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Synthesis of neutral and zwitterionic phosphinomethylpyrrolato complexes of nickel

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ABSTRACT

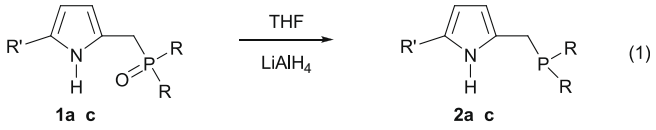
Potassium salts of the new 2-phosphinomethyl-1*H*-pyrroles, K[$R_2PCH_2C_4H_3N$] (R = Ph, Cy) react with (η^3-allyl)nickel bromide to give the chelate complexes ($R_2PCH_2C_4H_3N$)Ni(allyl), whereas the sterically hindered 2-diphenylphosphinomethyl-5-*t*-butyl-1*H*-pyrrole and (η^3-allyl)nickel bromide afford a phosphine adduct (HNC_4H_2-5-Bu^t-2-CH_2PPh_2)Ni(allyl)Br which is stabilized by an intramolecular NH···Br hydrogen bond. The addition of $B(C_6F_5)_3$ to ($R_2PCH_2C_4H_3N$)Ni(allyl) leads to an electrophilic attack in 5-position of the pyrrole ring, to give the thermally unstable zwitterions (η^3-C_3H_5)Ni[NC_4H_3(2-CH_2PR_2)-5-$B(C_6F_5)_3$] which catalyse the isomerisation of 1-hexene. The addition of $B(C_6F_5)_3$ is reversible, and slow ligand rearrangement to Ni(N-P)$_2$ products appears to be the major catalyst deactivation pathway.

1. Introduction

Nickel(II) complexes with a variety of chelating ligands have been much studied, mainly in connection with their activity as ethylene oligomerization catalysts. Nickel P–O chelates form the basis of the Shell Higher Olefins Process (SHOP) [1–3]. Some nickel allyl and benzyl chelate complexes show also good polymerisation activity [4,5]. The range of ligands has recently been extended to include new bidentate [6–12] and tridentate [13] P–N systems. We have recently reported the facile synthesis of the new phosphorylmethylpyrrolato ligands [$R_2P(O)$–CH_2pyr]$^-$ by the reaction of sec-phosphines with pyrrole aldehydes [14]. We report here their reduction to the corresponding phosphines, the formation and structure of their nickel allyl complexes and their activation to give alkene isomerisation catalysts [15].

2. Results and discussion

The reduction of 2-phosphorylmethyl-1*H*-pyrroles (**1a**–**c**) with $LiAlH_4$ in THF at room temperature for a period of 24 h affords the corresponding phosphine derivatives **2** in 45–61% yield (Eq. (1)). Extending the reaction times to up to a week did not result in substantial increases in yield. The compounds were isolated as off-white to pale-yellow solids.



1a c **2a c** (1)

a R = Ph, R' = H
b R = Ph, R' = Bu^t
c R = Cy, R' = H

yield 45 61 %

Ligands with mono-substituted pyrrole rings (**2a** and **2c**) undergo facile deprotonation with potassium hydride to give the corresponding potassium salts K[$R_2PCH_2C_4H_3N$], which react with (η^3-allyl)nickel bromide to give the chelate complexes **3a** and **3c** as orange (R = Ph) or yellow (R = Cy) solids (Eq. (2)). The ^{1}H NMR spectra of complexes **3a**, **c** show five individual signals for the five protons in the η^3-allylic group at room temperature; there is therefore no facile π–σ–π flipping of the allyl ligand under these conditions. The two *syn*-protons show different coupling patterns, since the one *trans* to P shows coupling to P whereas the one *trans* to N does not. The CH_2P protons are diastereotopic and appear as two doublets of doublets, which further corroborates the restricted rotation of the allyl ligand in **3**. The anti-H atom of the allyl ligand in **3c** is hidden by the cyclohexyl signals but was identified by ^{1}H/^{1}H correlation experiments.

Crystals suitable for X-ray diffraction were grown from diethyl ether solution at −30 °C (Fig. 1). Although some *trans* effect on the Ni–C bond lengths to the allyl ligand might have been expected, the effect is negligible within the standard deviations.

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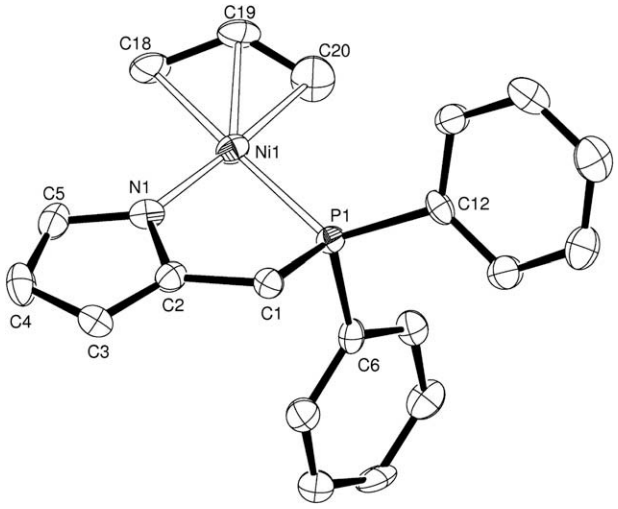
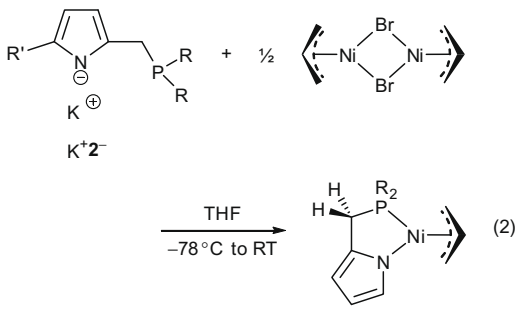
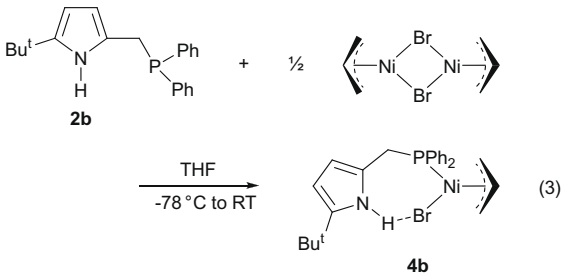


Fig. 1. Molecular structure of **3a**, showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–N(1) 1.880(5), Ni(1)–C(18) 2.023(6), Ni(1)–C(19) 1.979(10), Ni(1)–C(20) 2.008(8), Ni(1)–P(1) 2.1638(17); N(1)–Ni(1)–P(1) 85.79(16), C(18)–Ni(1)–C(20) 74.0(3), N(1)–Ni(1)–C(20) 173.1(3), C(18)–Ni(1)–P(1) 171.5(2).



Somewhat surprisingly, the more sterically hindered ligand **2b** failed to react with potassium hydride in THF and could be recovered unchanged. However, treatment of **2b** in diethyl ether with (η^3-allyl)nickel bromide led to a colour change to dark brown, and a dark-orange product **4b** was isolated. Whereas **3a** gave a ^{31}P NMR chemical shift of δ 42.5, **4b** was clearly different and showed a ^{31}P singlet resonance at δ 19.5. The complex was identified crystallographically as a phosphine adduct of (allyl)NiBr (Eq. (3)). Although the crystal quality was limited and the final *R*-factors were not as low as normally expected, the structure is clear and shows a nickel atom with square-planar geometry coordinated to an η^3-allyl, a bromide and a phosphine ligand. There is no bonding interaction to the nitrogen atom of the pyrrole ring; instead, there is a well-defined intramolecular hydrogen bond between the pyrrole N–H group and the bromide ligand: Br–H(32) 2.61 Å, N(32)–Br 3.411(16) Å (Fig. 2).



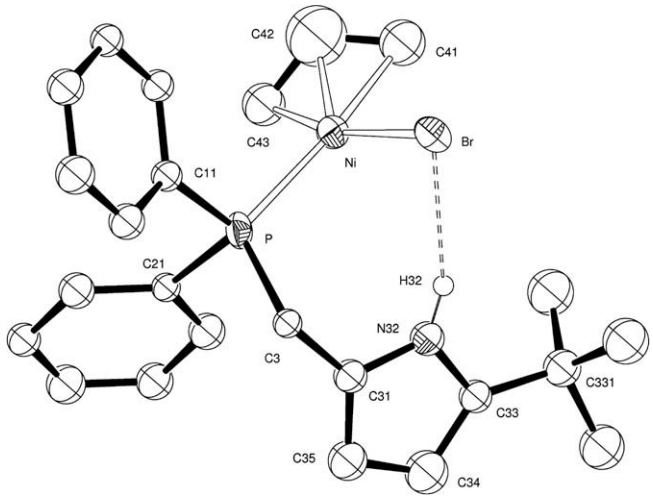


Fig. 2. Molecular structure of **4b** showing the atomic numbering scheme. Ellipsoids are drawn at 50 % probability. Hydrogen atoms except H(32) have been omitted for clarity.

The complexes **3a** and **3c** do not react with either ethylene or hex-1-ene. However, with $B(C_6F_5)_3$ they give the catalytically active zwitterionic products **5a** (R = Ph) and **5c** (R = Cy), respectively.

Some time ago Erker et al. reported the abstraction of a pyrrolate ligand from $Cp_2ZrMe(NC_4H_4)$ by $B(C_6F_5)_3$ to give the $[(1\text{-pyrrolyl})B(C_6F_5)_3]^-$ anion [16] and synthesized 5*H*-pyrrole-$B(C_6F_5)_3$ complex by acidification of $(Et_2O)_2Li[(1\text{-pyrrolyl})B(C_6F_5)_3]$ [17], while Resconi and co-workers undertook a detailed study of the reaction of $B(C_6F_5)_3$ with pyrroles, indoles, imidazoles and pyrazoles [18–20]. In all these cases, with the exception of N-alkyl pyrroles, the boron adds to the nitrogen atom. It seemed reasonable therefore to assume that in the case of complexes **3** attack by $B(C_6F_5)_3$ would also take place on the nitrogen of the N–P chelate, to give a product of structure **I** or **II** (Chart 1). Failing this, the electrophilic borane could be expected to react with one of the nucleophilic termini of the allyl ligand, to give 14-, 16- or 18-electron zwitterions of types **III**–**V**.

However, the spectroscopic data of **5** were inconsistent with any of these structures. The ^{11}B NMR spectra of **5a** and **5c** consisted of relatively sharp singlets with chemical shift values that are indicative of $B(C_6F_5)_3$ bonded to a carbon atom, whereas N-bonded B shows quadrupolar broadening [21,22]. For **5a**, there was a new signal centred at δ 4.75 in the ^{1}H NMR spectrum for a methylene group with an AB pattern and a large geminal H–H coupling constant of 24.9 Hz but no coupling to phosphorus. The ^{13}C NMR signal which correlates with these protons (δ 76.4) also did not couple to

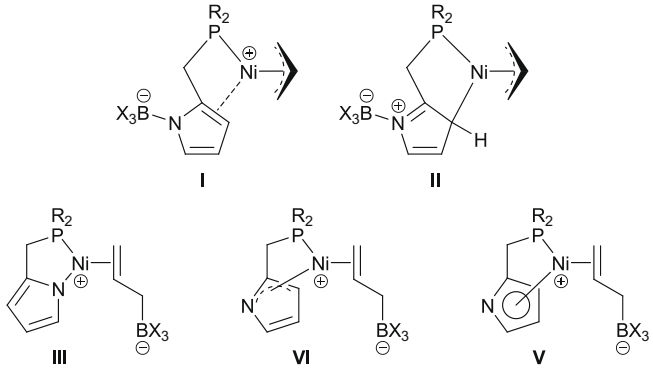
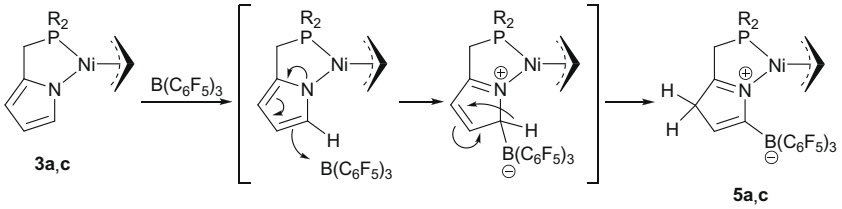


Chart 1.



Scheme 1.

Table 1
Isomerisation of hex-1-ene.[a]

Catalyst precursor	Time (min)	Conversion (%)[b]	% *Z*-hex-2-ene[c]	% *E*-hex-2-ene[c]	% *Z*-hex-3-ene[c]
3a	120	100	15	64	21
3c	480	90	43	47	10

[a] Conditions: 1.7 μm catalyst, 1.7 mmol hex-1-ene, Ni/B ratio 1.5, C_6D_6 (0.5 mL), 20 °C.
[b] Determined by integrations of the ^1H NMR spectra.
[c] Product distribution calculated from the ^{13}C NMR integrals.

phosphorus. These observations are consistent with the presence of acidic sp^3 protons in 5-membered N-heterocyclic compounds [18,19]. The ^1H NMR signals for the diastereotopic CH_2P group were found as two multiplets centred at δ 2.51 and 2.74; the corresponding ^{13}C signal appears as a doublet (J_{C-P} = 26.6 Hz) and its coupling pattern is, as expected, altered in the $^1H\{^{31}P\}$ NMR spectrum (these ^1H NMR signals do not in fact become simple doublets of doublets as a small coupling exists between this ABX system and the AB methylene system situated on the 3-position of the pyrrole ring, as shown by 2D COSY NMR). The carbon in 2-position of the pyrrolyl ring can be identified as a highly deshielded doublet at δ 186.57 ($^2J_{C-P}$ = 9.2 Hz). The data therefore point to the formation of a zwitterion with a $B(C_6F_5)_3$ moiety bound to an sp^2-C-atom in 5-position of the heterocycle, accompanied by an allylic 1,3-shift of an H atom (Scheme 1).

Compounds **5** do not undergo alkene insertion chemistry but catalyse the isomerisation of hex-1-ene to products with internal double bonds, in the manner of acid catalysts. Complex **5a**, which contains the less basic phosphine donor, showed both improved catalytic activity and higher selectivity for *E*-hex-2-ene. **5a** also yielded a higher conversion to the *Z*-hex-3-ene isomer, with traces of *E*-hex-3-ene also present (Table 1). No such isomerisation took place with $B(C_6F_5)_3$ alone. The catalyst is recyclable. After complete conversion of hex-1-ene by **3a**/$B(C_6F_5)_3$, all volatiles were removed and a second reaction batch of solvent and substrate was added. Although the conversion was reduced slightly (to 81% in 120 min), the product ratios remained unchanged.

Leaving the reaction of **5a** to stand for 3 days resulted in a black precipitate of nickel metal, accompanied by red crystals of $Ni(Ph_2PCH_2\text{-}2\text{-}C_4H_3N)_2$ (**6a**). This suggests that the formation of **5a** from **3a** and $B(C_6F_5)_3$ is reversible, and that under these conditions **3a** can slowly disproportionate into the bis-ligand complex **6a** and thermally labile Ni(allyl)$_2$. The structure of **6a** is shown in Fig. 3. The complex is square-planar, with an angle sum about the Ni centre of 360.78(10)°.

3. Conclusion

The reduction of phosphorylmethylpyrroles $R_2P(O)CH_2\text{-}2\text{-}C_4H_3N\text{-}5\text{-}R'$ gives the new N–P chelate ligands $R_2P(O)CH_2\text{-}2\text{-}C_4H_3N\text{-}5\text{-}R'$ (R = Ph or Cy; R′ = H or Bu^t). The mono-substituted pyrroles are readily deprotonated and react with (allyl)nickel bromide to give the expected chelates (N–P)Ni(η^3-allyl). Pyrroles

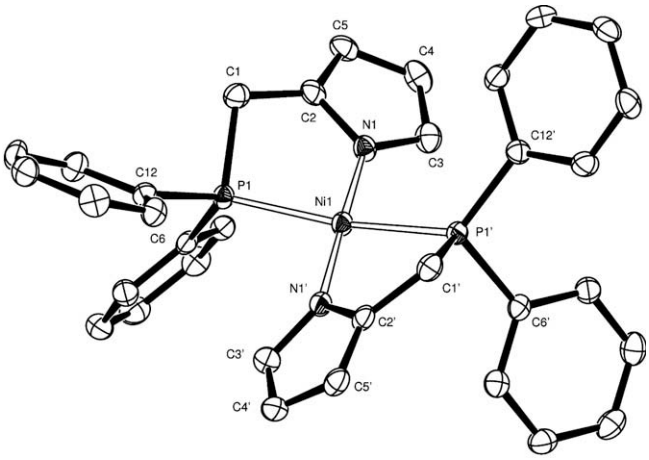


Fig. 3. Molecular structure of **6a**·C_6H_6 showing 50% probability ellipsoids. One molecule of benzene and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–N(1′) 1.8791(15), Ni(1)–P(1) 2.2123(5); N(1)–Ni(1)–P(1) 82.86(5), N(1)–Ni(1)–N(1′) 176.20(9), P(1)–Ni(1)–P(1′) 168.28(3), N(1)–Ni(1)–P(1′) 97.53(5).

with *t*-butyl substituents in *ortho*-position to N proved unexpectedly resistant to deprotonation under the same conditions. The complexes Ni(allyl)(κ^2-$R_2PCH_2C_4H_3$) react with $B(C_6F_5)_3$ *via* attack in 5-position of the pyrrole ring, accompanied by a 1,3-hydride shift. The resulting zwitterionic complex catalyses the isomerisation of hex-1-ene to predominantly *E*-hex-2-ene at room temperature in high conversions.

4. Experimental

4.1. General procedures

Syntheses were performed under nitrogen using standard Schlenk line techniques. Solvents were distilled from sodium-benzophenone (diethyl ether, THF), sodium–potassium alloy (light petroleum, b.p. 40–60 °C), or CaH_2 (dichloromethane). NMR solvents ($CDCl_3$, CD_2Cl_2, C_6D_6) were dried over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. Hex-1-ene was dried over sodium–potassium alloy for a minimum of 6 h, distilled and degassed before use. [Ni(η^3-allyl)(μ-Br)]$_2$ [23,24], $B(C_6F_5)_3$ [25,26], 2-diphenylphosphorylmethyl-1*H*-pyrrole [14], 2-diphenylphosphorylmethyl-5-*t*-butyl-1*H*-pyrrole [14] and 2-dicyclohexylphosphorylmethyl-1*H*-pyrrole [14] were synthesised using literature procedures; for the ligand precursor synthesis see also the Supporting Information. Dicyclohexyl phosphine oxide was made using standard literature procedures and reduced to the corresponding dicyclohexyl phosphine with $LiAlH_4$ in THF [27]. NMR spectra were recorded using a Bruker DPX-300 spectrometer with a 5 mm BBO probe. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C), ^{19}F is relative to $CFCl_3$. Nitrogen was purified

by passing through columns of supported P_2O_5, with moisture indicator, and activated 4 Å molecular sieves. Elemental analyses were performed by London Metropolitan University.

4.2. Ligand synthesis

4.2.1. Preparation of 2-diphenylphosphinomethyl-1H-pyrrole (**2a**)

2-Diphenylphosphorylmethyl-1*H*-pyrrole (**1a**) (5.63 g, 20.0 mmol) was dissolved in THF (250 cm^3) and slowly added to $LiAlH_4$ (2.34 g, 61.7 mmol). The suspension was stirred for 3 d and excess $LiAlH_4$ was hydrolysed with degassed, aqueous NH_4Cl (120 cm^3). The mixture was agitated for 15 min and left to separate. The aqueous layer was washed with THF (2×100 cm^3) and the combined organic phases dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give 3.5 g of crude product, which was then extracted with diethyl ether (100 cm^3). The solvents were evaporated to give the product as a pale-yellow solid (2.37 g, 45%). From the reaction residue 1.13 g (20%) of the starting material was recovered. Anal. Calc. for $C_{17}H_{16}NP$; C, 76.97; H, 6.08; N, 5.28. Found: C, 76.54; H, 5.87; N, 5.21%. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 7.92 (br s, 1H, NH), 7.73–7.38 (m, 10H, Ph), 6.61 (s, 1H, pyrrole), 6.04 (s, 1H, pyrrole), 5.87 (s, 1H, pyrrole), 3.47 (s, 2H, PCH_2). ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 138.71 (d, $^2J_{C-P}$ = 14.7 Hz, Ph), 134.23 (d, J_{C-P} = 18.1 Hz, aromatic C–P), 132.91 (Ph), 127.28 (Ph), 126.98 (d, $^3J_{C-P}$ = 6.7 Hz, pyrrole CH) 117.14 (d, $^2J_{C-P}$ = 7.01 Hz, pyrrole C), 108.61 (d, $^4J_{C-P}$ = 5.4 Hz, pyrrole CH), 107.33 (pyrrole CH), 27.87 (d, J_{C-P} = 15.0 Hz, PCH_2). ^{31}P{^{1}H} NMR (121 MHz, 300 K, $CDCl_3$,): δ −16.28.

4.2.2. Preparation of 2-diphenylphosphinomethyl-5-t-butyl-1H-pyrrole (**2b**)

The compound was made as described for **1a**, using 2-diphenylphosphorylmethyl-5-*t*-butyl-1*H*-pyrrole (**1b**). The crude product was extracted into petrol and volatiles were removed to give the pure product as a white sticky solid, 0.53 g (61%). Anal. Calc. for $C_{21}H_{24}NP$: C, 78.48; H, 7.53; N, 4.36. Found; C, 78.58; H, 7.54; N, 4.44%. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 8.65 (br s, 1H, NH), 7.43–7.35 (m, 10H, Ph), 5.77 (s, 1H, pyrrole), 5.72 (s, 1H, pyrrole), 3.41 (s, 2H, PCH_2), 1.13 (s, 9H, Bu^t). ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 141.12 (Ph), 138.51 (d, $^2J_{C-P}$ = 15.0 Hz, Ph), 132.78 (d, J_{C-P} = 18.2 Hz, aromatic C–P), 128.81 (Ph), 128.51 (d, $^3J_{C-P}$ = 6.6 Hz, pyrrole CH), 125.02 (d, $^2J_{C-P}$ = 7.01 Hz, pyrrole C), 106.61 (d, $^4J_{C-P}$ = 5.5 Hz, pyrrole CH), 102.21 (pyrrole C), 31.21 (*C*Me$_3$), 30.37 (C*Me*$_3$), 27.91 (d, J_{C-P} = 15.0 Hz, PCH_2). ^{31}P{^{1}H} NMR (121 MHz, 300 K, $CDCl_3$,): δ −15.41.

4.2.3. Preparation of 2-dicyclohexylphosphinomethyl-1H-pyrrole (**2c**)

The compound was made as described for **2a**, using 2-dicyclohexylphosphorylmethyl-1*H*-pyrrole (**1d**). The crude product was extracted into light petroleum and volatiles were removed to give the title product in 90% purity (by NMR) as an off-white solid, (0.45 g, 48%). ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 8.27 (br s, 1H, NH), 6.68 (s, 1H, pyrrole CH) 6.10 (br s, 1H, pyrrole), 5.93 (br s, 1H, pyrrole), 2.82 (s, 2H, PCH_2), 1.90–1.03 (m, 22H, Cy). ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 129.10 (d, $^2J_{C-P}$ = 8.4 Hz, pyrrole C), 116.21 (pyrrole CH), 114.18 (pyrrole CH), 108.28 ($^3J_{C-P}$ = 4.2 Hz, pyrrole CH), 33.31 (d, $^3J_{C-P}$ = 12.9 Hz, Cy), 29.81 (d, $^2J_{C-P}$ = 13.0 Hz, Cy), 28.69 (d, $^4J_{C-P}$ = 8.5 Hz, Cy), 27.33 (d, J_{C-P} = 19.2 Hz, Cy), 20.42 (d, J_{C-P} = 18.3 Hz, PCH_2). ^{31}P{^{1}H} NMR (121 MHz, 300 K, $CDCl_3$,): δ −6.65.

4.3. Synthesis of complexes

4.3.1. Preparation of (^{3}-C_3H_5)Ni($NC_4H_3CH_2PPh_2$) (**3a**)

To a suspension of the potassium salt of 2-diphenylphosphinomethyl-1*H*-pyrrole (**2a**) (0.20 g, 0.66 mmol) in THF (25 cm^3) was added [(η^3-allyl)NiBr]$_2$ (0.120 g, 0.33 mmol) in THF (15 cm^3) at −50 °C. The reaction mixture changed from deep-red to orange. The mixture was allowed to reach room temperature and left to stir for 6 h. Volatiles were removed *in vacuo* and the resultant brown solid was extracted as a yellow solution in diethyl ether (2×50 cm^3). On concentration and cooling the product was observed as yellow needles suitable for X-ray diffraction (0.170 g, 71%). Anal. Calc. for $NiC_{20}H_{20}NP$: C, 65.98; H, 5.54; N, 3.85. Found: C, 65.71; H, 5.66; N, 3.97%. ^{1}H NMR (300 MHz, 300 K, C_6D_6): δ 7.47–7.41 (m, 4H, Ph), 7.10–7.01 (m, 7H, Ph + pyrrole), 7.00 (m, 1H, pyrrole), 6.74 (m, 1H, pyrrole), 4.97–4.92 (m, 1H, allyl), 4.15–4.12 (m, 1H, allyl CH_{anti}), 3.67 (dd, 1H, $^2J_{H-P}$ = 9.7 Hz, ^2J = 15.0 Hz, C*H*HP), 3.55 (dd, 1H, $^2J_{H-P}$ = 9.8 Hz, ^2J = 15.0 Hz, C*H*HP), 3.03 (dd, 1H, $^3J_{H-P}$ = 5.2 Hz, ^2J = 10.6 Hz, allyl CH_{syn}), 2.87–2.80 (m, 1H, allyl CH_{anti}), 1.56 (d, 1H, ^2J = 12.0 Hz, allyl, CH_{syn}). ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 137.19 (d, $^2J_{C-P}$ = 8.8 Hz, pyrrole C), 133.49 (d, J_{C-P} = 22.5 Hz, aromatic C–P), 133.49 (d, J_{C-P} = 23.1 Hz, aromatic C–P), 132.42 (d, $^2J_{C-P}$ = 12.1 Hz, Ph), 132.08 (d, $^2J_{C-P}$ = 12.1 Hz, Ph), 131.46 (d, $^4J_{C-P}$ = 2.7 Hz, pyrrole CH), 130.18 (d, $^4J_{C-P}$ = 1.7 Hz, Ph), 128.77 (d, $^3J_{C-P}$ = 6.6 Hz, Ph), 128.66 (d, $^3J_{C-P}$ = 7.1 Hz, Ph), 111.25 (allyl), 110.82 (pyrrole CH), 103.81 (d, $^3J_{C-P}$ = 10.4 Hz, pyrrole CH), 67.67 (d, $^2J_{C-P}$ = 24.4 Hz, allyl H_2C_{trans}), 46.78 (d, $^2J_{C-P}$ = 3.8 Hz, allyl H_2C_{cis}), 32.43 (d, J_{C-P} = 25.8 Hz, PCH_2). ^{31}P{^{1}H} NMR (121 MHz, 300 K, C_6D_6): δ 42.47.

4.3.2. Preparation of (^{3}-C_3H_5)Ni(NC_4H_3-2-CH_2PCy_2) (**3c**)

The compound was made as described for **3a**, using the potassium salt of 2-dicyclohexylphosphinomethyl-1*H*-pyrrole (**2c**). On removal of all volatiles the crude product was observed as a yellow solid (0.15 g, 80%). Anal. Calc. for $NiC_{20}H_{32}NP$: C, 63.86; H, 8.57; N, 3.72. Found: C, 63.75; H, 8.91; N, 3.63%. ^{1}H NMR (300 MHz, 300 K, C_6D_6): δ 7.28–7.25 (m, 1H, pyrrole CH), 6.99–6.97 (m, 1H, pyrrole CH), 6.70–6.68 (m, 1H, pyrrole CH), 5.06–4.91 (m, 1H, allyl), 4.17–4.14 (m, 1H, allyl CH_{anti}), 3.13 (dd, 1H, $^3J_{H-P}$ = 5.9 Hz, ^2J = 8.9 Hz, allyl CH_{syn}), 2.96 (dd, 1H, $^2J_{H-P}$ = 10.6 Hz, ^2J = 16.3 Hz, C*H*HP), 2.82 (dd, 1H, $^2J_{H-P}$ = 9.9 Hz, ^2J = 16.3 Hz, C*H*HP), 2.64–2.58 (m, 1H, allyl CH_{anti}), 1.79–0.96 (23H, cyclohexyl + 1 allyl CH_{syn}). ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 138.46 (d, $^2J_{C-P}$ = 8.2 Hz, pyrrole *C*), 130.85 (d, ^4J = 2.2 Hz, pyrrole CH), 110.45 (pyrrole CH), 110.00 (allyl), 102.76 (d, ^3J = 9.9 Hz, pyrrole CH), 68.12 (d, $^2J_{C-P}$ = 20.3 Hz, allyl H_2C_{trans}), 46.78 (d, $^2J_{C-P}$ = 6.0 Hz, allyl H_2C_{cis}), 33.67 (d, J_{C-P} = 22.3 Hz, Cy), 33.43 (d, J_{C-P} = 22.0 Hz, Cy), 28.73 (d, $^3J_{C-P}$ = 6.5 Hz, Cy), 28.64 (d, $^3J_{C-P}$ = 7.3 Hz, Cy), 26.83 (d, $^2J_{C-P}$ = 12.5 Hz, Cy) 26.77 (d, $^2J_{C-P}$ = 13.3 Hz, Cy), 26.50 (d, $^4J_{C-P}$ = 5.7 Hz, Cy) 26.00 (d, $^4J_{C-P}$ = 5.0 Hz, Cy) 22.50 (d, J_{C-P} = 22.7 Hz, PCH_2). ^{31}P{^{1}H} NMR (121 MHz, 300 K, C_6D_6): δ 59.35.

4.3.3. Preparation of (^{3}-C_3H_5)NiBr(2-Ph_2PCH_2(5-Bu^t)C_4H_2NH) (**4b**)

To a solution of **2b** (0.20 g, 0.62 mmol) in THF was added slowly a solution of [(η^3-allyl)NiBr]$_2$ (0.12 g, 0.33 mmol) in THF (50 cm^3) to give a dark brown solution. Volatiles were removed *in vacuo* and the product exacted as a dark-orange solution in diethyl ether. The filtrate was cooled to −35 °C for 48 h to give **4b** as orange crystals suitable for X-ray diffraction, yield (0.14 g, 45%). Anal. Calc. for $NiC_{24}H_{29}BrNP$: C, 57.53; H, 5.83; N, 2.80. Found: C, 57.79; H, 6.16; N, 3.07%. ^{1}H NMR (300 MHz, 300 K, C_6D_6): δ 10.32 (br s, 1H, NH), 7.40–7.27 (m, 10H, Ph), 5.97 (br s, 1H, pyrrole CH), 5.64 (br s, 1H, pyrrole CH), 4.84–4.79 (m, 1H, allyl), 3.78 (br s, 1H, allyl CH_{anti}), 3.41 (d, 2H, $^2J_{H-P}$ = 7.0 Hz, CH_2P), 2.67 (br s, 1H, allyl CH_{syn}), 1.51 (s, 9H, Bu^t), 1.35 (m, 1H allyl CH_{anti}), 0.97 (d, 1H, ^2J = 6.6 Hz, allyl CH_{syn}). ^{31}P{^{1}H} NMR (121 MHz, 300 K, C_6D_6): δ 19.48.

4.3.4. (^{3}-C_3H_5)Ni[NC_4H_3(2-CH_2PPh_2)-5-B(C_6F_5)$_3$] (**5a**)

Tris(pentafluorophenyl)borane (0.036 g, 0.07 mmol) in deuterated benzene (0.2 cm^3) was added to **3a** (0.020 g, 0.06 mmol) in

deuterated benzene (0.4 cm^3) in an NMR tube to give an orange solution of compound **5a**. The compounds could not be crystallised, and attempted isolation resulted in a black oil. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 7.43–7.09 (m, 10H, Ph) 6.72 (br s, 1H, ring CH), 4.80 (d, 1H, ^2J = 24.9 Hz, one of ring CH_2), 4.71 (d, 1H, ^2J = 24.9 Hz, one of ring CH_2), 4.52 (m, 1H, allyl), 3.66–3.63 (m, 1H, allyl CH_{anti}), 2.75–2.73 (m, 1H, C*H*HP), 2.69 (br s, 1H, allyl CH_{anti}), 2.54–2.48 (m, 1H, C*H*HP), 2.23 (dd, 1H, $^3J_{H-P}$ = 5.4 Hz, ^2J = 8.6 Hz, allyl CH_{syn}), 1.42 (d, 1H, ^2J = 15.6 Hz, allyl CH_{syn}). ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 185.80 (d, $^2J_{C-P}$ = 9.2 Hz, ring $H_2CC{=}N$), 156.15 (*C*H=C), 148.14 ($^1J_{C-F}$ = 232.0 Hz, C–F), 137.48 ($^1J_{C-F}$ = 240.1 Hz, C–F), 134.51 ($^1J_{C-F}$ = 256.2 Hz, C–F), 132.11–130.41 (m, Ph), 114.52 (allyl), 76.36 (ring CH_2), 70.23 (d, $^2J_{C-P}$ = 18.8 Hz, allyl H_2C_{trans}), 50.00 (allyl H_2C_{cis}), 33.91 ($^3J_{C-P}$ = 25.5 Hz, PCH_2). ^{11}B NMR (96 MHz, 300 K, C_6D_6): δ −15.25. ^{19}F NMR (282 MHz, 300 K, C_6D_6): δ −130.05 (d, 2F, $^3J_{F-F}$ = 22.8 Hz, *o*-F), −160.60 (t, 1F, $^3J_{F-F}$ = 20.6 Hz, *p*-F), −164.84, −164.97 (m, 2F, *m*-F). $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, C_6D_6): δ 42.51.

4.3.5. (^{3}-C_3H_5)Ni[NC_4H_3(2-CH_2PCy_2)-5-$B(C_6F_5)_3$] (**5c**)

$B(C_6F_5)_3$ (0.036 g, 0.07 mmol) in deuterated benzene (0.2 cm^3) was added to (η^3-C_3H_5)Ni($NC_4H_3CH_2PCy_2$) (**3d**) (0.021 g, 0.06 mmol) in deuterated benzene (0.4 cm^3) in an NMR tube to give an orange solution of **5c**. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 6.71 (br s, 1H, ring CH), 4.73 (d, 1H, ^2J = 24.4 Hz, one of ring CH_2), 4.58 (d, 1H, ^2J = 24.4 Hz, one of ring CH_2), 4.45 (m, 1H, allyl), 3.63–3.61 (m, 1H, allyl CH_{anti}), 2.51 (br s, 1H, allyl CH_{anti}), 2.26 (dd, 1H, $^3J_{H-P}$ = 5.6, ^2J = 8.5 Hz, allyl CH_{syn}), 1.97–1.90 (m, 2H, CH_2P), 1.58–0.96 (m, 23H, Cy + allyl CH_{syn}). ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 186.50 (d, $^2J_{C-P}$ = 8.5 Hz, $H_2CC{=}N$), 148.21 ($^1J_{C-F}$ = 232.8 Hz, C–F), 138.48 ($^1J_{C-F}$ = 240.8 Hz, C–F), 136.51 ($^1J_{C-F}$ = 261.2 Hz, C–F), 128.12 (*C*H=C), 113.30 (allyl), 76.19 (ring CH_2), 70.41 (d, $^2J_{C-P}$ = 18.4 Hz, allyl H_2C_{trans}), 45.10 (allyl H_2C_{cis}), 32.51 (d, J_{C-P} = 22.4 Hz, Cy), 28.18 (d, $^2J_{C-P}$ = 10.0 Hz, Cy), 26.12 (d, $^3J_{C-P}$ = 5.5 Hz, Cy), 25.57 (Cy), 25.15 (d, J_{C-P} = 20.5 Hz, PCH_2).^{11}B NMR (96 MHz, 300 K, C_6D_6): δ −15.29. ^{19}F NMR (282 MHz, 300 K, C_6D_6): δ −130.25 (d, 2F, $^3J_{F-F}$ = 22.2 Hz, *o*-F), −160.70 (t, 1F, $^3J_{F-F}$ = 20.7 Hz, *p*-F), −164.92, −164.06 (m, 2F, *m*-F). $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, C_6D_6): δ 59.85.

4.3.6. $Ni(NC_4H_3$-2-$CH_2PPh_2)_2$ (**6a**)

Leaving a solution of **5a** and hex-1-ene in benzene for a 48 h period caused the precipitation of the title complex as dark red crystals suitable for X-ray crystallography. The complex was observed as a mixture of *trans* and *cis* isomers (~1:1) by NMR spectroscopy. Anal. Calc. for $NiC_{34}H_{30}N_2P_2$: C, 69.54; H, 5.15; N, 4.77. Found: C, 69.72; H, 4.89; N, 4.95%. ^1H NMR (300 MHz, 300 K, $CDCl_3$): δ 7.67–7.14 (m, 40H, Ph), 6.98–6.96 (m, 2H, pyrrole), 6.15–6.12 (m, 2H, pyrrole), 6.01–5.99 (m, 2H, pyrrole), 5.97–5.94 (m, 4H, pyrrole), 5.85–5.80 (m, 2H pyrrole), 3.69–3.65 (m, 4H, CH_2P), 3.61–3.58 (m, 4H, CH_2P). $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, $CDCl_3$): δ 42.42, 31.17.

4.4. X-ray crystallography

Samples were suspended in perfluoronated polyether oil, mounted on glass fibres and transferred directly to the cold N_2 stream of the diffractometer. Data for compound **3a** were collected on a Bruker–Nonius KappaCCD diffractometer, and for compounds **4b** and **6a** were collected on an Oxford Diffraction Xcalibur diffractometer with Sapphire-3 CCD detector; both diffractometers were equipped with molybdenum targets [λ(Mo Kα) = 0.71069 Å]. Data collection and processing were carried out using APEX2 and SAINT [28], DENZO and SCALEPACK (**3a**) [29], or CRYSALIS CCD and RED (**4b** and **6a**) [30].

Table 2
Crystal and refinement data.

Compound	**3a**	**4b**	**6a**·C_6H_6
Empirical formula	$C_{20}H_{20}NNiP$	$C_{24}H_{29}BrNNiP$	$C_{34}H_{30}N_2NiP_2{\cdot}C_6H_6$
Formula weight	364.03	501.07	665.36
Temperature (K)	120(2)	140(1)	140(2)
Crystal size (mm)	0.01 × 0.13 × 0.24	0.13 × 0.22 × 0.36	0.20 × 0.45 × 0.50
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*Pbca*	*C*2/*c*
a (Å)	8.4825(5)	11.5013(3)	12.9628(3)
b (Å)	9.9139(5)	15.2545(3)	14.2974(3)
c (Å)	11.3723(7)	27.0832(7)	17.8256(4)
α (°)	108.024(3)	90	90
β (°)	100.524(3)	90	104.097(2)
γ (°)	100.965(3)	90	90
V (Å^3)	862.43(9)	4751.7(2)	3204.20(12)
Z	2	8	4
Number of reflections collected	12 696	41 106	21 560
Number of unique reflections	3916	2212	3701
R_{int}	0.100	0.090	0.032
R_1 [$I > 2\sigma(I)$]	0.092	0.112	0.033
wR_2 (all data)	0.192	0.247	0.092

Structures were determined by direct methods using SHELXS (**3a** and **4b**) [31] or SIR-92 (**6a**) [32]. In all cases refinement was carried out by full-matrix least-squares methods using SHELXL-97 [31] within the WinGX suite [33]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model. Crystal and refinement data are collected in Table 2.

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Appendix A. Supplementary data

CCDC 731719, 731720 and 731721 contain the supplementary crystallographic data for complexes **3a**, **4b** and **6a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.033.

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