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Synthesis of allyl- and aryl-iminopyrrolyl complexes of nickel †

Ronan M. Bellabarba,[a] Pedro T. Gomes *[a] and Sofia I. Pascu[b]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: pedro.gomes@ist.utl.pt*

[b] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*

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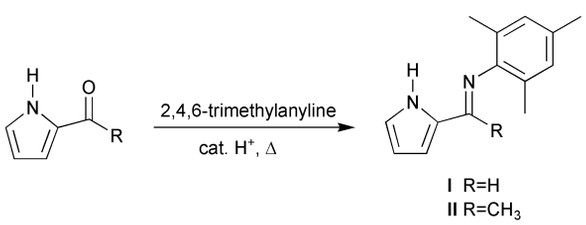
The 2-iminopyrrole ligand precursors 2-$C_4H_3NH[(R)C{=}N(2,4,6\text{-}C_6H_2Me_3)]$ (R = H, **I**; R = Me, **II**) were synthesised and react with NaH to give the corresponding sodium salts **1** and **2**, respectively. Salt **2** reacts with $[NiPhBr(PPh_3)_2]$ to yield [NiPh(acetiminopyrrolyl)(PPh_3)] **3**. Ligand precursors **II** and **2** react, respectively, with equimolar amounts of $[NiMe_2(TMEDA)]$ and $[NiBr_2(NCMe)_2]$ to give [Ni(acetiminopyrrolyl)$_2$] **4**. Both **1** and **2** react with $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ to give complexes $[Ni(\eta^3\text{-}C_3H_5)$(iminopyrrolyl)] **5** and **6**. The crystal structures of ligand precursor **II** and of complex **3** are reported and compared. Complex **3** was tested for catalytic activity for the oligomerisation of ethylene and showed only moderate activity.

Introduction

In recent years, many papers have been published in which bidentate chelating ligands containing an imine and a donor moiety have been used as precursors to the synthesis of new organometallic complexes as precatalysts for olefin polymerisation.[1] However, metal complexes of ligands containing both an imine and a pyrrolyl moiety are uncommon. These complexes may be formed using two different strategies: either by *in situ* formation of the imine and concomitant complexation to the metal centre *via* a template-type synthesis,[2,3] or by prior formation of the imine and reaction to form the desired metal complex.[4–10] The advantages of the latter strategy is that ancillary ligands can be also attached to the metal centre, whilst with the metal template synthesis bis(iminopyrrolyl)metal complexes appear to be the favoured products. This type of complex has been studied for olefin polymerisation catalysis in several projects.[6–9] Following Grubbs *et al.* work on neutral nickel(II) catalysts for olefin polymerisation,[11,12] we decided to synthesise new iminopyrrolyl complexes of nickel in view of their potential interest as olefin polymerisation catalysts. At the end of this study we came across patents where similar ligand precursors and nickel complexes are claimed.[13,14]

Results and discussion

Two (arylimino)pyrrole ligands were synthesised by condensation of 2-(formyl)pyrrole or 2-(acetyl)pyrrole with mesitylaniline (Scheme 1). The synthesis of the formimines was relatively straightforward and standard conditions could be employed, but the synthesis of the acetimines required forcing conditions and resulted in low yields (*ca.* 35%).



Scheme 1 Synthetic route to the ligand precursors **I** and **II**.

These ligands were characterised by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The crystal structure of the acetimine ligand precursor (**II**) was determined in order to confirm the structure (Fig. 1) and to compare it with the metal complexes, and relevant bond distances and angles are given in Table 1. As can be seen from Table 1, the pyrrole ring shows a longer bond distance between C4 and C5 than between any other carbons of the ring, the shortest bond in the ring being between N1 and C6. The angle between C3–N1–C6 is 109.37(12)°, whilst the imine C2–N2 distance is 1.2846(19) Å and the angle at N2 is 118.91(12)°. The co-planarity of the pyrrole ring with the acetimine group (torsion angle N1–C2–C3–N1 of 1.3°) and a distance C2–C3 of 1.450(2) Å, shorter than normal values of a typical C–C single bond, points to an extension of the pyrrole ring π-electronic delocalisation towards its acetimino substituent. The sterical hindrance produced by the two methyl substituents in the 2 and 6 positions of the mesityl ring makes it nearly perpendicular (83.2°) to the acetiminopyrrole plane defined by atoms N1, C3, C2 and N2. These features only change slightly upon coordination, as will be discussed below.

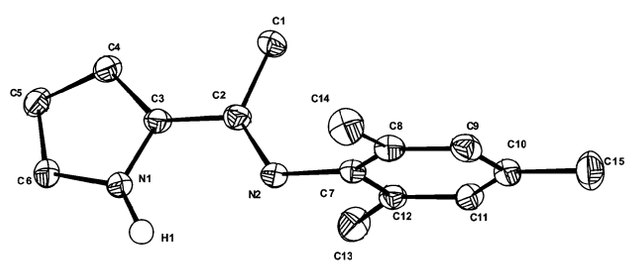


Fig. 1 Molecular structure of the ligand precursor **II**.

Treatment of the ligands **I** and **II** with sodium hydride results in the formation of the pyrrolyl sodium salts **1** and **2**, respectively. These ligand precursors were generally prepared immediately before reaction with the appropriate nickel substrate, and only characterised in the case of **2** by ^1H NMR spectroscopy to confirm the site of deprotonation.

Treatment of $[NiPhBr(PPh_3)_2]$ with one equivalent of **2** results in the formation of **3** (Scheme 2). However, this reaction is not clean, as a certain amount of **4** (as determined by ^1H NMR) and of $[Ni(PPh_3)_4]$ (determined by elemental analysis) were also formed in all cases independently of precautions taken to exclude moisture or control the reaction by cooling.

In an attempt to synthesise [NiMe(acetiminopyrrolyl)$(NCCH_3)$], the product **4** was also formed, in quantitative yield (based on **I**), in the reaction of $[NiMe_2(TMEDA)]$ with one equivalent of **I** in acetonitrile (Scheme 3). **3** was characterised by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, elemental analysis and its identity was confirmed by mass spectrometry.

† Dedicated to Professor J. J. R. Fraústo da Silva on the occasion of his 70th birthday.

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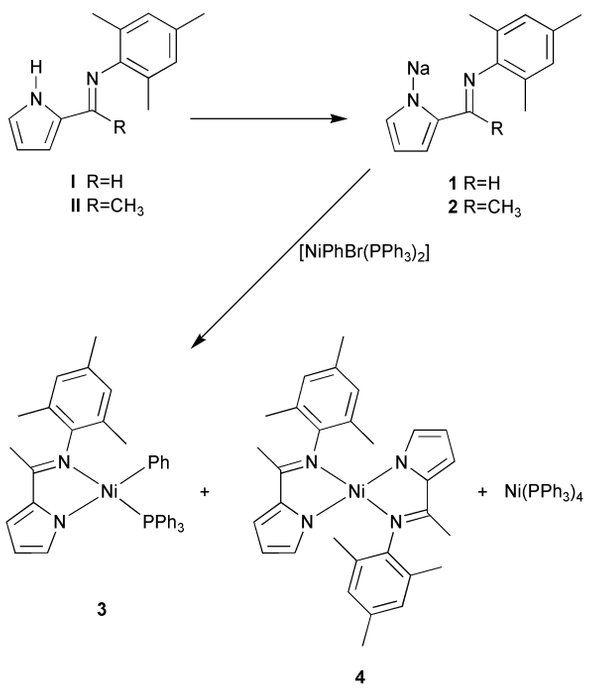
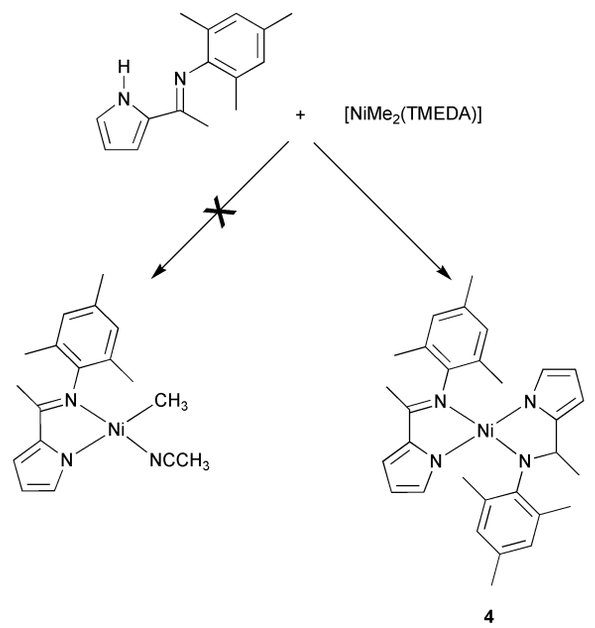
Table 1 Selected bond distances (Å) and angles (°) for ligand precursor acetiminopyrrole **II** and the complex [NiPh(acetiminopyrrolyl)(PPh_3)] **3**

	II	**3**		**II**	**3**
N2–C2	1.2846(19)	1.302(3)	C2–N2–C7	118.91(12)	120.2(2)
N2–C7	1.4266(19)	1.435(3)	N1–C3–C2	122.28(13)	114.8(2)
C1–C2	1.507(2)	1.501(3)	N2–C2–C3	119.74(13)	115.7(2)
C2–C3	1.450(2)	1.427(3)	C1–C2–C3	116.46(13)	120.7(2)
C3–C4	1.387(2)	1.387(4)	C2–C3–C4	130.25(13)	134.4(2)
C4–C5	1.410(2)	1.397(4)	N1–C3–C4	107.36(13)	110.6(2)
C5–C6	1.374(2)	1.396(4)	C3–C4–C5	107.51(13)	106.3(2)
N1–C6	1.3617(19)	1.353(3)	C4–C5–C6	107.15(13)	106.4(2)
N1–C3	1.3747(18)	1.386(3)	N1–C6–C5	108.61(13)	111.4(2)
Ni1–P1	–	2.1478(7)	C3–N1–C6	109.37(12)	105.3(2)
Ni1–N1	–	1.940(2)	N1–Ni1–N2	–	82.87(9)
Ni1–N2	–	1.959(2)	P1–Ni1–C16	–	88.10(7)
Ni1–C16	–	1.900(3)	P1–Ni1–N1	–	98.79(6)
C16–C17	–	1.398 (4)	N2–Ni1–C16	–	91.43(9)
C17–C18	–	1.392(4)	P1–Ni1–N2	–	174.10(7)
C18–C19	–	1.386(5)	N1–Ni1–C16	–	166.76(11)
C19–C20	–	1.379(5)			
C20–C21	–	1.396(4)			
C21–C16	–	1.399(4)			



Scheme 2 Synthesis of **3** and side-products.



Scheme 3

On the basis of these observations it would appear that Ni complexes containing two iminopyrrolyl ligands, such as **4**, are favoured products.

The complex **3** was characterised by ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy, and peaks assigned by using selective ^{1}H–^{1}H decoupling techniques. Satisfactory elemental analysis was obtained and suitable crystals for X-ray diffractometry were grown. The structure is shown in Fig. 2 and selected bond distances and angles are given in Table 1. The sum of all the angles around the nickel centre is *ca.* 360°, indicating this atom is in an essentially square-planar conformation (Fig. 3), albeit distorted by the ligand (angle between the planes defined by N1, Ni1, N2 and P1, Ni1, C16 is 13.4°). The acetiminopyrrolyl chelating ligand occupies two *cis* positions and the triphenylphosphine group is located *trans* to the mesitylimine moiety due to steric reasons. The phenyl ligand is virtually perpendicular to the square plane (88.5°) and the mesityl substituent of the imine also retains its perpendicularity to this plane (79.4°). Comparison of the data in Table 1 also highlights some structural differences between the free ligand and when it is coordinated. The first feature to note is that the acetiminopyrrolyl ligand bite angle described by N1–Ni–N2 is very acute, at 82.87(9)°. This

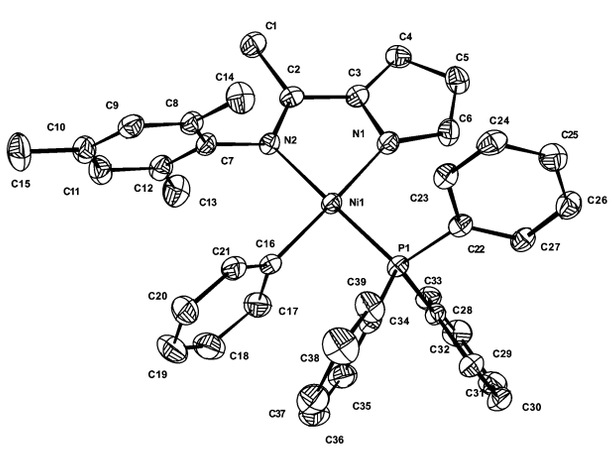


Fig. 2 Molecular structure of the complex **3**.

value is obtained at expenses of decreases of 3.8 and, mainly, 7.7° in the angles defined by N2–C3–C2 or N1–C3–C2 in relation to those observed in the organic ligand precursor **II**. Also, the angle at the pyrrolyl nitrogen C3–N1–C6 is decreased by almost 4° upon coordination, which is compensated by an increase of 2.7 and 3.3° of the pyrrolyl angles at C6 and C3,

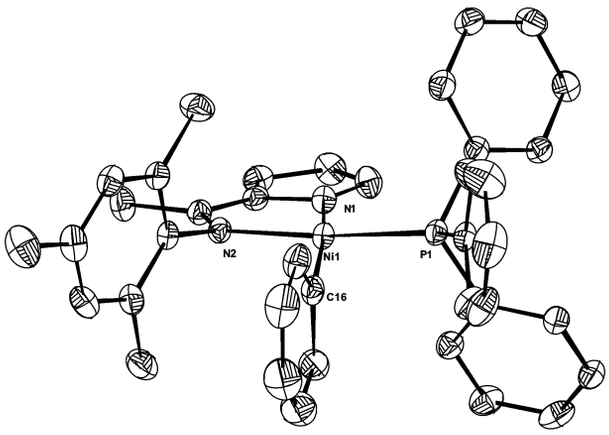
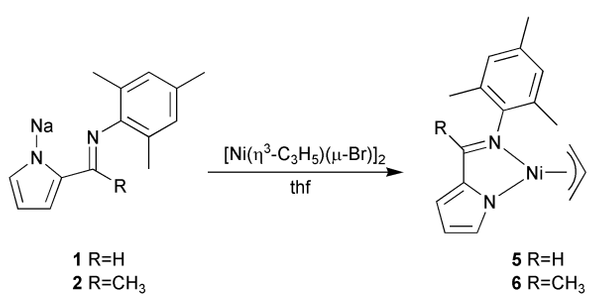


Fig. 3 Alternative view of the molecular structure of complex **3**. ORTEP diagram showing the square planar geometry about the Ni(II) centre.

respectively. In general, the bond lengths within the pyrrole ring or in the acetiminic moiety appear not to be very significantly affected. The N1–C6 distance decreases slightly, as does the C4–C5 distance, whilst the N1–C3 and the C5–C6 distances increase. The angle at the iminic nitrogen C2–N2–C7 remains almost the same, and the imine double bond C2–N2 only slightly increases upon coordination, indicating that π-back-donation from the nickel centre to this group is not strong.

Preliminary experiments in which the complex **3** was tested for catalytic ability in the polymerisation of olefins showed it as inactive. However, when in the presence of a phosphine scavenger like $[Ni(COD)_2]$ (1 equivalent), it promotes oligomerisation of ethylene at 25 and 50 °C, in toluene, to a mixture of unsaturated hydrocarbons. The activity at 25 °C is estimated to be 1.25×10^3 g oligomer (mol Ni)$^{-1}$ h^{-1} bar^{-1}, which is lower than the values observed for the oligomerisation of ethylene with catalysts based on the analogue systems Ni salicylaldimine/$[Ni(COD)_2]$ (5.7×10^3–8.2×10^4 g oligomer (mol Ni)$^{-1}$ h^{-1} bar^{-1})[11,12] or the Ni diimine/MAO systems (5.5×10^4–6.2×10^5 g oligomer (mol Ni)$^{-1}$ h^{-1} bar^{-1}).[15,16] We emphasise, however, that the value herein reported corresponds to non-optimised oligomerisation conditions (temperature, pressure and **3**/$[Ni(COD)_2]$ ratio). Blank experiments revealed that $[Ni(COD)_2]$ alone is inactive at both temperatures.

Reaction of two equivalents of **1** with $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ cleanly yields **5** (Scheme 4) as orange crystals, which was characterised by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and elemental analysis; ^{1}H–^{1}H decoupling techniques and a COSY-NMR experiment permitted assignments of the ^{1}H NMR resonances.



1 R=H
2 R=CH_3

5 R=H
6 R=CH_3

Scheme 4 Synthesis of complexes **5** and **6**.

The complex **6** (Scheme 4) was prepared in a similar fashion by the reaction of **2** with $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$, isolated as a yellow microcrystalline product, and characterised by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and elemental analysis.

^{1}H–^{1}H COSY, NOE and selective decoupling NMR experiments were carried out and the ^{1}H NMR resonances of **2**, **3** and **6** were assigned by comparison between them. These experiments showed that the peak occurring at δ 2.91 and 2.98 for complexes **5** and **6**, respectively, are the *syn*-protons closest to the pyrrole ring. The resonance at δ 7.01 and 7.12, respectively, was shown to correspond to the proton occupying the 2-position on the pyrrole ring. Interestingly, in the case of **5**, a *syn*- and an *anti*-allyl proton are isochronous at around δ 2.0; however, these resonances are partially masked by the mesityl *p*-CH_3 resonance. This is not the case in **6** where all four allyl CH_2 resonances are well separated. Both the allyl ligands in **5** and **6** are non-fluxional.

Experimental

All manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders by Air Liquide, and purified by passage through 4Å molecular sieves. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae and mixtures were filtered in a similar way using modified cannulae that could be fitted with glass fibre filter disks. Unless otherwise stated, reagents were purchased from commercial suppliers (Aldrich, Fluka *et sim.*) and used without further purification. All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium/benzophenone for toluene, benzene, thf and diethyl ether; calcium hydride for hexanes, dichloromethane and *o*-dichlorobenzene. Deuterated solvents were dried by storage over 4 Å molecular sieves and degassed by the freeze–pump–thaw method. Mass spectra were obtained from the IST mass spectrometry service. Nuclear magnetic resonance spectra were recorded on a Varian Unity 300 spectrometer, at the following frequencies: ^{1}H at 299.995 MHz; ^{13}C at 75.4296 MHz; ^{31}P at 121.417 MHz. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane (^{1}H and ^{13}C, $\delta = 0$) or 85% H_3PO_4 (^{31}P, $\delta = 0$). All chemical shifts are quoted in δ (ppm) and coupling constants are given in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), heptet (h), multiplet (m), broad (br). Elemental analyses were obtained from the IST elemental analysis service. Masses are quoted in grams (g) for quantities above 1 g and milligrams (mg) for smaller amounts. The compounds 2-formylpyrrole, 2-acetylpyrrole,[17] $[NiPhBr(PPh_3)_2]$,[18] and $[NiMe_2(TMEDA)]$[19] were synthesised according to the literature procedure. $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ was prepared[20] by oxidative addition of allyl bromide to $[Ni(COD)_2]$.[21]

Preparation of (1*H*-pyrrol-2-ylmethylene)(2,4,6-trimethylphenyl)amine, formimine, I

2-Formylpyrrole (1.00 g, 10.6 mmol), mesitylaniline (1.58 g, 11.5 mmol), a catalytic amount of *p*-toluenesulphonic acid and enough $MgSO_4$ to remove any water from the reaction mixture were suspended in absolute ethanol (5 ml) in a 50 ml round bottom flask fitted with a condenser and a $CaCl_2$ guard tube. The mixture was heated to reflux overnight, during which time the solution turned yellow–orange. The mixture was allowed to cool, CH_2Cl_2 was added and the suspension was filtered through Celite, and washed through with more CH_2Cl_2. After removal of all volatiles, the product was recrystallised from refluxing hexane to yield 2.01 g (90%) of a microcrystalline yellow solid. Anal. found (calc. for $C_{14}H_{16}N_2$): C 79.28 (79.21); H 7.76 (7.60); N 13.22 (13.20)%. NMR: δ_H ($CDCl_3$): 10.60 (1H, br s, pyrrole NH), 7.94 (1H, s, N=CH), 6.89 (2H, s, phenyl H), 6.59 (1H, s, pyrrole 5-H), 6.54 (1H, s, pyrrole 3-H), 6.20 (1H, m, pyrrole 4-H), 2.29 (3H, s, mesityl *p*-CH_3), 2.12 (6H, s, mesityl *o*-CH_3); δ_C ($CDCl_3$): 153.25 (N=CH), 148.27 (*ipso*-C), 133.45 (pyrrole quat. C), 130.36 (mesityl quat. *p*-C), 129.08 (mesityl *m*-CH), 128.35 (mesityl quat. *o*-C), 123.87 (pyrrole 5-CH),

116.72 (pyrrole 4-CH or 3-CH), 110.34 (pyrrole 3-CH or 4-CH), 21.02 (mesityl *p*-CH_3), 18.57 (mesityl *o*-CH_3).

Synthesis of [1-(1*H*-pyrrol-2-yl)ethylidene](2,4,6-trimethylphenyl)amine, acetimine, II

2-Acetylpyrrole (purified by vacuum sublimation at 140 °C, 10^{-2} mbar) (1.08 g, 10 mmol) and mesitylaniline (1.49 g, 11 mmol, 1.54 ml) were placed in a 100 ml round bottom flask with a catalytic amount of *p*-toluenesulphonic acid under nitrogen. A calcium chloride guard tube was fitted on top of the flask, and it was immersed as far as possible in an oil bath. The bath was heated to 140 °C overnight. After the flask was allowed to cool, the remaining aniline was eliminated by trap-to-trap distillation, and the iminopyrrole was vacuum-sublimed into a water condenser. Any further impurities could be removed by recrystallisation from the minimum amount of boiling hexane. A second crop of crystals from the mother-liquor can be obtained by evaporation and washing with cold hexane. Combined isolated yield: 758 mg (35%). Anal. found (calc. for $C_{15}H_{18}N_2$): C 79.77 (79.61); H 8.16 (8.02); N 12.37 (12.38)%. NMR: δ_H ($CDCl_3$): 9.80 (1H, br s, pyrrole NH), 6.83 (2H, s, mesityl CH), 6.75 (1H, s, pyrrole 5-H), 6.61 (1H, m, pyrrole 3-H), 6.21 (1H, m, pyrrole 4-H), 2.24 (3H, s, N=CCH_3), 1.95 (6H, s, mesityl *o*-CH_3), 1.91 (3H, s, mesityl *p*-CH_3); δ_C (pyridine-d_5): 158.12 (N=*C*CH_3), 147.13 (mesityl *ipso*-C), 133.29 (pyrrole quat. C), 131.50 (mesityl quat. *p*-C), 128.97 (mesityl CH), 126.48 (mesityl quat. *o*-C), 122.76 (pyrrole 5-CH), 112.72 (pyrrole 4-CH or 3-CH), 109.75 (pyrrole 3-CH or 4-CH), 20.76 (mesityl *p*-CH_3), 18.11 (mesityl *o*-CH_3), 16.77 (N=C*C*H_3).

Synthesis of the sodium salt of [1-(1*H*-pyrrol-2-yl)ethylidene]-(2,4,6-trimethylphenyl)amine, 2

NaH (55 mg, 60% dispersion in mineral oil, 1.38 mmol) was placed in a Schlenk tube under nitrogen, washed twice with hexanes and suspended in thf. The iminopyrrole **II** (271 mg, 1.2 mmol) was slowly added as a solid under a counterflow of nitrogen, and immediate evolution of hydrogen occurred. After the addition was completed, the suspension was stirred for 90 min and then filtered into another Schlenk tube. The yellow solution was concentrated to about 5 ml, and excess hexane was added. After a few seconds, the product began to precipitate out of solution. The material was allowed to settle for 15 min, then the supernatant was filtered off and the solid pumped to dryness. Yield: 180 mg, 0.73 mmol, 60%. NMR: δ_H (pyridine-d_5): 7.62 (1H, s, pyrrole 5-H), 7.34 (1H, m, pyrrole 3-H), 6.80 (1H, m, pyrrole 4-H), 6.78 (2H, s, mesityl CH), 2.25 (3H, s, N=CCH_3), 2.16 (3H, s, mesityl *p*-CH_3), 1.90 (6H, s, mesityl *o*-CH_3).

Synthesis of [NiPh(acetiminopyrrolyl)(PPh_3)], 3

The sodium salt **2** (164 mg, 0.66 mmol) was suspended in toluene, with a few drops of thf to dissolve it. $Ni(PPh_3)_2(Ph)Br$ (485 mg, 0.66 mmol) was dissolved in toluene and cooled to −80 °C. The sodium salt was added to the nickel complex, and the resulting suspension was stirred for 3 h, during which time the reaction mixture attained a temperature of *ca*. 0 °C. The mixture was then pumped to dryness, and the following workup procedure was applied. The residue was washed once with hexanes and once with a very small quantity of diethyl ether. The residue was then extracted into diethyl ether until it was almost colourless. NMR experiments showed that the hexane extract contained very little of the desired product, whilst the diethyl ether extract contained it. Washing this residue with hexane afforded a yellow solid, which was dried under vacuum. Yield: 120 mg (30%). Anal. found (calc. for $C_{39}H_{37}N_2PNi$): C 74.74 (75.14); H 6.18 (5.98); N 4.11 (4.49)%. NMR: δ_H (C_6D_6): 7.66 (6H, m, PPh_3 *m*-H), 7.02 (2H, m, NiPh *o*-H), 6.80–6.90 (9H, m, PPh_3 *o*,*p*-H), 6.78 (1H, m, pyrrole 5-H), 6.48 (2H, s, mesityl-H), 6.36 (1H, m, NiPh *p*-H), 6.27 (2H, m, NiPh *m*-H), 6.20 (1H, m, pyrrole 3-H), 5.96 (1H, br, pyrrole 4-H), 2.32 (6H, s, mesityl-*o*-CH_3), 1.98 (3H, s, N=CCH_3), 1.66 (3H, s, mesityl-*p*-CH_3); δ_C (C_6D_6): 170.49 (N=*C*CH_3), 153.64 (d, $^1J_{PC}$ = 48 Hz, C–P), 144.08 (*ipso*-C), 143.23 (aryl quat. C), 138.64 (aryl CH), 136.58 (aryl CH), 135.08 (aryl CH), 134.93 (aryl CH), 133.66 (pyrrole quat. C), 133.11 (aryl quat. C), 132.52 (aryl CH), 130.98 (aryl quat. C), 130.07 (aryl CH), 125.28 (aryl CH), 121.52 (pyrrole 5-CH), 115.70 (pyrrole 4-CH or 3-CH), 111.68 (pyrrole 3-CH or 4-CH), 20.83 (mesityl *p*-CH_3), 19.20 (mesityl *o*-CH_3), 16.04 (N=C*C*H_3); δ_P (C_6D_6): 31 (s).

Synthesis of Ni(acetiminopyrrolyl)$_2$, 4

Ni(TMEDA)Me_2 (165 mg, 0.81 mmol) was dissolved in acetonitrile and cooled to −45 °C. The iminopyrrole **II** (183 mg, 0.81 mmol) was dissolved in acetonitrile and added slowly and dropwise to the nickel complex. The solution was allowed to warm to room temperature and stirred overnight. After filtration, the solvent was removed. During the removal of the solvent, the colour changed from yellow to orange to red. The dry material was a red microcrystalline solid. Washing with hexanes, extraction and crystallisation from diethyl ether yielded a red crystalline solid. Yield: 148 mg (72%, relative to ligand). Anal. found (calc. for $C_{30}H_{34}N_4Ni$): C 69.37 (70.75); H 7.00 (6.73); N 10.67 (11.00)%; MS: *m*/*z* 508 (M^+), 493 ($M^+ - CH_3$), 442 ($M^+ - C_4H_4N$), 400 ($M^+ - C_9H_{11}$), 349 [$M^+ - C_{11}H_{14}$], 284 [$M^+ - C_{15}H_{17}N_2$]. NMR: δ_H (C_6D_6): 6.64 (2H, s, mesityl CH), 6.58 (1H, m, pyrrole 5-H), 6.01 (1H, m, pyrrole 3-H), 5.00 (1H, br, pyrrole 4-H), 2.39 (6H, s, mesityl-*o*-CH_3), 2.01 (3H, s, N=CCH_3), 1.38 (3H, s, mesityl-*p*-CH_3); δ_C (C_6D_6): 170.5 (N=*C*CH_3), 143.4 (mesityl *ipso*-C), 142.5 (aryl quat. *p*-C), 135.9 (pyrrole CH), 135.8 (pyrrole quat. C), 133.4 (aryl quat. *o*-C), 129.5 (aryl *m*-CH), 117.0 (pyrrole CH), 111.4 (pyrrole CH), 21.0 (mesityl *p*-CH_3), 18.8 (mesityl *o*-CH_3), 15.0 (N=C*C*H_3).

Synthesis of Ni(η^3-C_3H_5)(formiminopyrrolyl), 5

NaH (144 mg, 60% dispersion in mineral oil, 3.6 mmol) was placed in a Schlenk tube under nitrogen, washed twice with hexanes and suspended in thf. The iminopyrrole **I** (245 mg, 1.16 mmol) was slowly added as a solid under a counterflow of nitrogen, and immediate evolution of hydrogen occurred with concomitant generation of a bright pink colour. The suspension was stirred for 1 h then slowly added by filtration into a thf solution of [Ni(η^3-C_3H_5)(μ-Br)]$_2$ (207 mg, 0.58 mmol) at −70 °C. The solution rapidly turned orange and cloudy, and was allowed to warm to room temperature. All volatiles were removed under vacuum, and the residue was extracted with hexanes until the extracts were colourless. The resulting solution was concentrated and cooled to −80 °C to yield the product as orange crystals. Yield: 68%. If desired a second crop can be obtained by concentrating the mother-liquor and further cooling to −80 °C. Anal. found (calc. for $C_{17}H_{20}N_2Ni$): C 65.87 (65.64); H 6.57 (6.48); N 8.92 (9.01)%. NMR: δ_H (C_6D_6): 7.01 (1H, br, pyrrole 5-H) 6.87 (1H, s, N=CH), 6.80 (1H, m pyrrole 3-H), 6.71 (1H, br, aryl H), 6.68 (1H, (br), mesityl H), 6.50 (1H, m, pyrrole 4-H), 5.18–4.85 (1H, m, allyl central H), 2.91 (1H, m, allyl *syn*-H), 2.19 (3H, s, mesityl *o*-CH_3), 2.11 (3H, s, mesityl *o*-CH_3), 2.03–1.99 (5H, s + m, mesityl *p*-CH_3 + allyl *syn* + *anti*-H), 1.78 (1H, m, allyl *anti*-H); δ_C (C_6D_6): 162.5 (N=CH), 149.1 (mesityl *ipso*-C), 141.8 (mesityl quat. *p*-C), 139.9 (allyl CH), 134.2 (pyrrole quat. C), 130.3 (mesityl quat. *o*-C), 130.1 (mesityl quat. *o*-C), 129.0 (mesityl *m*-CH), 128.7 (mesityl *m*-CH), 118.0 (pyrrole CH), 113.4 (pyrrole CH), 111.0 (pyrrole CH), 58.8 (allyl CH_2), 50.1 (allyl CH_2), 20.8 (mesityl *p*-CH_3), 18.7 (mesityl *o*-CH_3), 18.6 (mesityl *o*-CH_3).

Synthesis of Ni(η^3-C_3H_5)(acetiminopyrrolyl), 6

NaH (96 mg, 60% dispersion in mineral oil, 2.4 mmol) was placed in a Schlenk tube under nitrogen, washed twice with

hexanes and suspended in thf. The acetiminopyrrole **II** (318 mg, 1.4 mmol) was slowly added as a solid under a counterflow of nitrogen, and immediate evolution of hydrogen occurred. The suspension was stirred for 1 h then slowly added by filtration into a thf solution of $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ (252 mg, 0.7 mmol) at −70 °C. The mixture went yellow and cloudy during this time and was allowed to warm to room temperature. After 90 min, the mixture was evaporated under vacuum to yield a dark yellow oil. The residue was extracted with hexanes until the washings were colourless, and the solution was concentrated and cooled to −80 °C to yield yellow crystals of the desired product. A second crop can be obtained by concentrating and cooling the mother-liquor. Combined yield: 91%. Anal. found (calc. for $C_{18}H_{22}N_2Ni$): C 66.45 (66.51); H 7.00 (6.82) N 8.48 (8.62)%. NMR: δ_H (C_6D_6): 7.12 (1H, m, pyrrole 5-H), 6.90 (1H, m), pyrrole 3-H), 6.77 (1H, br, mesityl H), 6.75 (1H, br, mesityl H), 6.62 (1H, m, pyrrole 4-H), 5.15–5.04 (1H, m, allyl central H), 2.98 (1H, m, allyl *syn*-H), 2.22 (3H, s, mesityl *o*-CH_3), 2.18 (3H, s, mesityl *o*-CH_3), 2.10 (1H, m, allyl *anti*-H), 2.03 (3H, s, imine CH_3), 1.92 (1H, m, allyl *syn*-H), 1.82 (1H, m, allyl *anti*-H), 1.62 (3H, s, mesityl *p*-CH_3); δ_C (C_6D_6): 170.48 (N=*C*CH_3), 146.83 (*ipso*-C), 138.70 mesityl quat. *p*-C) 138.51 (allyl CH), 134.01 (pyrrole quat. C), 129.97 (mesityl quat. *o*-C), 129.84 (mesityl quat. *o*-C), 129.14 (mesityl *m*-CH), 128.85 (mesityl *m*-CH), 115.84 (pyrrole CH), 112.12 (pyrrole CH), 110.93 (pyrrole CH), 54.86 (allyl CH_2), 49.64 (allyl CH_2), 20.83 (mesityl *p*-CH_3), 18.40 (mesityl *o*-CH_3), 18.30 (mesityl *o*-CH_3), 16.68 (N=C*C*H_3).

Oligomerisation tests

Oligomerisation tests with ethylene were carried out in flame dried 250 ml crown capped glass pressure bottles, sealed with neoprene septa, and pump filled with nitrogen atmosphere. To these reaction bottles 50 ml of toluene (dried over Na/K alloy) were added and the solvent saturated with ethylene at a constant pressure of 2 bar (absolute pressure). This value was kept constant during the polymerisation runs. A solution of $Ni(COD)_2$ (9.4 μmol in 1 ml of toluene), used as a co-catalyst, was added *via* a glass syringe. The solutions were thermostated to 20 or 50 °C and allowed to equilibrate for 15 min. After this period of time, a toluene solution of nickel catalyst **3** (9.4 μmol in 1 ml of toluene) was added to the reaction mixture. The oligomerisation reactions were terminated after 2 h by quenching the mixture with 150 ml of a 2% HCl–methanol solution, and no polymer precipitated from the reaction solution. Aliquots of these solutions were analysed by gas–liquid chromatography (Chrompack GC PONA capillary column (0.53 mm × 30 m); oven temperature program: 40 °C/15 min, 10 °C min^{-1} ramp, 200 °C/20 min) showing the presence of peaks corresponding to a mixture of ethylene oligomers, the total amount being estimated by integration. The reaction mixture was extracted with distilled water (3 × 100 ml) and the organic phase volatiles were removed under vacuum to yield an oily liquid colourless product. This fraction was analysed by ^{1}H NMR spectroscopy showing resonances corresponding to olefinic, methine, methylene and methyl protons (δ 6.47, 5.37, 4.93, 2.39–1.53, 1.24 and 0.83). Blank tests were carried out using either $Ni(COD)_2$ or compound **3** alone, at the same pressure of ethylene and temperatures used for their mixtures, showing no catalytic activity in the oligo- or polymerisation of ethylene.

Crystal structure determination

Experimental. Crystals of compound **II** were grown by cooling a hexane solution to −20 °C. Crystals of compounds **3** were grown from a diethyl ether solution which was slowly cooled to −20 °C. In all cases, the crystals were isolated by filtration, and a specimen crystal selected under an inert atmosphere, covered with polyfluoroether, and mounted on the end of a glass fibre. Crystal data are summarised in Table 2.

Table 2 Crystallographic data for compounds **II** and **3**

	II	**3**
Chemical formula	$C_{15}H_{18}N_2$	$C_{39}H_{37}N_2NiP$
M_r	226.32	623.42
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions:		
a/Å	7.1279(2)	11.7076(2)
b/Å	15.0718(4)	13.0259(2)
c/Å	12.4133(3)	21.3494(3)
β/°	92.6733(12)	98.1760(12)
V/Å^3	1332.11(6)	3222.73(9)
Z	4	4
D_c/g cm^{-3}	1.128	1.285
T/K	150(2)	150(2)
μ/mm^{-1}	0.067	0.682
Reflection collected	5816	7381
Independent reflections	3049	4081
R_{int}	0.01	0.02
R	0.0530	0.0339
R_w	0.0575	0.0370

Criterion for observation: $I > 3\sigma(I)$.

Data collection and processing. All data were collected at 150(2) K on a Nonius KappaCCD, with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), as summarised in Table 2. The images were processed with the DENZO and SCALEPACK programs.[22]

Structure solution and refinement. The crystal structures were solved by direct methods using the programs SIR92.[23] The structures of compounds **II** and **3** were refined using full-matrix least squares on all F data using the CRYSTALS[24] and CAMERON[25] software packages. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions with isotropic thermal parameters. In the case of compound **II**, The NH hydrogen atom H1 was located in a difference Fourier map and its coordinates and isotropic thermal parameter subsequently refined. All other hydrogen atoms were positioned geometrically, the orientations of the methyl groups H11–H13, H131–H133, H141–H143 and H151–H153 having been determined by examination of a difference Fourier map. A Chebychev polynomial weighting scheme[26] with the parameters 1.190, 0.871 and 0.730 was applied to the crystal structure of compound **II** giving a final R factor of 0.0530 and R_w = 0.0575 with a maximum residual electron density of 0.54 e $Å^{-3}$. A similar weighting scheme was applied to the structure of **3** using the parameters 0.250, 0.0981 and 0.0658. This yielded a final R factor of 0.0339 and R_w = 0.0370 with a maximum residual electron density of 0.31 e $Å^{-3}$. Empirical absorption corrections were applied.[27]

CCDC reference numbers 212400 and 212401.

See http://www.rsc.org/suppdata/dt/b3/b311323j/ for crystallographic data in CIF or other electronic format.

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