.

4.3. 4-(2,6-Diisopropyl-phenylimino)-3,3-dimethyl-pent-1-en-2-olato-η¹O](η¹-CH₂Ph)(PMe₃)₂ nickel (1)

Potassium 4-(2,6-diisopropylphenylimino)-3,3-dimethyl-pent-2-en-2-olate (48.1 mg, 0.148 mmol) was dissolved in diethyl ether and added drop-wise to a diethyl ether solution of Ni(PMe₃)₂(η¹-CH₂Ph)Cl (50.0 mg, 0.148 mmol) at room temperature. The reaction was allowed to stir at room temperature overnight. The reaction mixture was filtered over celite and excess diethyl ether was removed to yield a red/orange solid in 88% yield. Compound **1** was purified via recrystallization from pentane at room temperature.

¹H NMR (399.95 MHz, [d₆]-benzene, 298 K): δ = 7.40 (d, 2H, J = 6.8 Hz, phenyl) 7.19–7.11 (m, 6H, phenyl/benzyl) 3.15 (sept,

2H, *i*Pr–CH), 1.74 (s, 3H, CH₃–C=N), 1.65 (s, 6H, 2CH₃), 1.29 (d, 6H, J = 6.8 Hz, *i*Pr–CH₃), 1.24 (d, 6H, J = 7.0 Hz, *i*Pr–CH₃) 0.85 (s, 18H, 2PMe₃). ¹³C NMR (100 MHz, C₆D₆, 298 K): δ = 176.41(CO), 148.03 (imine), 137.06, 130.34, 129.63, 124.58, 124.05, 123.91 (phenyl/benzyl-C), 53.07 (C–(CH₃)₂), 28.81(CH₂), 27.34 (CH₂-benzyl), 25.66 (*i*Pr–CH), 23.95 (CH₃C=N), 23.82 (C(CH₃)₂) 23.53 (*i*Pr–CH₃), 23.31 (*i*Pr–CH₃), 13.95 (2P(CH₃)₃). ³¹P NMR (162 MHz, C₆D₆, 25 °C): δ = –21.5. Elemental Anal. Calc.: C 65.32, H 9.08, N 2.38; found C 65.49, H 8.91, N 2.45%.

4.4. Bis(4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-1-en-2-olato)(η¹-CH₂Ph)₂Ni₂ (2)

Potassium 4-(2,6-diisopropylphenylimino)-3,3-dimethyl-pent-2-en-2-olate (62.2 mg, 0.191 mmol) was dissolved in diethyl ether and added dropwise to a diethyl ether solution of Ni(PMe₃)₂(η³-CH₂Ph)Cl (50.0 mg, 0.191 mmol) at room temperature. Upon addition of the potassium salt, a large amount of red precipitate was observed; the reaction was allowed to stir overnight at room temperature. After stirring overnight, the reaction mixture was placed into the freezer, to allow the fine precipitate to settle. The mixture was carefully decanted and the solid was washed several times with cold diethyl ether. The red/violet isolated solid was dried under vacuum. NMR spectroscopic analysis of this compound proved very difficult as the stability and solubility of this species was very poor. The isolated product was only slightly soluble in deuterated solvents such as d-benzene and d-toluene, and rapidly decomposes in THF and DCM. However crystals suitable for X-ray diffraction were obtained from the slow evaporation of a very dilute diethyl ether solution at –35 °C. Details for the X-Ray analysis can be seen in Table 1.

Elemental Anal. Calc.: C 71.52, H 7.77, N 3.27; found C 71.08, H 7.22, N 3.19%.

4.5. 4-(2,6-Diisopropyl-phenylimino)-3,3-dimethyl-pent-1-en-2-olato-κ²N,O](η¹-CH₂Ph)(PMe₃) nickel (3)

Potassium 4-(2,6-diisopropyl-phenylimino)-3,3-dimethyl-pent-2-en-2-olate (54.0 mg, 0.166 mmol) in toluene-pentane (1.5:1 g) was added drop-wise to a stirring toluene-pentane (1.5:1) solution

Table 1
Crystallographic data for compounds **1**, **2**, and **3**.

Compound	1	2	3
Empirical formula	C ₃₂ H ₅₂ NOP ₂ Ni	C ₂₆ H ₃₅ NONi	C ₂₉ H ₄₄ NOPNi
Molecular weight	587.69	871.4	512.33
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n	C2/c
Unit cell parameters			
<i>a</i> (Å)	16.615(4)	9.828(3)	30.212(5)
<i>b</i> (Å)	11.621(3)	18.279(5)	10.6388(16)
<i>c</i> (Å)	17.460(4)	13.601(4)	18.662(3)
α (°)	90	90	90
β (°)	90.351(8)	109.168(4)	109.214(2)
γ (°)	90	90	90
<i>V</i> (Å ³)	3371.1(15)	2308.0(11)	5664.2(15)
<i>Z</i>	4	4	8
<i>D</i> _{calc} (mg m ³)	1.159	1.256	1.202
λ (Mo Kα) (mm ^{–1})	0.693	0.710	0.762
Crystal size (mm)	0.3 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.25 × 0.15 × 0.1
Habit	Blades	Blades	Blades
Color	Red/orange	Red	Dark orange
θ range (°)	2.11–26.42	1.77–26.71	2.04–26.37
Parameters refined	546	561	314
<i>R</i> (000)	1272	936	2208
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0630 0.1421	0.0641, .1153	0.0675, 0.1418
Maximum and minimum density (e Å ^{–3})	1.275 and –0.548	0.601 and –1.160	1.058 and –0.367

of Ni(PMe₃)(η³-CH₂Ph)Cl (43.0 mg, 0.164 mmol) and was allowed to stir at room temperature for 12 h. The reaction mixture was filtered over celite and excess solvent was removed under vacuum to give a red solid. Trituration with pentane and crystallization at –35 °C overnight gave the desired product as a dark orange solid in 82% yield.

¹H NMR (399.95 MHz, [d₆]-benzene, 298 K): δ = 7.39 (broad s, 3H, phenyl), 7.20–7.02 (m, 5H, benzyl), 3.23 (sept, 2H, J = 6.8 Hz, *i*Pr–CH), 1.75 (s, 3H, CH₃), 1.73 (s, 6H, 2CH₃), 1.34 (d, 6H, J = 6.8 Hz, *i*Pr–CH₃), 1.28 (s, 2H, CH₂-benzyl), 1.21 (d, 6H, J = 7 Hz, *i*Pr–CH₃) 0.77 (d, 9H, J = 8.2 Hz, P(CH₃)₃). ¹³C NMR (100 MHz, C₆D₆, 298 K): δ = 176.41(CO), 148.03 (imine), 137.06, 130.34, 129.63, 124.58, 124.05, 123.91 (phenyl/benzyl-C), 53.07 (C–(CH₃)₂), 28.81(CH₂), 27.34 (CH₂-benzyl), 25.66 (*i*Pr–CH), 23.95 (CH₃C=N), 23.82 (C(CH₃)₂), 23.53 (*i*Pr–CH₃), 23.31 (*i*Pr–CH₃), 13.95 (2P(CH₃)₃). ³¹P NMR (162 MHz, C₆D₆, 25 °C): δ = –21.2.

Elemental Anal. Calc.: C 67.99, H 8.66, N 2.73; found C 67.96, H 8.58, N 2.63%.

4.6. Polymerization reactions

Polymerizations were conducted in the following manner using pre-catalysts **1**, **2**, or **3**. An autoclave reactor (100 mL) was loaded inside a glovebox with pre-catalyst (5 μmol Ni), B(C₆F₅)₃ (5 eq., 25 μmol) and toluene, such that the final volume of the toluene solution was 30 mL. The reactor was sealed inside the glovebox. The reactor was removed from the glovebox and attached to an ethylene line and the gas was fed continuously into the reactor at 100 psi. Several polymerization reactions were setup in this manner. While the ethylene pressure remained constant between runs, the temperature was varied. Two temperature profiles were examined at 20 °C and 40 °C. These temperatures were maintained throughout the reaction using either an ice bath or the heating element of the reactor. After a reaction time of 20 min, the ethylene was vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried overnight under vacuum. GPC analysis determined the average molecular weight and PDI's and DSC determined the melting temperature.

Supplementary material

CCDC 680085, 679917, 679916 contain the supplementary crystallographic data for compounds **1**, **2**, and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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