View Article Online / Journal Homepage / Table of Contents for this issue

Chelating *N*-pyrrolylphosphino-*N′*-arylaldimine ligands: synthesis, ligand behaviour and applications in catalysis

Carly E. Anderson,†[a] Andrei S. Batsanov,[b] Philip W. Dyer,*‡[a] John Fawcett[a] and Judith A. K. Howard[b]

Received 14th August 2006, Accepted 19th September 2006
First published as an Advance Article on the web 2nd October 2006
DOI: 10.1039/b611652c

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

Two families of variously-substituted *N*-pyrrolylphosphino-*N′*-arylaldimine ligands, 2-(aryl–N=CH)C_4H_3N–PR_2 {**3a–d** R = Ph; **4a–d** R = $Pr^i{}_2N$}, have been prepared from the corresponding pyrrolylaldimines **2**. The donor characteristics/basicity of *P–N*-chelating **3** and **4** have been assessed using a combination of $^{31}P\{^1H\}$ NMR and IR spectroscopies through study of the magnitudes of $^1J_{SeP}$ for the phosphorus(V) selenides **7** and **8**, and measurement of ν_{CO} for the complexes [RhCl(CO)(**3**,**4**-κ^2-*P*,*N*)] (**5**, **6**), respectively. The synthesis of the palladium(II) complexes [$PdCl_2$(**3**,**4**-κ^2-*P*,*N*)] (**9**, **10**) was readily achieved from reaction of **3** or **4** with [$PdCl_2(MeCN)_2$] in CH_2Cl_2. X-Ray crystallographic studies of **13d** and **14b** confirm the chelating nature of the *P–N* ligands, which adopt a distorted 'envelope' conformation, and highlight the potentially significant steric demands of these metal scaffolds. Reaction of equimolar quantities of **3** with [$NiBr_2$(DME)] in MeCN afforded [$NiBr_2$(**3**-κ^2-*P*,*N*)] (**15**), while the same reaction undertaken in CH_2Cl_2 with **3c** gave rise to the homoleptic bis(pyrrolatoimine) derivative [Ni{2-(mes–N=CH)C_4H_3N}$_2$] (**16**) in 45% yield, following *P–N* bond cleavage. Complex **16c** was characterised in the solid-state by X-ray crystallography. No identifiable metal-containing complexes could be obtained on reaction of **4** with a variety of sources of Ni(II). The palladium dichloride complexes **13** and **14** proved inactive in combination with MAO or $EtAlCl_2$ for ethylene polymerisation, and with methanesulfonic acid for CO/ethylene co-polymerisation. Contrastingly, the nickel complexes **15** in combination with 4.5 eq. $EtAlCl_2$ catalysed the formation of butenes and hexenes with moderate activity from ethylene at 1 bar.

Introduction

Ease and flexibility of synthesis are important considerations for ligand systems designed for applications in catalysis, facilitating study of the important correlation between catalyst structure, properties and performance. Bidentate *P–N* ligands have been particularly successful in this regard,[1,2] and have been exploited in a wide variety of metal-catalysed processes, including transfer hydrogenation,[3] asymmetric hydroformylation,[4] olefin oligomerisation/polymerisation,[5–8] co-polymerisation,[9,10] and coupling reactions.[11,12] The heteroditopic nature of such ligands has been used to engender both control and selectivity in reactions occurring at metal centres; the significant electronic asymmetry that is possible having a considerable impact.[13–16]

The formation of direct phosphorus–heteroatom bonds (*e.g.* from reaction of halophosphines with bifunctional nitrogen derivatives) is a versatile methodology for the preparation of chelating ligands, with the simplicity and considerable scope of *P–N* bond formation being especially valuable.[17–19] Indeed, amino-functionalised tertiary phosphines synthesised in this way make attractive ligand targets in their own right, as variation in the nature of the substituents at nitrogen can be used to considerably alter the steric and electronic character of the *P*-donor moieties.[20–23] This kind of strategy has been exploited in a number of recent studies, which demonstrate the utility of pyrrole-derived building blocks for the preparation of a range of bidentate P-containing ligands.[9,24–30] These pyrrolyl-substituted phosphine centres are strongly π-acidic, a feature that is of particular interest in catalysis involving both mono- and bi-dentate ligands.

Building on these reports and our previous work on *P–N*-chelating scaffolds,[10,31,32] we describe here the synthesis, preliminary coordination chemistry, and donor/basicity characteristics of a number of sterically demanding *N*-pyrrolylphosphino-*N′*-arylaldimine ligands, which combine electron-rich aldimine and tuneable phosphine donor moieties.[25] The application of these metal scaffolds in olefin oligomerisation is outlined.

Results and discussion

N-Pyrrolylphosphino-*N′*-arylaldimine ligand syntheses

The desired heteroditopic ligands were prepared in a two-step process. Firstly, a range of variously-substituted 2-pyrrole-*N′*-arylaldimines **2a–d** were prepared from 2-pyrrolecarbaldehyde (**1**) *via* condensation (*ca.* 18 h) under Dean and Stark conditions in the presence of a catalytic quantity of *para*-toluenesulfonic acid (*p*-TSA) (Scheme 1). The resulting aldimines were obtained

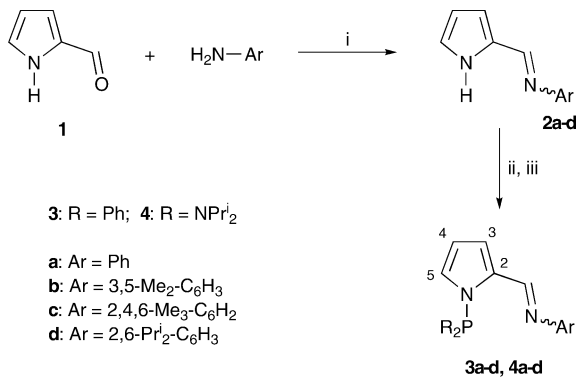
[a]*Department of Chemistry, University of Leicester, University Road, Leicester, UK LE1 7RH*
[b]*Department of Chemistry, Durham University, South Road, Durham, UK DH1 3LE*
† Current address: Department of Chemistry, Durham University, South Road, Durham, UK, DH1 3LE. Fax: 0191 384 4737; Tel: 0191 334 2150; E-mail: p.w.dyer@durham.ac.uk
‡ Current address: Department of Chemistry, Durham University, South Road, Durham, UK, DH1 3LE. Fax: 0191 384 4737; Tel: 0191 334 2150; E-mail: p.w.dyer@durham.ac.uk

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

as crystalline solids in moderate to good isolated yields (53–73%). It was found necessary to store all four derivatives under a nitrogen atmosphere to avoid degradation. Spectroscopic data for compounds **2** were consistent with their proposed structures, with the aldimine carbons giving rise to resonances at *ca.* 150 ppm by $^{13}C\{^1H\}$ NMR spectroscopy and both NH (~3200 cm^{-1}) and characteristic imine (~1585 cm^{-1}) absorption bands visible by IR spectroscopy.[33]



Scheme 1 *Reagents and conditions*: (i) toluene, *p*-TSA (cat.), reflux, Dean and Stark, 16–20 h; (ii) Bu^nLi, DME, −78 °C to RT, 1 h; (iii) Ph_2PCl (neat) or $(Pr^i_2N)_2PCl$, DME, 1 h. (Pyrrolyl numbering scheme included.)

The *P*-donor components were introduced by initial deprotonation of **2** by Bu^nLi in 1,2-dimethoxyethane (DME), followed by addition of the desired chlorophosphine (Scheme 1). This methodology was used to prepare two families of *P*–*N* ligands bearing either phenyl (**3a–d**) or diisopropylamino (**4a–d**) substituents at phosphorus, each being isolated in high yields (typically >80%), with the exception of **3b**, which despite repeated attempts could only be obtained cleanly in *ca.* 30% yield. Ligands **3** were obtained as viscous brown oils or waxy solids, while their counterparts **4** were obtained as beige crystalline solids following purification.

The use of Bu^nLi, as described above, proved essential since organic bases such as NEt_3 or DBU were found not to deprotonate the pyrrole nitrogen of **2** (even at elevated temperatures). This difficulty, relative to the comparative ease of reaction of Ph_2PCl with pyrrole, 2-pyrrole-*N*′-alkylaldimines or oxazoline-functionalised derivatives that require only NEt_3,[25,26,33] has tentatively been attributed to the presence of strong hydrogen bonding interactions of the pyrrole proton and the aldimine nitrogen centre.

Notably, although a number of attempts were made to prepare the *N*′-arylketimine analogues of **2** from 2-acetylpyrrole and the desired aniline using a range of differing methodologies, only a trace of the desired product could be detected in each case. The comparatively unreactive nature of the acetyl precursor relative to its aldehyde counterpart is presumed to result from a combination of additional steric constraints imposed by the methyl group and enhanced mesomeric deactivation of the carbonyl fragment by the ring nitrogen.[35]

Each of the phosphorus-donor ligands **3** and **4** exhibited a single resonance by $^{31}P\{^1H\}$ NMR spectroscopy (Table 1). As would be expected, the signals for the tris(amino)phosphines **4** (*ca.* +80 ppm) were observed at higher frequencies than those for **3** (*ca.* +48 ppm), a direct consequence of the presence of two additional electronegative amino substituents at phosphorus for **4**.[20] These data are comparable to those observed for related 7-*aza*-*N*-indolyl- and (keto-functionalised)-*N*-pyrrolylphosphines.[9,28,29,36] Within each of the two series of ligands **3** and **4**, the $^{31}P\{^1H\}$ NMR chemical shifts were largely independent of the nature of the aldimine substituent. The ^1H and $^{13}C\{^1H\}$ NMR spectra for all the ligands **3** and

Table 1 Selected spectroscopic data for compounds **2–4** and complexes **13**, **14**, **15a** and **16**

		N=CH		
Compound	$\delta(^{31}P)^a$/ppm	$\delta(^1H)^b$/ppm ($^4J_{PH}$/Hz)	$\delta(^{13}C)^c$ /ppm ($^3J_{PC}$/Hz)	$\nu_{CN}{}^d$/cm^{-1}
2a	—	8.32	150.5	1583
2b	—	8.25	149.9	1585
2c	—	7.96	153.7	1587
2d	—	8.05	153.0	1585
3a	47.5	8.68 (1.2)	149.9 (9.8)	1589[h]
3b	47.9	8.51 (2.4)	149.5 (10.3)[i]	1585[h]
3c	48.4[e]	8.35 (3.0)	156.6 (7.9)	1582[h]
3d	49.1	8.31 (1.8)	152.3 (6.8)	1588[h]
4a	84.4	8.99 (5.7)	152.0 (24.9)	1589[h]
4b	83.2	8.96 (5.6)	151.7 (24.4)	1584[h]
4c	82.8	8.67 (5.6)	154.5 (25.6)	1588[h]
4d	82.7	8.79 (5.7)[g]	152.9 (25.9)[i]	1585[h]
13a	66.5	8.23 (3.2)	154.5 (7.2)	1596
13b	65.8[f]	7.96 (2.9)	153.7 (7.0)	1597
13c	64.4	7.79 (3.0)	156.7 (7.7)	1590
13d	65.5	7.78 (3.3)	155.6 (7.9)	1597
14a	81.3	8.01 (3.0)	154.9 (7.5)	1601
14b	81.6	8.04 (3.0)	154.8 (7.6)	1600
14c	81.4[e]	7.76 (3.8)	156.4 (7.3)	1605
14d	80.9	7.83 (4.1)	155.4 (8.8)[i]	1599
15a	—	—	—	1596
16	—	7.17	162.4	1592

[a] 121.5 MHz, $CDCl_3$. [b] 300.1 MHz. [c] 75.5 MHz, $CDCl_3$. [d] Neat, ATR. [e] 162.0 MHz, $CDCl_3$. [f] 101.3 MHz, $CDCl_3$. [g] 400.1 MHz, $CDCl_3$. [h] KBr, CH_2Cl_2. [i] 100.1 MHz, $CDCl_3$.

View Article Online

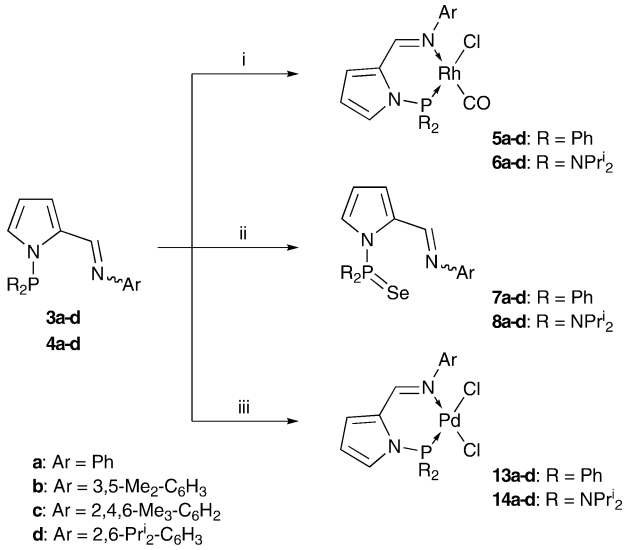
Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

4 were similar and comparable to those of **2**. A $^{4}J_{PH}$ coupling constant of *ca.* 6 Hz (confirmed by $^{1}H\{^{31}P\}$ NMR) is observed for **4** to the aldimine protons and lies at the upper end of the normally quoted scale (1–4 Hz). The aldimine carbons exhibit $^{3}J_{PC}$ coupling of *ca.* 9 Hz for **3** and *ca.* 24 Hz for **4**, a difference that is presumed to reflect the greater s-character at phosphorus for the tris(aminophosphines) **4** compared with that for **3** (*vide infra*).[20] The IR spectra of **3** and **4** exhibit a C=N stretch in the range 1584 to 1589 cm^{-1}, comparable with the parent compounds **2**.

Synthesis of rhodium(I) chloride carbonyl complexes of *N*-pyrrolylphosphino-*N*′-arylaldimines

Reaction of two equivalents of ligands **3** or **4** with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in $CDCl_3$ under an atmosphere of CO (necessary to prevent gradual decomposition in solution) was undertaken in a manner analogous to that reported previously (Scheme 2).[20,37] This afforded two series of complexes **5** and **6**, which were characterised *in situ* by NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy. The complexes were assigned a *P*–*N*-chelating structure, *cis*-[RhCl(CO)(3,4-κ^{2}-*P*,*N*)], in which the *P*-donor lies *cis* to the carbonyl, on the basis of the spectroscopic data and in accordance with *trans*-influence effects. The relatively large magnitudes of the $^{1}J_{RhP}$ (*ca.* 180–230 Hz) and $^{1}J_{RhC}$ (*ca.* 50–80 Hz) coupling constants (Table 2) are consistent with the proposed regiochemistry and those determined for related, structurally characterised complexes.[9,16,38] There was no spectroscopic evidence to suggest the formation of the *trans*-[RhCl(CO)(3,4-κ^{1}-*P*,*N*)$_2$] bis(phosphine) derivatives or the presence of unreacted $[Rh(\mu\text{-}Cl)(CO)_2]_2$.

Each set of rhodium complexes **5** and **6** presents a doublet by $^{31}P\{^{1}H\}$ NMR spectroscopy, for which the chemical shift and the magnitude of the $^{1}J_{RhP}$ coupling constant varies according to the nature of the substituents at phosphorus, with average values being *ca.* δ +90 ppm, $^{1}J_{RhP}$ 185 Hz (**5**; Ph_2P) and δ +117 ppm, $^{1}J_{RhP}$ 235 Hz (**6**; $\{Pr^{i}_2N\}_2P$). In both series $\Delta\delta$ [= δ(complex) − δ(ligand)] is positive. Although the magnitudes of $^{1}J_{RhP}$ are sometimes not particularly diagnostic,[20] the complexes bearing the tris(aminophosphine)-based ligands **6**, present the greater magnitudes, consistent with the greater s-character associated with the *P*-donor component of **4** *vs.* that of **3**.[9,20]



Scheme 2 *Reagents and conditions*: (i) 0.5 $[RhCl(CO)_2]_2$, $CDCl_3$, CO (1 atm), RT; (ii) Se, 80 °C, $CDCl_3$, 1 h; (iii) $[PdCl_2(COD)]$ or $[PdCl_2(MeCN)_2]$, CH_2Cl_2.

Table 2 Selected spectroscopic data for [RhCl(CO)(**3**,**4**-κ^{2}-*P*,*N*)] (**5**, **6**), phosphinopyrrolylaldimine selenides **7**, **8**, selenide derivatives **10**, **12** and related R_3P=Se derivatives

Compound	$\delta(^{31}P)^{a}$/ppm	$^{1}J_{MP}$/Hz	$\delta(^{13}C)^{b}$ *CO*/ppm ($^{1}J_{RhC}$/Hz)	$\nu_{CO}{}^{e}$/cm^{-1}
5a	92.9	185[c]	186.9 (65.2)	2017
5b	92.7	186[c]	187.5 (67.4)	2013
5c	90.9	185[c]	188.2 (70.0)	2018
5d	90.7	183[c]	188.2 (61.7)	2014
6a	117.9	233[c]	188.9 (79.6)	2005
6b	117.7	233[c]	189.1 (69.0)	2000
6c	117.8	236[c]	189.0 (69.1)	2002
6d	117.5	235[c]	189.1 (73.0)	2005
7a	56.7	820[d]	—	—
7b	56.7	821[d]	—	—
7c	56.0	820[d]	—	—
7d	55.9	823[d]	—	—
8a	58.2	846[d]	—	—
8b	58.2	848[d]	—	—
8c	59.9	860[d]	—	—
8d	60.4	850[d]	—	—
10	58.4	812[d]	—	—
12	60.4	842[d]	—	—
$SePMe_3$[39]	8.0	684[d]	—	—
$SePPh_3$[39]	34.1	736[d]	—	—
$SeP(NPr^{i})Ph_2$[20]	59.7	744[d]	—	—
$SeP(NPr^{i})_2Ph$[20]	70.2	759[d]	—	—
$SeP(NMe_2)_3$[40]	81.2	784[d]	—	—
$SeP(NEt_2)_2(NC_4H_4)$[41]	60.9	862[d]	—	—
$SeP(NMe_2)_2(NC_4H_4)$[41]	74.9	867[d]		

[a] 121.5 MHz, $CDCl_3$. [b] 100.6 MHz, $CDCl_3$. [c] M = Rh. [d] M = Se. [e] KBr, $CDCl_3$, CO.

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

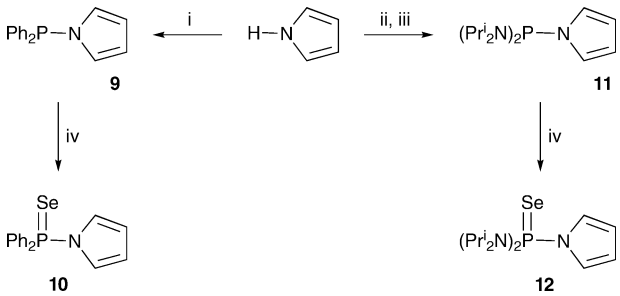
The carbonyl stretching frequencies determined for complexes of the type $[RhCl(CO)(PR_3)_2]$ have routinely been used to assess the electronic characteristics of monodentate phosphines,[15,20,37,42] and to a lesser extent bidentate diphosphine ligands.[43] Although this approach has been previously employed for evaluating heteroditopic *cis*-chelating *P–E* ligands (*E* = *N*, *O*),[15,16,28] these types of system potentially present a problem as a result of their asymmetry with respect to the 'reporter' CO unit, a situation that may give an inaccurate picture of the electronic character of the *P–N* entity as a whole and must therefore be used with caution.

The two series of IR data (**5a–d** and **6a–d**) are both entirely self-consistent with little alteration observed on changing the arylaldimine substituent (Table 2). As expected from previous analyses of the donor behaviour of aminophosphines,[20,21] the magnitude of ν_{CO} for the mono-aminophosphine series **5** (*ca.* 2015 cm^{-1}) is greater than that of the corresponding tris-amino set **6** (*ca.* 2003 cm^{-1}), as a result of lone pair donation from the diisopropylamino substituents to phosphorus in the latter series. However, the values of ν_{CO} for both **5** and **6** are considerably higher than those observed for the corresponding complexes of either Ph_2(pyrrolyl)P (**9**) {1992 cm^{-1}}, the related *P–N*-chelating aza-*N*-indolyldiphenylphosphine (1992 cm^{-1}), or the *P–O*-chelating 2-keto-functionalised *N*-pyrrolyldiphenylphosphine (1989 cm^{-1}).[9,24,28] These discrepancies suggest that the significantly greater steric demands imposed by the *N*-arylimine component combined with the greater σ-donor character of an imine *vs.* either an azaindole or a ketone noticeably influence the CO stretching frequency. Moreover, the inference concerning the donor character that can be made from the IR data for **5** and **6** are at odds with those made upon the basis of the magnitudes of $^1J_{RhP}$, which indicate a reversed ligand basicity. Thus, in order to further probe these apparent discrepancies in net donor character in greater depth, an alternative approach was sought.

Reactions of *N*-pyrrolylphosphino-*N*′-arylaldimines with Se

An inverse relationship exists between the σ-basicity of a phosphine and the magnitude of the ^{77}Se–^{31}P coupling constant that arises from the corresponding selenide derivative. This can be used to estimate the Lewis basicity of the parent P(III) compound.[20,44,45] Hence, in order to examine the donor behaviour of the *P*-component of ligands **3** and **4**, their corresponding phosphorus selenides, **7a–d** and **8a–d**, respectively, were prepared. These were synthesised cleanly by reaction of **3** and **4** with excess grey selenium in $CDCl_3$ at 80 °C (Scheme 2). For comparison, the corresponding unfunctionalised pyrrolylphosphine selenides **10** and **12** were prepared from pyrrole *via* the P(III) derivatives **9**[24] and **11**, respectively (Scheme 3). In contrast to the preparation of **9**,[34] more forcing conditions were required for the formation of **11**, namely the sequential reaction of pyrrole with KH and $(Pr^i_2N)_2PCl$; no reaction was obtained using NEt_3 in toluene at reflux. A hydride base proved essential since deprotonation with Bu^nLi followed by trapping with chlorophosphine afforded an intractable mixture of regioisomers, in accordance with related observations appearing in the literature.[35]

As expected, the *P*-diphenyl selenides **7** exhibited the lower magnitudes of $^1J_{SeP}$ (*ca.* 820 Hz), while the tris(aminophosphine) derivatives **8** showed values in the range 846–860 Hz (Table 2). Both sets of data are in reasonable agreement with those of the parent pyrrolylphosphine selenides, **10** ($^1J_{SeP}$ = 812 Hz) and **12** ($^1J_{SeP}$ = 842 Hz), and the previously reported systems $SeP(pyrrolyl)(NR_2)_2$ {R = Me, Et} ($^1J_{SeP}$ = *ca.* 865 Hz).[41] Furthermore the data from **7** and **8** indicate that addition of a pendant imine in the 2-position of the pyrrolyl rings has little impact on the basicity of the *P*-donor component of **3** and **4**.



Scheme 3 *Reagents and conditions*: (i) Ph_2PCl, NEt_3, toluene, 100 °C, 12 h; (ii) KH, THF, −78 °C to RT, 3 h; (iii) $(Pr^i_2N)_2PCl$, THF, RT, 12 h; (iv) Se, 80 °C, $CDCl_3$, 1 h.

Together, the $^1J_{SeP}$ data for **7** and **8** clearly confirm the expected trend in basicity, namely that the phosphine fragments of **3** are somewhat better donors than those of **4**, although both are comparatively poor donors (relative to alkyl or aryl phosphines), as a result of the presence of the electron-accepting pyrrolyl fragment. Furthermore, these data highlight an attenuation in basicity on introducing two diisopropylamino groups (−I effect) at *P*,[20,24] consistent with the lower σ-basicity of **4**.

Thus, it would appear that the relative donor ability of unsymmetrical scaffolds **3** and **4** as an ensemble is not accurately reflected by the carbonyl stretching frequencies of the rhodium complexes **5** and **6** and that the donor character of the *P*-component of these systems is akin to that of parent pyrrolyl phosphines **9** and **11**.

Palladium dichloride complexes of *N*-pyrrolylphosphino-*N*′-arylaldimine ligands 3 and 4

The synthesis of the $PdCl_2$ complexes **13** and **14** of these two new families of *P–N* ligands was undertaken with a view to screening their utility as proinitiators in olefin polymerisation. The desired *cis*-dichloride complexes were obtained in good to excellent yields (>70%) from reaction of one equivalent of **3** and **4** with $[PdCl_2(COD)]$ or the more labile $[PdCl_2(MeCN)_2]$, in either chloroform or dichloromethane; satisfactory mass spectrometric and elemental analyses were obtained in all cases. These new complexes are stable indefinitely in the solid state under air, but degrade slowly (days) in solution unless anaerobic conditions are ensured. The enhanced stability evident for the *P–N* bonds of the various metal-bound ligands, compared to that of the free pyrrolylaldimines, is in line with previous observations for coordinated aminophosphines.[20,29,31]

Each of the κ^2-*P*,*N* palladium(II) complexes displays a single resonance by $^{31}P\{^1H\}$ NMR spectroscopy at *ca.* +65 ppm for complexes of **3** and *ca.* +81 ppm for those of ligands **4** (Table 1). The diphenylphosphinopyrrolylaldimines **3** exhibit a significant coordination chemical shift upon complexation, Δδ *ca.* +17 ppm, to higher frequency. In contrast, the corresponding tris(aminophosphine) series of ligands **4** showed a much smaller and negative value of Δδ, *ca.* −2 ppm.

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

Table 3 Selected bond distances (Å) and angles (°) for **13d** and **14b**

13d		**14b**	
Pd(1)–Cl(1)	2.2855(5)	Pd(1)–Cl(1)	2.2776(11)
Pd(1)–Cl(2)	2.3487(5)	Pd(1)–Cl(2)	2.3499(10)
Pd(1)–P(2)	2.1959(5)	Pd(1)–P(1)	2.2081(11)
Pd(1)–N(1)	2.0593(15)	Pd(1)–N(2)	2.037(3)
P(1)–N(2)	1.7121(16)	P(1)–N(1)	1.717(3)
C(2)–C(3)	1.377(3)	P(1)–N(3)	1.658(3)
C(3)–C(4)	1.401(3)	P(1)–N(4)	1.631(3)
C(4)–C(5)	1.354(3)	C(1)–C(2)	1.359(6)
N(1)–C(1)	1.292(2)	C(2)–C(3)	1.388(6)
		C(3)–C(4)	1.358(5)
		N(2)–C(5)	1.277(5)
P(2)–Pd(1)–N(1)	92.34(4)	P(1)–Pd(1)–N(2)	91.33(9)
N(1)–Pd(1)–Cl(2)	91.47(4)	N(2)–Pd(1)–Cl(2)	90.15(9)
Cl(2)–Pd(1)–Cl(1)	90.998(18)	Cl(2)–Pd(1)–Cl(1)	89.42(4)
Cl(1)–Pd(1)–P(2)	85.402(19)	Cl(1)–Pd(1)–P(1)	89.44(4)
P(2)–N(2)–C(5)	127.31(13)	P(1)–N(1)–C(1)	127.3(3)
C(5)–N(2)–C(2)	107.10(15)	C(1)–N(1)–C(4)	106.9(3)
C(2)–N(2)–P(2)	124.39(13)	C(4)–N(1)–P(1)	124.9(3)

Few appreciable differences are observed between the ^{1}H NMR spectral data of the free and of the bound ligands. The most significant feature is a shift to lower frequency ($\Delta\delta$ *ca.* −0.4 to −1.2 ppm) for the aldimine proton resonances (Table 1), which was accompanied by a reduction in the magnitudes of the coupling of these protons to phosphorus for all the complexes except **13c**,**d**. An analogous attenuation in the aldimine carbon coupling to phosphorus was also noted, although there was no discernible trend associated with the changes in the chemical shift for this carbon atom by ^{13}C{^{1}H} NMR spectroscopy.

The molecular structures of complexes **13d** and **14b** were investigated by X-ray crystallography, with crystals being grown by slow evaporation from CH_2Cl_2 solutions (Figs. 1, 2 and Table 3). The gross molecular structures of both complexes are comparable, the palladium centres adopting near-square planar geometries with the anticipated κ^2-*P*,*N*-coordination of ligands **3** and **4** (in accordance with the spectroscopic data obtained).

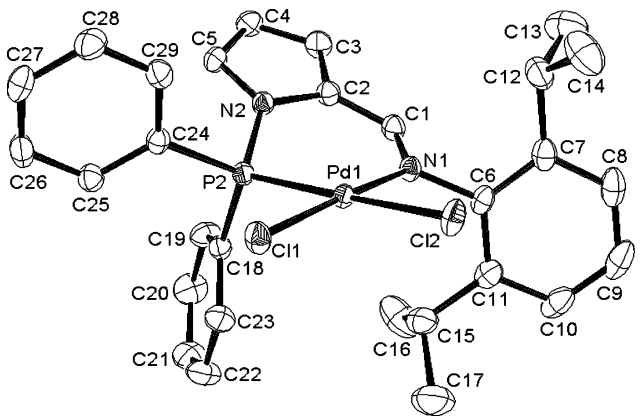


Fig. 1 Molecular structure of [$PdCl_2$(**3d**-κ^2-*P*,*N*)] (**13d**) with the thermal ellipsoids set at the 50% probability level.

In both **13d** and **14b** the six-membered metallacyclic ring is puckered, with the *P*–*N* ligand backbone adopting a distorted 'envelope' conformation. The differing *trans*-influences of the *N*- and *P*-donor units are clearly reflected by the inequivalence of

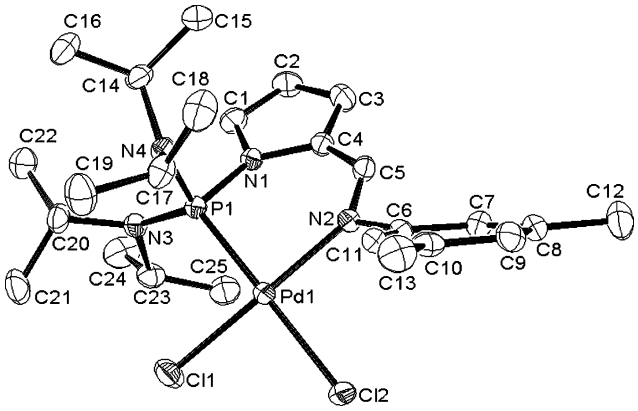


Fig. 2 Molecular structure of [$PdCl_2$(**4b**-κ^2-*P*,*N*)] (**14b**) with the thermal ellipsoids set at the 50% probability level (two solvent molecules omitted for clarity).

the two Pd–Cl bond distances of each complex, the bond *trans* to phosphorus being the longer, as expected.[46] The Pd–P bond distances for complex **13d** bearing the diphenylpyrrolylaldimine [2.1959(5) Å] is marginally shorter than that determined for the bis(diisopropyl)amino-functionalised ligand of **14b** [2.2081(11) Å]. In **13d**, the plane of the *N*-aryl ring lies at an angle of 72° to the Pd(1) coordination plane, while in **14b** the arylimine ring plane is near-perpendicular, 83°, to the coordination plane of palladium.

The crystallographically-determined *P*–*N* bite angles at palladium [**13d**: 92.34(4)°; **14b**: 91.33(9)°] are comparable, whilst the aldimine C=N bond distance for **13d** {1.292(2) Å} differs slightly from that of **14b** {1.277(5) Å}. In gross terms, however, both these sets of metric parameters are comparable to those observed in related phosphine-imine ligands, but lie towards the higher end of the ranges previously observed.[6,10,47–49]

Nickel dibromide complexes of *N*-pyrrolylphosphino-*N*′-arylaldimine ligands 3a–d

There is considerable literature precedent indicating that polymerisation initiators based on Ni(II) are considerably more active than their heavier Group 10 congeners.[50–52] Hence, the corresponding *P*–*N*-chelated nickel dibromide complexes [$NiBr_2$(**3**-κ^2-*P*,*N*)] (**15**) were prepared by reaction of equimolar quantities of ligands **3** with [$NiBr_2$(DME)] in MeCN, and isolated as green/brown solids in moderate yields (47–70%).

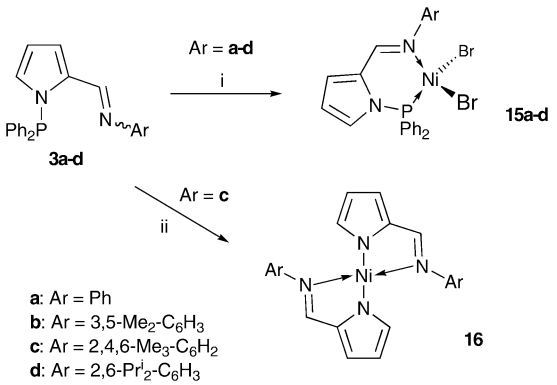
Each complex gave rise to an ion corresponding to [NiBr(**3**)]$^+$ by mass spectrometry and was found to be paramagnetic in solution. Despite numerous attempts, crystals of **15** suitable for study by X-ray diffraction could not be obtained. An alternative synthetic strategy involving displacement of triphenylphosphine from [$NiBr_2(PPh_3)_2$] proved successful for the preparation of **15b**, which was isolated in 71% yield following reaction of **3b** with the diphosphine complex in MeCN using a modification of a related literature procedure (Scheme 4).[53] Despite repeated attempts using a range of Ni(II) starting materials, reactions involving the tris(aminophosphine)aldimines **4** afford significant quantities of $Pr^i_2NH_2Br$ as the only identifiable product in each case, irrespective of the solvent employed. Notably, the reaction between equimolar quantities of **3c** and [$NiBr_2$(DME)] performed in CH_2Cl_2 under rigorously anaerobic and anhydrous conditions gives rise to the

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

homoleptic bis(pyrrolatoimine) Ni(II) complex *trans*-[Ni{2-(Mes–N=CH)C_4H_3N-κ^2-*N*,*N*}$_2$] (**16**) in near-quantitative isolated yield (45%) as a red/brown, air stable solid (Scheme 4).



Scheme 4 *Reagents and conditions*: (i) [$NiBr_2$(DME)], MeCN, RT, 3 h; (ii) [$NiBr_2$(DME)], CH_2Cl_2, RT, 3 h.

The observed solvent dependency of the reactions of **3** has been attributed to moderation of the reactivity of the Ni(II) species by the *in situ* formation of [$NiBr_2$(MeCN)$_2$]. In contrast to the behaviour of **3c**, which undergoes clean P–N bond cleavage and results in the formation of Ni(II) pyrrolato complexes, identical reactions between [$NiBr_2$(DME)] and **3a**,**b**,**d** in CH_2Cl_2 did not afford any tractable products.

Clearly the formation of **16** from **3c** must involve *P–N* bond cleavage, however both the mechanism for this process and the origins of its substrate specificity to **3c** remain elusive. Although attempts were made to probe the fate of the Ph_2P moiety by ^{31}P NMR spectroscopy, neither the formation of Ph_2PBr nor other P-containing products could be observed. A small number of examples of *P–N* bond cleavage of aminophosphines in the presence of Group 10 metal complexes have been observed previously.[20,54] However, in these reports *P–N* bond rupture was induced by either the deliberate addition of acids (*e.g.* HCl, ROH) or the presence of adventitious water. Although the reactions of **3** and **4** with [$NiBr_2$(DME)] were carried out under scrupulously dry conditions, the presence of trace quantities of protic impurities cannot be ruled out. Hence no definitive mechanism for the *P–N* bond rupture observed here can be presented.

The molecular structure of **16** was confirmed by X-ray diffraction (Fig. 3, Table 4). The asymmetric unit of **16** (Fig. 3) comprises one molecule (**A**) in a general position and a half of another molecule (**B**) whose Ni(2) atom lies at an inversion centre. The four-fold coordination of nickel in molecule **B** is thus rigorously square planar (*trans*), whereas molecule **A** experiences a slight distortion intermediate between tetrahedral and pyramidal. Thus, deviations of the four nitrogen atoms from their mean plane are: N(1) and N(3) −0.18, N(2) and N(4) 0.18 Å, whilst Ni(1) deviates from the same plane by 0.04 Å. The N(1)Ni(1)N(2) and N(3)Ni(1)N(4) planes form a dihedral angle of 16.6°. In molecule **B** the ring planes of both mesityl (Mes) substituents lie almost normal to the Ni(2) coordination plane (dihedral angle 85.2°), whereas in **A** the Mes substituents at N(1) and N(2) are inclined to the mean N(4) plane by 72° and 68°, respectively. All the N–Ni bond distances are slightly longer in the planar complex (**B**) than in its puckered counterpart (**A**).

Table 4 Selected bond distances (Å) and angles (°) for **16**

Molecule A		Molecule B	
Ni(1)–N(1)	1.9221(15)	Ni(2)–N(5)	1.9392(15)
Ni(1)–N(2)	1.9061(15)	Ni(2)–N(6)	1.9148(15)
Ni(1)–N(3)	1.9262(15)	C(1)–N(1)	1.303(2)
Ni(1)–N(4)	1.8983(15)	N(6)–C(32)	1.395(3)
N(1)–C(1)	1.307(2)	C(32)–C(33)	1.380(2)
N(1)–N(3)	1.403(3)	C(33)–C(34)	1.398(3)
N(2)–C(2)	1.388(2)	C(34)–C(35)	1.388(3)
C(2)–C(3)	1.400(3)	C(35)–N(6)	1.395(3)
C(3)–C(4)	1.387(3)		
C(4)–C(5)	1.399(3)		
N(2)–C(5)	1.352(2)		
N(4)–C(7)	1.382(2)		
C(7)–C(8)	1.399(3)		
C(8)–C(9)	1.390(3)		
C(9)–C(10)	1.394(3)		
C(10)–N(4)	1.350(2)		
N(2)–Ni(1)–N(1)	83.80(6)	N(5)–Ni(2)–N(6)	83.68(6)
N(1)–Ni(1)–N(4)	96.56(6)	N(5)–Ni(2)–N(6′)	96.32(6)
N(4)–Ni(1)–N(3)	83.80(7)	C(31)–N(5)–C(41)	115.99(15)
N(2)–Ni(1)–N(3)	97.74(6)	Ni(2)–N(5)–C(31)	112.12(12)
C(1)–N(1)–Ni(1)	113.03(13)	Ni(2)–N(5)–C(41)	131.19(12)
Ni(1)–N(1)–C(11)	128.14(12)		
C(1)–N(1)–C(11)	118.83(15)		
C(21)–N(3)–Ni(1)	128.07(12)		
C(21)–N(3)–C(6)	119.00(16)		
C(6)–N(3)–Ni(1)	112.92(12)		

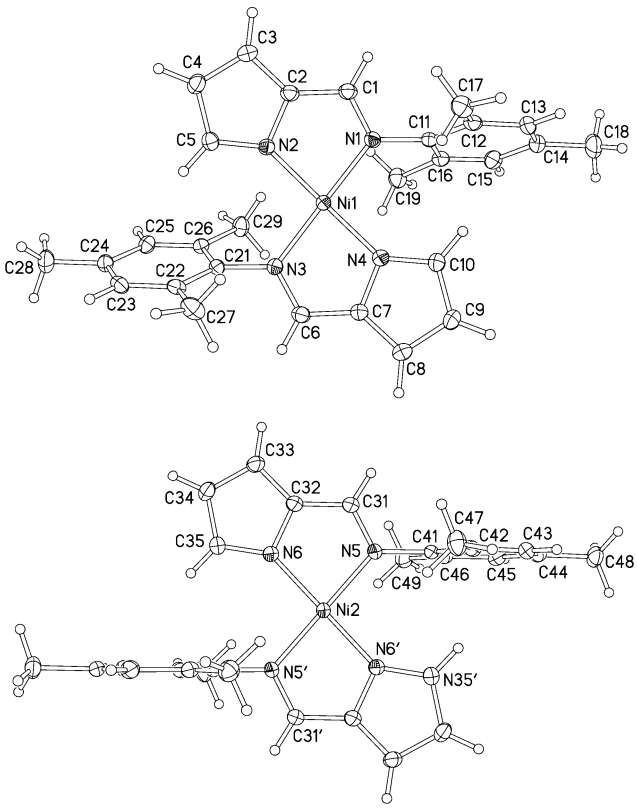


Fig. 3 Molecular structure of [Ni{2-(Mes-N=CH)C_4H_3N-κ^2-*N*,*N*)$_2$] (**16**) showing molecule **A** (top) and **B** (bottom) with the thermal ellipsoids set at the 50% probability level. Primed atoms are generated by the inversion centre.

A number of the corresponding bis(pyrrolato-*N*-alkylimine) Ni(II) complexes have been previously prepared in a 'one-pot'

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

fashion from $NiSO_4 \cdot 2H_2O$, 2-acetylpyrrole and an alkyl amine.[55] Their structures are entirely comparable to that of **16**, with the bulk of the *N*-alkyl substituent determining the extent of deviation from square planar coordination at Ni. The palladium congeners of **16** have also been prepared, *e.g.* [Pd{2-(aryl–N=CH)C_4H_3N}$_2$], whose structures are analogous to those of the square planar form of **16**.[56]

Despite the existence of both a square planar and a distorted form of **16** in the solid state, in solution the complex is diamagnetic, with its NMR spectroscopic data being consistent with a symmetrical *trans* structure. Relative to the parent pyrrole **2c**, the proton and carbon resonances for the CH=N moiety of **16** are shifted to lower and higher frequencies, respectively (Table 1).

Attempted CO/ethylene copolymerisation reactions

Previous studies have indicated that *P*–*N*-chelating phosphino-(phenylpyridin-2-yl methylene)amine complexes of Pd(II) are highly chemoselective proinitiators for alkene hydrocarboxylation in methanol.[10] Their success has been attributed to the flexible nature of the ligand, which readily allows it to adopt 90 or 120° bite-angles, as a result of its flexible six-membered ring chelation. To further explore this hypothesis, it was of interest to screen the considerably more rigid, yet still six-membered chelate-forming complexes **13** and **14** for CO/ethylene polymerisation activity.

Methanol solutions of **13** and **14** were heated to 90 °C under a 1 : 1 CO–C_2H_4 atmosphere (40 bar) in the presence of four equivalents of methane sulfonic acid for periods of 3 h.[10] Although a slight gas uptake was detected in all cases, GC-MS analysis of the crude reaction mixtures did not reveal the formation of any new products. After each run, initiator decomposition was apparent from significant deposits of 'palladium black' within the autoclave. It should be noted, however, that both **13** and **14** have been shown to be stable in methanolic solution in the presence of methane sulfonic acid under the reaction conditions for short periods of time.

This lack of carbonylation activity for complexes of **3** and **4** is somewhat surprising, certainly in light of successful polyketone formation initiated by a range of palladium complexes of phosphine-imine scaffolds and, in particular, those using structurally-related chelating aza-*N*-indolylphosphines.[6,8,9] One possible explanation for the difference in behaviour of **3** and **4** compared with that of the aza-*N*-indolyl-based scaffolds could lie in the nature of the *N*-donor component; aryl imine *vs.* aromatic heterocyclic nitrogen, respectively. While pyridines are both good σ-donors and π-acceptors,[57] non-conjugated imines have essentially no acceptor character,[58] a difference that affects the strength of the Pd–nitrogen interaction (imines potentially being more labile) and in turn the reactivity of the metal centre.

Ethylene oligomerisation reactions

Following various reports of the use of *P*–*N* ligands in olefin polymerisation, an investigation of the utility of the sterically demanding, non-enolisable ligands **3** and **4** as metal scaffolds in ethylene polymerisation was undertaken.[52,59–62] Here, it was of interest to explore whether (a) the tris(amino) ligand series **4** that locates significant steric constraints close to the axial sites of the metals' square coordination planes, would favour high molecular mass polymer formation,[50] and (b) what the effect of the comparatively poor σ-donor character (*vide supra*) of ligands **3** and **4** would be upon the rate of chain termination by β-hydride elimination.

Treating toluene solutions of palladium complexes **13** and **14** (5×10^{-5} mol) with 500 equivalents of MAO at ambient temperature led to initiator decomposition, as signified by the rapid formation (minutes) of 'palladium black' for both systems. The resulting suspensions showed no activity towards ethylene (1 or 10 bar, ambient temperature). These observations are consistent with those reported for certain related bidentate phosphine-imine scaffolds bound to Pd(II).[63] Since it is well established that the oligo-/poly-merisation activity of late transition metal complexes of *P*–*N* ligands is intimately linked to the nature of the Lewis acidic co-initiator,[61] an alternative activation procedure was invoked. Despite a distinct colour change (orange to yellow) on addition of 4.5 equivalents of $EtAlCl_2$ to toluene solutions of **13** and **14** (5×10^{-5} mol), the resulting species again proved inactive for the polymerisation of ethylene (1 or 10 bar, ambient temperature). However, unlike the reactions with MAO, no 'palladium black' was found to have formed at the end of the polymerisation tests.

Contrastingly, activation of the corresponding Ni(II) derivatives **15** (5×10^{-5} mol) by 4.5 equivalents of $EtAlCl_2$ (in toluene) led to the formation of initiators that rapidly convert ethylene (1 bar, ambient temperature, 0.5 h) to mixtures of butenes and hexenes (identified by GC-MS) as the only organic products, in initially very exothermic reactions (reaching *ca.* 80 °C). The alkenes are obtained as isomeric mixtures as a result of well-established Ni-catalysed double bond isomerisation. This behaviour is consistent with that observed previously for Ni(II) complexes of other *P*–*N* chelates.[61,62,64] No higher molecular weight polyolefin products were formed. Degradation of the initiator systems derived from **15a–c** was evident from the slow, gradual precipitation of a brown, water-soluble solid in varying amounts. In contrast, no decomposition was observed using proinitiator **15d** over the course of the reaction.

Notably, the substitution pattern about the imine moiety impacts directly upon both the selectivity and the activity of the various initiator systems derived from **15**, although it is difficult to establish any conclusive structure–property correlations with this small data set. However, it is clear that proinitiators **15a**,**b**,**d** all exhibit a very marked selectivity for the formation of butenes (Table 5, entries 1, 2 and 4), while the mesityl-bearing derivative **15c** demonstrates an inverse selectivity favouring production of hexenes (entry 3). The levels of activity (total for all products) of complexes **15** may be classified as 'moderate' on the scale established by Gibson and co-workers.[59] Both the selectivity and activity of the systems based on **15** are comparable to that reported previously for an isoelectronic phosphonite-derived *P*–*N* chelate system.[65]

Upon activation by 4.5 eq. $EtAlCl_2$ the mesityl-substituted bis(pyrrolatoaryl imine) derivative **16** exhibits a very slight activity for the dimerisation of ethylene at 1 bar (Table 6, entry 5). The extremely low activity of **16** for the formation of butenes compared with the efficacy of complexes **15a**,**b**,**d** indicates that under the polymerisation conditions employed, complexes **15** are not converted to their bis(pyrrolatoimine) counterparts on the time-scale of the catalytic tests.

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

Table 5 Ethylene di- and tri-merisation studies[a]

Entry	Proinitiator[b]	Activator [eq.]	*P*/bar	Initial *T*[c]/°C	Selectivity (%)[d] C_4	Selectivity (%)[d] C_6	Activity[e,f]
1	**15a**	$EtAlCl_2$ [4.5]	1	20	92	8	3.8
2	**15b**	$EtAlCl_2$ [4.5]	1	20	72	28	51.5
3	**15c**	$EtAlCl_2$ [4.5]	1	20	8	92	17.1
4	**15d**	$EtAlCl_2$ [4.5]	1	20	83	17	56.9
5	**16**	$EtAlCl_2$ [4.5]	1	20	100	0	~1

[a] *Reaction conditions*: toluene (50 cm^3), reaction time 30 min. [b] 5×10^{-5} mol. [c] No cooling applied. [d] C_n fraction defined as the (amount of C_n olefins)/(total amount of olefins) × 100. [e] Average productivity (two runs) expressed in g(total product) mmol $(Ni)^{-1}$ h^{-1} bar^{-1}. [f] Determined by quantitative GC using nonane as internal standard.

Summary

Pyrrole-substituted in the 2-position makes a useful building block for the straightforward preparation of various heteroditopic chelating ligands with a range of substitution patterns. Here, the synthesis of two families of *N*-pyrrolylphosphinoarylimines that bear phenyl (**3**) or diisopropylamino (**4**) groups at phosphorus have been described. Both ligand sets **3** and **4** readily form rigid κ^2-*P*,*N* six-membered chelates with Rh(I) and Pd(II). In contrast, only the [$NiBr_2$(**3**-κ^2-*P*,*N*)] (**15**) complexes could be prepared. The use of rhodium carbonyl chloride complexes to probe the donor character of chelating heteroditopic ligands should be used with caution, since both steric and electronic factors can impact in an unpredictable manner upon the observed values of ν_{CO}.

Despite the structural similarity between the *N*-pyrrolylphosphino-*N*′-arylaldimine ligands reported here and a variety of other *P*–*N* chelate systems that have been reported previously, palladium dichloride complexes of **3** and **4** proved inactive for CO/C_2H_4 copolymerisation. In contrast, following activation by $EtAlCl_2$ the Ni(II) complexes **15** afford initiators that exhibit moderate activity for the formation of isomeric mixtures of butenes and hexenes from ethylene under mild conditions. Although bulky arylimine substituents (known to support the formation of high molecular weight polyolefin products) were present in ligands **3**, the comparatively unhindered diphenylphosphino moiety proved insufficient to prevent rapid β-hydride elimination and hence permitted only ethylene di- and tri-merisation.

The utility of ligands **3** and **4** in other catalytic applications is under active investigation.

Experimental

General considerations

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a nitrogen-filled glove box, unless stated otherwise. All NMR-scale reactions were conducted using NMR tubes fitted with J. Young tap valves. Solvents were freshly distilled under nitrogen from sodium/benzophenone (Et_2O, toluene, and DME), from sodium (hexane, pentane), from magnesium turnings (MeOH), from calcium hydride (CH_2Cl_2) or from P_2O_5 ($CDCl_3$) and deoxygenated prior to use. Sonication was achieved by suspending the desired reaction vessel in a water-filled Grant Ultrasonic Bath XB2.

Palladium and rhodium salts were used on loan from Johnson Matthey. Pyrrole-2-carbaldehyde and 2-acetylpyrrole were purchased from Avocado, gaseous chemicals from BOC and all other chemicals from Aldrich. All solid reagents were used as received. Where appropriate, liquid reagents were dried, distilled and deoxygenated prior to use. Gases were passed through a drying column (silica/$CaCO_3$/P_2O_5) prior to use. The starting materials $(Pr^i_2N)_2PCl$,[66] $[PdCl_2(COD)]$,[67] $[PdCl_2(MeCN)_2]$,[68] $[RhCl(CO)_2]_2$,[69] and $Ph_2PNC_4H_4$[34] were prepared according to literature procedures or slight modifications thereof.

Routine NMR spectra were collected on a Bruker AM250, DPX300 or Varian Inova 500 at ambient probe temperatures (~290 K) unless stated otherwise, and NOE spectra on a Bruker AMX400. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (^1H), ^{13}C shift of the solvent (^{13}C), or to external aqueous 85% H_3PO_4 (^{31}P). Solvent proton shifts (ppm): $CDCl_3$, 7.27 (s). Solvent carbon shifts (ppm): $CDCl_3$, 77.2 (t). In ^1H NMR spectra, ^{31}P coupled resonances were verified by running ^1H $\{^{31}P\}$ experiments. ^{13}C NMR spectra were assigned with the aid of DEPT 135 and ^1H–^{13}C correlation experiments. Chemical shifts are reported in ppm and coupling constants in Hz. While $^1J_{SeP}$ coupling constants are negative,[70] only the magnitudes are reported here, since direct measurements are not possible from the ^{31}P NMR spectra and only relative differences in magnitude are of relevance.

FAB (3-nitrobenzyl alcohol matrix) and EI mass spectra were recorded on a Kratos Concept 1H instrument, while MALDI (dithranol matrix) were obtained on an Applied Biosystems Voyager-DE STR instrument and are all reported in (*m*/*z*). The isotope distributions for all parent ion peaks for metal complexes were verified *via* comparison with a theoretical isotope pattern. Elemental analyses were performed by Mr S. Boyer at the London Metropolitan University or by Mrs J. Dostal of the Analytical Services Department, Durham University. Infrared spectra were collected on a Perkin Elmer 1600 spectrophotometer using KBr discs, or a solution cell with KBr windows or *via* ATR-FTIR on a Perkin Elmer Spectrum ONE instrument. GC/MS were obtained using a Thermo Finnegan Trace instrument (Agilent HP-5MS 30 m column, internal diameter 0.25 mm, film thickness 0.25 μm).

Syntheses and reactions

Phenyl(1*H*-pyrrol-2-ylmethylene)amine 2a. A modification of the literature procedure was employed.[33] Under air, aniline (4.0 cm^3, 43.3 × 10^{-3} mol) was added to a solution of

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

pyrrole-2-carbaldehyde (**1**) (3.80 g, 40.0 × 10^{-3} mol) in toluene (100 cm^3). A catalytic quantity of *p*-TSA (0.1 g, 0.7 × 10^{-3} mol) was added and the mixture heated to reflux under Dean–Stark conditions for 17 h. The toluene was then removed *in vacuo*, replaced with CH_2Cl_2 and the solution filtered to remove *p*-TSA. The CH_2Cl_2 was removed under reduced pressure and the resulting dark brown solid was then washed with hexane (3 × 10 cm^3) to remove excess aniline and dried *in vacuo* to afford **2a** (4.25 g, 63%) as a dark brown crystalline solid following recrystallisation from methanol (Anal. Calc. for $C_{11}H_{10}N_2$: C, 77.61; H, 5.93; N, 16.46. Found: C, 77.42; H, 6.02; N, 16.26%); δ_H (300.1 MHz, $CDCl_3$) 6.31 (t, $^3J_{HH}$ = 3.0 Hz, 1H, H^4), 6.76 (d, $^3J_{HH}$ = 3.0 Hz, 1H, H^3), 6.84 (s, 1H, H^5), 7.15 (m, 3H, *m*/*p*-C_6H_5), 7.30 (m, 2H, *o*-C_6H_5), 8.32 (s, 1H, CH=N), 10.27 (br s, $\nu_{1/2}$ = 30.0 Hz, 1H, pyrrolyl NH); δ_C (75.5 MHz, $CDCl_3$) 110.8 (s, C^4), 117.8 (s, C^3), 121.2 (s, *m*-C_6H_5), 124.4 (s, *p*-C_6H_5), 125.9 (s, C^5), 129.6 (s, *o*-C_6H_5), 130.8 (s, C^2), 150.5 (s, CH=N), 151.8 (s, *i*-PhC); MS (FAB$^+$): *m*/*z* 171 (MH^+); IR (ATR, neat): = 3221 (ν_{NH}), 1583 (ν_{CN}) cm^{-1}. The product is hygroscopic and must be stored under a dry nitrogen atmosphere to prevent degradation.

(3,5-Dimethylphenyl)(1*H*-pyrrol-2-ylmethylene)amine 2b. Using conditions analogous to those for the preparation of **2a**, 3,5-dimethylaniline (4.75 cm^3, 38.1 × 10^{-3} mol) was reacted with **1** (3.43 g, 36.1 × 10^{-3} mol) in toluene (100 cm^3) in the presence of *p*-TSA (0.1 g, 0.71 × 10^{-3} mol) at reflux under Dean–Stark conditions for 20 h. Subsequently, compound **2b** (5.18 g, 72%) was isolated as a dark brown crystalline solid following recrystallisation from methanol (Anal. Calc. for $C_{13}H_{14}N_2$: C, 78.74; H, 7.13; N 14.13. Found: C, 78.90; H, 7.33; N, 14.17%); δ_H (400.1 MHz, $CDCl_3$) 2.39 (s, 6H, $(CH_3)_2C_6H_3$), 6.37 (t, $^3J_{HH}$ = 2.8 Hz, 1H, H^4), 6.56 (s, 1H, *p*-C_6H_3), 6.72 (d, $^3J_{HH}$ = 2.6 Hz, 1H, H^3), 6.84 (s, 1H, H^5), 7.09 (s, 2H, *o*-C_6H_3), 8.25 (s, 1H, CH=N), 9.88 (br s, $\nu_{1/2}$ 42.0 Hz, 1H, pyrrolyl NH); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 21.4 (s, *m*-C_6H_3), 110.5 (s, C^4), 117.5 (s, C^3), 118.8 (s, *o*-C_6H_3), 124.4 (s, *p*-C_6H_3), 127.4 (s, C^5), 130.5 (s, C^2), 138.9 (s, *m*-C_6H_3), 149.9 (s, CH=N), 151.3 (s, *i*-C_6H_3); MS (FAB$^+$) *m*/*z* 199 (MH^+); IR (ATR, neat) 3282 (ν_{NH}), 1585 (ν_{CN}) cm^{-1}. The product is hygroscopic and must be stored under a dry nitrogen atmosphere to prevent degradation.

(2,4,6-Trimethylphenyl)(1*H*-pyrrol-2-ylmethylene)amine 2c. Using conditions analogous to those for the preparation of **2a**, 2,4,6-trimethylaniline (4.95 cm^3, 35.2 × 10^{-3} mol) was added to **1** (3.09 g, 32.5 × 10^{-3} mol) in toluene (100 cm^3) and *p*-TSA (0.1 g, 0.71 × 10^{-3} mol) was added and the mixture heated to reflux under Dean–Stark conditions for 16 h. Subsequently, compound **2c** (4.36 g, 63%) was isolated as a mid-brown-coloured crystalline solid following recrystallisation from methanol (Anal. Calc. for $C_{14}H_{16}N_2$: C, 79.19; H, 7.61; N, 13.20. Found: C, 79.22; H, 7.51; N, 13.27%); δ_H (250.1 MHz, $CDCl_3$) 2.13 (s, 6H, *o*-$(CH_3)_2C_6H_2$), 2.30 (s, 3H, *p*-$CH_3C_6H_2$), 6.29 (t, $^3J_{HH}$ = 2.5 Hz, 1H, H^4), 6.61 (d, $^3J_{HH}$ = 1.4 Hz, 1H, H^3), 6.82 (d, $^3J_{HH}$ = 1.4 Hz, 1H, H^5), 6.89 (s, 2H, *m*-C_6H_2), 7.96 (s, 1H, CH=N); δ_C {^{1}H} (62.9 MHz, $CDCl_3$) 18.6 (s, *o*-$(CH_3)_2C_6H_2$), 21.1 (s, *p*-$CH_3C_6H_2$), 110.3 (s, C^4), 117.0 (s, C^3), 124.3 (s, C^5), 128.5 (s, *o*-C_6H_2), 129.2 (s, *m*-C_6H_2), 130.3 (s, *p*-C_6H_2), 133.6 (s, C^2), 148.6 (s, *i*-C_6H_2), 153.7 (s, CH=N); MS (FAB$^+$) *m*/*z* 213 (MH^+); IR (ATR, neat) 3131 (ν_{NH}), 1587 (ν_{CN}) cm^{-1}. The product is hygroscopic and must be stored under a dry nitrogen atmosphere to prevent degradation.

(2,6-Diisopropylphenyl)(1*H*-pyrrol-2-ylmethylene)amine 2d. A modification to the literature procedure was used.[71] Under air, 2,6-diisopropylaniline (6.65 cm^3, 35.3 × 10^{-3} mol) was added to a solution of **1** (3.10 g, 32.6 × 10^{-3} mol) in toluene (100 cm^3). A catalytic quantity of *p*-TSA (0.1 g, 0.7 × 10^{-3} mol) was added and the mixture heated to reflux under Dean–Stark conditions for 16 h. The toluene was then removed *in vacuo*, replaced with CH_2Cl_2 and the solution filtered to remove *p*-TSA. The CH_2Cl_2 was removed *in vacuo*. Following recrystallisation from MeOH, **2d** (4.39 g, 53%) was obtained as a dark cream-coloured crystalline solid (Anal. Calc. for $C_{17}H_{22}N_2$: C, 80.25; H, 8.73; N, 11.01. Found: C, 80.43; H, 8.50; N, 11.07%); δ_H (300.1 MHz, $CDCl_3$) 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H, *o*-$((CH_3)_2CH)_2C_6H_3$), 3.20 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, *o*-$((CH_3)_2CH)_2C_6H_3$), 6.06 (s, 1H, H^4), 6.17 (s, 1H, H^3), 6.66 (d, $^3J_{HH}$ = 1.4 Hz, 1H, H^5), 7.26 (m, 3H, *m*/*p*-C_6H_3), 8.05 (s, 1H, CH=N); δ_C {^{1}H} (62.9 MHz, $CDCl_3$): δ 24.0 (s, *o*-C_6H_3), 28.4 (s, *o*-C_6H_3), 110.2 (s, C^4), 117.0 (s, C^3), 123.6 (s, *m*-C_6H_3), 124.4 (s, *p*-C_6H_3), 124.9 (s, C^5), 130.3 (s, C^2), 139.3 (s, *o*-C_6H_3), 148.9 (s, *i*-C_6H_3), 153.0 (s, CH=N); MS (FAB$^+$) *m*/*z* 255 (MH^+); IR (ATR, neat) 3232 (ν_{NH}), 1585 (ν_{CN}) cm^{-1}. The product is hygroscopic and must be stored under a dry nitrogen atmosphere to prevent degradation.

Attempted preparation of phenyl[1-(1*H*-pyrrol-2-yl)ethylidene]-amine. Under air, aniline (1.81 cm^3, 16.8 × 10^{-3} mol) was added to a solution of **1** (2.00 g, 18.3 × 10^{-3} mol) in toluene (100 cm^3). A catalytic quantity of *p*-TSA (0.1 g, 0.7 × 10^{-3} mol) was added and the mixture heated to reflux under Dean–Stark conditions for 14 h. The toluene was removed *in vacuo* to afford a dark brown crystalline solid, which following recrystallisation from methanol afforded bright purple needles that, upon further analysis, were shown to be predominately **1** with only traces of the desired ketimine. Attempts were made to isolate the imine by further recrystallisation from methanol, but without success. Similarly, no tractable products resulted using 3,5-dimethylaniline, 2,4,6-trimethylaniline or 2,6-diisopropylaniline.

(1-Diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)phenylamine 3a. A solution of **2a** (1.10 g, 6.5 × 10^{-3} mol) in DME (20 cm^3) was cooled to −78 °C with stirring. Bu^nLi (4.03 cm^3, 6.5 × 10^{-3} mol; 1.6 mol dm^{-3} solution in hexanes) was added, the resulting solution allowed to stir at −78 °C for 0.5 h and then allowed to warm slowly to RT. Ph_2PCl (1.18 cm^3, 6.4 × 10^{-3} mol) was added by syringe and the mixture allowed to stir at RT for 18 h. The volatile components were then removed *in vacuo*, CH_2Cl_2 added and the solution filtered. The CH_2Cl_2 was then removed under vacuum and the product dried *in vacuo* to yield a red–brown tar. Hexane (10 cm^3) was then added, the red–black tar triturated and the mixture filtered to afford **3a** (1.92 g, 84%) as a waxy dark brown solid (Anal. Calc. for $C_{23}H_{19}N_2P$: C, 77.94; H, 5.41; N, 7.91. Found: C, 78.11; H, 5.61; N, 8.11%); δ_H (300.1 MHz, $CDCl_3$): δ 6.38 (t, $^3J_{HH}$ = 2.4 Hz, 1H, H^4), 6.55 (m, 1H, H^3), 7.03 (m, 3H, *m*/*p*-C_6H_5), 7.09 (m, 1H, H^5), 7.16 (m, 2H, *o*-C_6H_5), 7.34 (m, 4H, PC_6H_5), 7.44 (m, 6H, *p*-C_6H_5), 8.68 (d, $^4J_{PH}$ = 1.2 Hz, 1H, CH=N); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 112.7 (s, C^4), 118.0 (s, C^3), 121.2 (s, *m*-C_6H_5), 125.6 (s, *p*-C_6H_5), 129.0 (d, $^3J_{PC}$ = 6.8 Hz, *m*-C_6H_5P), 129.3

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

(s, *p*-C_6H_5P), 130.2 (s, *o*-C_6H_5), 130.4 (s, C^5), 132.8 (d, $^2J_{PC}$ = 21.9 Hz, *o*-C_6H_5P), 137.0 (d, $^1J_{PC}$ = 14.7 Hz, *i*-C_6H_5P), 137.2 (s, C^2), 149.9 (d, $^3J_{PC}$ = 9.8 Hz, CH=N), 152.2 (s, *i*-C_6H_5); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) + 47.5 (s); MS (FAB$^+$) *m*/*z* 355 (MH^+); IR (KBr, CH_2Cl_2) 1589 (ν_{CN}), 897 ($\nu_{PN(pyrl)}$) cm^{-1}.

(3,5-Dimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine 3b. Using an analogous procedure to that used to prepare **3a**, reaction of **2b** (1.70 g, 8.6 × 10^{-3} mol) in DME (20 cm^3) with Bu^nLi (5.40 cm^3, 8.6 × 10^{-3} mol; 1.6 mol dm^{-3}, solution in hexanes) followed by addition of Ph_2PCl (1.58 cm^3, 8.6 × 10^{-3} mol) afforded, after stirring for 23 h and appropriate purification, **3b** (0.90 g, 27%) as a thick orange oil. Further distillation led to decomposition of **3b**, hence analytical data are reported for the crude material. (Anal. Calc. for $C_{25}H_{23}N_2P$: C, 78.50; H, 6.07; N, 7.33. Found: C, 75.07; H, 5.38; N, 6.34%); δ_H (400.1 MHz, $CDCl_3$) 2.15 (s, 6H, *m*-(CH_3)$_2C_6H_3$), 6.20 (t, $^3J_{HH}$ = 3.4 Hz, 1H, H^4), 6.39 (m, 1H, H^3), 6.49 (s, 2H, *o*-C_6H_5), 6.65 (s, 1H, *p*-C_6H_3), 6.92 (s, 1H, H^5), 7.20 (m, 4H, PC_6H_5), 7.23 (m, 6H, PC_6H_5), 8.51 (d, $^4J_{PH}$ = 2.4 Hz, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$): δ 21.7 (s, *m*-(CH_3)$_2C_6H_3$), 112.7 (s, C^4), 117.5 (s, C^3), 119.0 (s, *p*-C_6H_3), 127.3 (s, *o*-C_6H_3), 129.0 (d, $^3J_{PC}$ = 6.6 Hz, *m*-C_6H_5P), 130.1 (s, C^5), 130.2 (s, *p*-C_6H_5P), 132.7 (d, $^2J_{PC}$ = 21.9 Hz, *o*-C_6H_5P), 136.0 (d, $^1J_{PC}$ = 13.5 Hz, *i*-C_6H_3P), 137.2 (s, C^2), 138.8 (s, *m*-C_6H_3), 149.5 (d, $^3J_{PC}$ = 10.3 Hz, CH=N), 152.2 (s, *i*-C_6H_3); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) + 47.9 (s); MS (FAB$^+$) *m*/*z* 383 (MH^+); IR (KBr, CH_2Cl_2) 1585 (ν_{CN}), 897 ($\nu_{PN(pyrl)}$) cm^{-1}.

(2,4,6-Trimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-methylene)amine 3c. Using an analogous procedure to that used to prepare **3a**, reaction of **2c** (1.11 g, 5.2 × 10^{-3} mol) in DME (20 cm^3) with Bu^nLi (3.30 cm^3, 1.6 mol dm^{-3}, solution in hexanes) followed by the addition of Ph_2PCl (0.96 cm^3, 5.2 × 10^{-3} mol) afforded, after stirring for 14 h and appropriate purification, **3c** (1.45 g, 70%) as a red–brown oil (Anal. Calc. for $C_{26}H_{25}N_2P$: C, 78.75; H, 6.37; N, 7.07. Found: C, 78.81; H, 6.77; N, 7.27%); δ_H (300.1 MHz, $CDCl_3$) 2.21 (s, 6H, *o*-(CH_3)$_2C_6H_2$), 2.31 (s, 3H, *p*-$CH_3C_6H_2$), 6.65 (t, $^3J_{HH}$ = 3.3 Hz, 1H, H^4), 6.85 (m, 1H, H^3), 6.89 (s, 2H, *m*-C_6H_2), 7.22 (m, 1H, H^5), 7.59 (m, 4H, PC_6H_5), 7.71 (m, 6H, PC_6H_5), 8.35 (d, $^4J_{PH}$ = 3.0 Hz, 1H, CH=N); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 19.2 (s, *o*-(CH_3)$_2C_6H_2$), 21.3 (s, *p*-$CH_3C_6H_2$), 116.4 (s, C^4), 117.9 (s, C^3), 129.0 (s, *p*-C_6H_5P), 129.5 (d, $^3J_{PC}$ = 6.8 Hz, *m*-C_6H_5P), 130.1 (s, C^5), 130.4 (s, *o*-C_6H_2), 130.6 (s, *m*-C_6H_2), 132.7 (d, $^1J_{PC}$ = 12.1 Hz, *i*-C_6H_5P), 133.0 (s, *p*-C_6H_2), 133.2 (d, $^2J_{PC}$ = 22.1 Hz, *o*-C_6H_5P), 136.5 (s, C^2), 149.4 (s, *i*-C_6H_2), 156.6 (d, $^3J_{PC}$ = 7.9 Hz, CH=N); δ_P {^{1}H} (162.0 MHz, $CDCl_3$) +48.4 (s); MS (FAB$^+$) *m*/*z* 397 (MH^+); IR (KBr, CH_2Cl_2) 1582 (ν_{CN}), 896 ($\nu_{PN(pyrl)}$) cm^{-1}.

(2,6-Diisopropylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine 3d. Using an analogous procedure to that used to prepare **3a**, reaction of **2d** (1.01 g, 4.0 × 10^{-3} mol) in DME (20 cm^3) with Bu^nLi (2.50 cm^3, 4.0 × 10^{-3} mol; 1.6 mol dm^{-3}, solution in hexanes) followed by Ph_2PCl (0.73 cm^3, 4.0 × 10^{-3} mol) afforded, after stirring for 14 h and extraction, **3d** (1.51 g, 86%) as a beige waxy solid, that was not amenable to further purification and hence data are recorded for the crude material (Anal. Calc. for $C_{29}H_{31}N_2P$: C, 79.41; H, 7.14; N, 6.39. Found: C, 77.51; H, 7.04; N, 6.93%); δ_H (300.1 MHz, $CDCl_3$) 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 12H, *o*-((CH_3)$_2$C*H*)$_2C_6H_3$), 2.80 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, *o*-((CH_3)$_2$C*H*)$_2C_6H_3$), 6.38 (t, $^3J_{HH}$ = 3.3 Hz, 1H, H^4), 6.51 (m, 1H, H^3), 7.02 (m, 1H, H^5), 7.30 (m, 4H, PC_6H_5), 7.43 (m, 6H, PC_6H_5), 8.31 (d, $^4J_{PH}$ = 1.8 Hz, 1H, CH=N); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 23.7 (s, *o*-((CH_3)$_2$CH)$_2C_6H_3$), 27.7 (s, *o*-((CH_3)$_2$*C*H)$_2C_6H_3$), 112.1 (s, C^4), 118.1 (s, C^3), 122.8 (s, *m*-C_6H_3), 123.1 (s, C^5), 123.4 (s, *p*-C_6H_3), 129.0 (d, $^3J_{PC}$ = 6.8 Hz, *m*-C_6H_5P), 130.2 (s, *p*-C_6H_5P), 132.9 (d, $^2J_{PC}$ = 22.6 Hz, *o*-C_6H_5P), 136.0 (s, *o*-C_6H_3), 137.5 (d, $^1J_{PC}$ = 17.4 Hz, *i*-C_6H_5P), 138.5 (s, C^2), 149.8 (s, *i*-C_6H_3), 152.3 (d, $^3J_{PC}$ = 6.8 Hz, CH=N); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +49.1 (s); MS (FAB$^+$): *m*/*z* 439 (MH^+); IR (KBr, CH_2Cl_2) 1588 (ν_{CN}), 895 ($\nu_{PN(pyrl)}$) cm^{-1}.

(Bis(diisopropylamino)phosphanyl)(1*H*-pyrrol-2-ylmethylene)-phenylamine 4a. A solution of **2a** (1.12 g, 6.6 × 10^{-3} mol) in DME (20 cm^3) was cooled to −78 °C with stirring. Bu^nLi (4.15 cm^3, 6.6 × 10^{-3} mol; 1.6 mol dm^{-3}, solution in hexanes) was added and the resulting solution allowed to stir at −78 °C for 0.5 h and then allowed to warm slowly to RT. A solution of (Pr^i_2N)$_2PCl$ (1.76 g, 6.6 × 10^{-3} mol) in DME (20 cm^3) was added *via* cannula and the resulting mixture allowed to stir at RT for 16 h. The DME was then removed *in vacuo*, CH_2Cl_2 added, and the solution filtered. Removal of CH_2Cl_2 under vacuum and drying *in vacuo* afford **4a** (2.01 g, 76%) as a mid-brown-coloured crystalline solid (Anal. Calc. for $C_{23}H_{37}N_4P$: C, 68.95; H, 9.33; N, 13.99. Found: C, 69.02; H, 9.25; N, 13.75%); δ_H (300.1 MHz, $CDCl_3$) 1.09 (d, $^3J_{HH}$ = 6.6 Hz, 12H, ((CH_3)$_2$CH)$_2$N)), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 12H, ((CH_3)$_2$CH)$_2$N)), 3.55 (sept, $^3J_{HH}$ = 6.6 Hz, 4H, (CH_3)$_2$C*H*)$_2$N), 6.36 (s, 1H, H^4), 7.14 (d, $^3J_{HH}$ = 3.9 Hz, 1H, H^3), 7.20 (d, $^3J_{HH}$ = 7.5 Hz, 3H, *m*/*p*-C_6H_5), 7.25 (s, 1H, H^5), 7.37 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-C_6H_5), 8.99 (d, $^4J_{PH}$ = 5.7 Hz, 1H, CH=N); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 23.8 (d, $^3J_{PC}$ = 12.6 Hz, ((CH_3)$_2$CH)$_2$N)), 24.0 (d, $^3J_{PC}$ = 12.6 Hz, ((CH_3)$_2$CH)$_2$N)), 47.0 (d, $^2J_{PC}$ = 13.6 Hz, ((CH_3)$_2$*C*H)$_2$N)), 111.2 (s, C^4), 113.6 (s, C^3), 121.4 (s, *m*-C_6H_5), 125.1 (s, *p*-C_6H_5), 127.9 (s, C^5), 129.2 (s, *o*-C_6H_5), 134.7 (s, C^2), 152.0 (d, $^3J_{PC}$ = 24.9 Hz, CH=N), 153.0 (s, *i*-C_6H_5); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +84.4 (s); MS (FAB$^+$) *m*/*z* 400 (M^+); IR (KBr, CH_2Cl_2) 1589 (ν_{CN}), 897 ($\nu_{PN(pyrl)}$) cm^{-1}.

(3,5-Dimethylphenyl)(bis(diisopropylamino)phosphanyl)(1*H*-pyrrol-2-ylmethylene)amine 4b. Using an analogous procedure to that for the preparation of **4a**, derivative **2b** (1.13 g, 5.7 × 10^{-3} mol) as a solution in DME (20 cm^3) was reacted with Bu^nLi (3.6 cm^3, 5.8 × 10^{-3} mol; 1.6 mol dm^{-3}, solution in hexanes) and a solution of (Pr^i_2N)$_2PCl$ (1.51 g, 5.7 × 10^{-3} mol) in DME (20 cm^3). Following purification, **4b** (2.19 g, 90%) was isolated as a brown crystalline solid (Anal. Calc. for $C_{25}H_{41}N_4P$: C, 70.04; H, 9.66; N, 13.07. Found: C, 69.94; H, 9.60; N, 12.91%); δ_H (300.1 MHz, $CDCl_3$) 1.10 (d, $^3J_{HH}$ = 6.6 Hz, 12H, ((CH_3)$_2$CH)$_2$N), 1.27 (d, $^3J_{HH}$ = 6.6 Hz, 12H, ((CH_3)$_2$CH)$_2$N), 2.34 (s, 6H, *m*-$CH_3C_6H_3$), 3.54 (sept, $^3J_{HH}$ = 6.6 Hz, 4H, ((CH_3)$_2$C*H*)$_2$N)$_2$), 6.34 (s, 1H, H^4), 6.83 (s, 1H, *p*-C_6H_3), 6.84 (s, 2H, *o*-C_6H_3), 7.12 (d, $^3J_{HH}$ = 2.9 Hz, 1H, H^3), 7.23 (s, 1H, H^5), 8.96 (d, $^4J_{PH}$ = 5.6 Hz, 1H, CH=N); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 21.8 (s, *m*-$CH_3C_6H_3$), 24.1 (d, $^3J_{PC}$ = 13.6 Hz, ((CH_3)$_2$CH)$_2$N), 47.3 (d, $^2J_{PC}$ = 13.6 Hz, ((CH_3)$_2$CH)$_2$N), 111.2 (s, C^4), 113.5 (s, C^3), 119.3 (s, *o*-C_6H_3), 126.9 (s, C^5), 127.9 (s, *p*-C_6H_3), 134.8 (s, C^2), 138.8 (s, *m*-C_6H_3), 151.7 (d, $^3J_{PC}$ = 24.4 Hz, CH=N), 153.4 (s, *i*-C_6H_3); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +83.2 (s); MS (FAB$^+$) *m*/*z* 428 (M^+); IR (KBr, CH_2Cl_2) 1584 (ν_{CN}), 897 ($\nu_{PN(pyrl)}$) cm^{-1}.

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

(2,4,6-Trimethylphenyl)(bis(diisopropylamino)phosphanyl)(1*H*-pyrrol-2-ylmethylene)amine 4c. Using an analogous procedure to that for the preparation of **4a**, compound **2c** (1.56 g, 7.4 × 10^{-3} mol) in DME (20 cm^3) was reacted with Bu^nLi (4.6 cm^3, 7.4 × 10^{-3} mol; 1.6 mol dm^{-3}, solution in hexanes) and $(Pr^i_2N)_2PCl$ (1.97 g, 7.4 × 10^{-3} mol) in DME (20 cm^3). Following purification **4c** (2.84 g, 87%) was obtained as a light brown crystalline solid (Anal. Calc. for $C_{26}H_{43}N_4P$: C, 70.54; H, 9.81; N, 12.66. Found: C, 70.31; H, 10.00; N, 12.72%); δ_H (300.1 MHz, $CDCl_3$): δ 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $((CH_3)_2CH)_2N$), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $((CH_3)_2CH)_2N$), 2.13 (s, 6H, *o*-$CH_3C_6H_2$), 2.28 (s, 3H, *p*-$CH_3C_6H_2$), 3.55 (sept, $^3J_{HH}$ = 6.6 Hz, 4H, $((CH_3)_2CH)_2N$), 6.36 (s, 1H, H^4), 6.86 (s, 2H, *m*-C_6H_2), 7.15 (d, $^3J_{HH}$ = 3.5 Hz, 1H, H^3), 7.23 (s, 1H, H^5), 8.67 (d, $^4J_{PH}$ = 5.6 Hz, 1H, CH=N); δ_C {^{1}H} (75.5 MHz, $CDCl_3$) 18.8 (s, *o*-$CH_3C_6H_2$), 21.2 (s, *p*-$CH_3C_6H_2$), 24.1 (d, $^3J_{PC}$ = 13.3 Hz, $((CH_3)_2CH)_2N$), 47.2 (d, $^2J_{PC}$ = 13.3 Hz, $((CH_3)_2CH)_2N$), 110.9 (s, C^4), 112.7 (s, C^3), 127.4 (s, C^5), 127.8 (s, *o*-C_6H_2), 128.8 (s, *m*-C_6H_2), 132.3 (s, *p*-C_6H_2), 134.4 (s, C^2), 150.1 (s, *i*-C_6H_2), 154.5 (d, $^3J_{PC}$ = 25.6 Hz, CH=N); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +82.8 (s); MS (FAB$^+$) *m*/*z* 443 (MH^+); IR (KBr, CH_2Cl_2) 1588 (ν_{CN}), 896 ($\nu_{PN(pyrl)}$) cm^{-1}.

(2,6-Diisopropylphenyl)(bis(diisopropylamino)phosphanyl)(1*H*-pyrrol-2-ylmethylene)amine 4d. Following a procedure analogous to that used to prepare **4a**, compound **2d** (1.33 g, 5.2 × 10^{-3} mol) in DME (20 cm^3) was treated with Bu^nLi (3.3 cm^3, 5.3 × 10^{-3} mol; 1.6 mol dm^{-3}, solution in hexanes) followed by $(Pr^i_2N)_2PCl$ (1.40 g, 5.2 × 10^{-3} mol) in DME (20 cm^3). Following work-up and purification **4d** (2.23 g, 88%) was isolated as a light brown solid after drying *in vacuo* (Anal. Calc. for $C_{29}H_{49}N_4P$: C, 71.84; H, 10.21; N, 11.56. Found: C, 71.97; H, 10.10; N, 11.49%); δ_H (400.1 MHz, $CDCl_3$): δ 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $((CH_3)_2CH)_2N$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $((CH_3)_2CH)_2C_6H_3$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $((CH_3)_2CH)_2N$), 3.24 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, *o*-$((CH_3)_2CH)_2C_6H_3$), 3.72 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $((CH_3)_2CH)_2N$), 6.50 (s, 1H, H^4), 7.23 (m, 1H, H^3), 7.28 (s, 2H, *m*-C_6H_3), 7.29 (s, 1H, *p*-C_6H_3), 7.38 (d, $^3J_{HH}$ = 3.5 Hz, 1H, H^5), 8.79 (d, $^4J_{PH}$ = 5.7 Hz, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$): δ 23.1 (d, $^3J_{PC}$ = 13.2 Hz, $((CH_3)_2CH)_2N$), 23.3 (d, $^3J_{PC}$ = 13.2 Hz, $((CH_3)_2CH)_2N$), 27.3 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 46.1 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 46.4 (d, $^2J_{PC}$ = 13.2 Hz, $((CH_3)_2CH)_2N$), 110.3 (s, C^4), 112.3 (s, C^3), 122.4 (s, *m*-C_6H_3), 122.9 (s, *p*-C_6H_3), 126.7 (s, C^5), 133.8 (s, C^2), 138.0 (s, *o*-C_6H_3), 149.6 (s, *i*-C_6H_3), 152.9 (d, $^3J_{PC}$ = 25.9 Hz, CH=N); δ_P {^{1}H} (121.5 MHz, $CDCl_3$): δ +82.7 (s); MS (FAB$^+$): *m*/*z* = 485 (MH^+); IR (KBr, CH_2Cl_2) 1585 (ν_{CN}), 897 ($\nu_{PN(pyrl)}$) cm^{-1}.

(1-Diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)phenylamine rhodium carbonyl chloride 5a. In a glove box, a Young's tap NMR tube was charged with **3a** (0.044 g, 1.2 × 10^{-4} mol), $[Rh(CO)_2Cl]_2$ (0.025 g, 6.4 × 10^{-5} mol) and sealed before transferring to a Schlenk line. $CDCl_3$ (0.6 cm^3) was added and the tube freeze/thaw degassed, back-filled with nitrogen and sealed. After 0.5 h, when gas evolution had ceased, the solution was freeze/thaw degassed, back-filled with CO and sealed; δ_H (300.1 MHz, $CDCl_3$): δ 6.40 (t, $^3J_{HH}$ = 3.0 Hz, 1H, H^4), 6.62 (s, 1H, H^3), 7.01 (s, 1H, H^5), 7.10 (t, $^3J_{HH}$ = 6.9 Hz, 1H, *o*-C_6H_5), 7.14 (s, 1H, *p*-C_6H_5), 7.22 (m, $^3J_{HH}$ = 8.1 Hz, 1H, *m*-C_6H_5), 7.45 (m, 4H, PC_6H_5), 7.51 (m, 6H, PC_6H_5), 7.89 (d, $^4J_{PH}$ = 2.4 Hz, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$): δ 114.5 (s, C^4), 122.2 (s, C^3), 123.7 (s, *m*-PhC), 127.2 (s, *p*-C_6H_5), 129.1 (s, *p*-C_6H_5P), 129.4 (d, $^3J_{PC}$ = 11.5 Hz, *m*-C_6H_5P), 129.6 (s, C^5), 132.2 (s, *o*-C_6H_5), 133.0 (d, $^2J_{PC}$ = 10.4 Hz, *o*-C_6H_5P), 133.1 (d, $^1J_{PC}$ = 10.8 Hz, *i*-C_6H_5P), 142.7 (s, C^2), 152.5 (s, *i*-C_6H_5), 156.3 (d, $^3J_{PC}$ = 6.1 Hz, CH=N), 186.9 (d, $^1J_{CRh}$ = 65.2 Hz, RhCO); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +92.9 (d, $^1J_{RhP}$ = 185 Hz); IR (KBr, $CDCl_3$) 1586/1568 (ν_{CN}), 2017 (ν_{CO}) cm^{-1}.

(3,5-Dimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine rhodium carbonyl chloride 5b. Using the procedure as described for **5a** with **3b** (0.045 g, 1.2 × 10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.023 g, 5.9 × 10^{-5} mol): δ_H (300.1 MHz, $CDCl_3$) 2.20 (s, 6H, *m*-$CH_3C_6H_3$), 6.42 (s, 1H, H^4), 6.62 (s, 1H, H^3), 6.68 (s, 2H, *o*-C_6H_3), 6.75 (s, 1H, *p*-C_6H_3), 7.00 (s, 1H, H^5), 7.42 (m, 4H, PC_6H_5), 7.50 (m, 6H, PC_6H_5), 7.87 (d, $^4J_{PH}$ = 2.4 Hz, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$) 21.6 (s, *m*-$CH_3C_6H_3$), 114.8 (s, C^4), 120.0 (s, C^3), 121.4 (s, *o*-C_6H_3), 129.0 (s, *p*-C_6H_3), 129.4 (d, $^3J_{PC}$ = 11.1 Hz, *m*-C_6H_5P), 129.6 (s, *p*-C_6H_5P), 131.1 (s, C^5), 132.8 (d, $^2J_{PC}$ = 14.7 Hz, *o*-C_6H_5P), 133.1 (s, *i*-C_6H_5P), 138.3 (s, *m*-C_6H_3), 142.6 (s, C^2), 152.1 (s, *i*-C_6H_3), 156.1 (d, $^3J_{PC}$ = 6.1 Hz, CH=N), 187.5 (d, $^1J_{CRh}$ = 67.4 Hz, RhCO); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +92.7 (d, $^1J_{RhP}$ = 186 Hz); IR (KBr, $CDCl_3$) 1586/1567 (ν_{CN}), 2013 (ν_{CO}) cm^{-1}.

(2,4,6-Trimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-methylene)amine rhodium carbonyl chloride 5c. Using the procedure as described for **5a** with **3c** (0.043 g, 1.1 × 10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.021 g, 5.4 × 10^{-5} mol): δ_H (300.1 MHz, $CDCl_3$) 1.95 (s, 6H, *o*-$CH_3C_6H_2$), 2.15 (s, 3H, *p*-$CH_3C_6H_2$), 6.34 (t, $^3J_{HH}$ = 3.5 Hz, 1H, H^4), 6.63 (s, 1H, H^3), 6.72 (s, 2H, *m*-C_6H_2), 6.92 (m, 1H, H^5), 7.41 (m, 4H, PC_6H_5), 7.47 (m, 6H, PC_6H_5), 7.68 (d, $^4J_{PH}$ = 2.7 Hz, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$) 19.5 (s, *o*-$CH_3C_6H_2$), 21.2 (s, *p*-$CH_3C_6H_2$), 114.6 (s, C^4), 120.5 (s, C^3), 128.9 (s, *p*-C_6H_5P), 129.0 (s, *m*-C_6H_2), 129.3 (d, $^3J_{PC}$ = 11.9 Hz, *m*-C_6H_5P), 130.4 (s, *o*-C_6H_2), 131.4 (s, C^5), 132.6 (d, $^2J_{PC}$ = 14.2 Hz, *o*-C_6H_5P), 133.1 (s, *p*-C_6H_2), 133.3 (d, $^1J_{PC}$ = 13.7 Hz, *i*-C_6H_5P), 148.3 (s, C^2), 152.9 (s, *i*-C_6H_2), 157.9 (d, $^3J_{PC}$ = 6.8 Hz, CH=N), 188.2 (d, $^1J_{RhC}$ = 70.0 Hz, RhCO); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +90.9 (d, $^1J_{RhP}$ = 185 Hz); IR (KBr, $CDCl_3$) 1572 (ν_{CN}), 2018 (ν_{CO}) cm^{-1}.

(2,6-Diisopropylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine rhodium carbonyl chloride 5d. Using the procedure as described for **5a** with **3d** (0.054 g, 1.2 × 10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.024 g, 6.2 × 10^{-5} mol): δ_H (300.1 MHz, $CDCl_3$) 0.69 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 1.20 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 2.95 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, *o*-$((CH_3)_2CH)_2C_6H_3$), 6.43 (t, $^3J_{HH}$ = 3.3 Hz, H^4), 6.63 (s, 1H, H^3), 6.92 (m, 1H, H^5), 7.01 (s, 2H, *m*-C_6H_3), 7.06 (s, 1H, *p*-C_6H_3), 7.41 (m, 4H, PC_6H_5), 7.45 (m, 6H, PC_6H_5), 7.74 (d, $^4J_{PH}$ = 2.4 Hz, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$) 23.4 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 24.6 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 28.9 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 114.4 (s, C^4), 123.2 (s, *m*-C_6H_3), 123.8 (s, C^3), 127.0 (s, *p*-C_6H_3), 129.0 (s, *p*-C_6H_5P), 129.3 (d, $^3J_{PC}$ = 11.5 Hz, *m*-C_6H_5P), 131.6 (s, C^5), 132.5 (d, $^2J_{PC}$ = 14.3 Hz, *o*-C_6H_5P), 132.7 (d, $^1J_{PC}$ = 18.0 Hz, *i*-C_6H_5P), 133.4 (s, *o*-C_6H_3), 141.3 (s, C^2), 147.9 (s, *i*-C_6H_3), 157.4 (d, $^3J_{PC}$ = 7.0 Hz, CH=N), 188.2 (dd, $^1J_{CRh}$ = 61.7 Hz, $^2J_{CP}$ = 18.6 Hz, RhCO); δ_P {^{1}H} (121.5 MHz, $CDCl_3$) +90.7 (d, $^1J_{RhP}$ = 183 Hz); IR (KBr, $CDCl_3$) 1587/1570 (ν_{CN}), 2014 (ν_{CO}) cm^{-1}.

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

(Bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)-phenylamine rhodium carbonyl chloride 6a. Using the procedure as described for **5a** with **4a** (0.041 g, 1.0×10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.020 g, 5.1×10^{-5} mol): δ_H (300.1 MHz, $CDCl_3$) 1.19 (d, $^3J_{HH} = 6.3$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.35 (d, $^3J_{HH} = 6.3$ Hz, 12H, $((CH_3)_2CH)_2N$), 4.40 (dsept, $^3J_{HH} = 6.3$ Hz, $^3J_{PH} = 11.7$ Hz, 4H, $((CH_3)_2CH)_2N$), 6.37 (t, $^3J_{HH} = 3.3$ Hz, 1H, H^4), 6.87 (s, 1H, H^3), 7.17 (m, 3H, *m*/*p*-C_6H_5), 7.29 (t, $^3J_{HH} = 7.8$ Hz, 2H, *o*-C_6H_5), 7.49 (s, 1H, H^5), 7.94 (d, $^4J_{PH} = 2.7$ Hz, 1H, CH=N); $\delta_C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) 24.1 (d, $^3J_{CP} = 2.7$ Hz, $((CH_3)_2CH)_2N$), 50.2 (d, $^2J_{PC} = 12.1$ Hz, $((CH_3)_2CH)_2N$), 112.5 (s, C^4), 124.0 (s, *o*-C_6H_5), 126.5 (s, *p*-C_6H_5), 128.3 (s, *m*-C_6H_5), 129.2 (s, C^3), 130.3 (s, C^5), 130.4 (s, C^2), 153.0 (s, *i*-C_6H_5), 155.8 (d, $^3J_{PC} = 6.4$ Hz, CH=N), 188.9 (dd, $^1J_{RhC} = 79.6$ Hz; $^2J_{PC} = 21.5$ Hz, RhCO); $\delta_P\{^1H\}$ (121.5 MHz, $CDCl_3$) +117.9 (d, $^1J_{RhP} = 233$ Hz); IR (KBr, $CDCl_3$) 1590 (ν_{CN}), = 2005 (ν_{CO}) cm^{-1}.

(3,5-Dimethylphenyl)(bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)amine rhodium carbonyl chloride 6b. Using the procedure as described for **5a** with **4b** (0.049 g, 1.1×10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.022 g, 5.7×10^{-5} mol): δ_H NMR (300.13 MHz, $CDCl_3$) 1.25 (d, $^3J_{HH} = 7.1$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.40 (d, $^3J_{HH} = 7.1$ Hz, 12H, $((CH_3)_2CH)_2N$), 2.31 (s, 6H, *m*-$CH_3C_6H_3$), 4.44 (dsept, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 12.0$ Hz, 4H, $((CH_3)_2CH)_2N$)), 6.42 (t, $^3J_{HH} = 3.3$ Hz, 1H, H^4), 6.83 (s, 2H, *o*-C_6H_3), 6.85 (s, 1H, *p*-C_6H_3), 6.92 (s, 1H, H^3), 7.53 (d, $^3J_{HH} = 1.8$ Hz, H^5), 7.98 (d, $^4J_{PH} = 2.7$ Hz, 1H, CH=N); $\delta_C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) 21.7 (s, *m*-$CH_3C_6H_3$), 24.1 (d, $^3J_{CP} = 4.1$ Hz, $((CH_3)_2CH)_2N$), 25.1 (d, $^3J_{CP} = 4.1$ Hz, $((CH_3)_2CH)_2N$), 50.2 (d, $^2J_{PC} = 12.1$ Hz $((CH_3)_2CH)_2N$), 112.5 (s, C^4), 121.7 (s, *o*-C_6H_3), 128.6 (s, *p*-C_6H_3), 129.2 (s, C^3), 130.4 (s, C^5), 130.8 (s, *m*-C_6H_3), 138.1 (s, C^2), 153.4 (s, *i*-C_6H_3), 155.8 (d, $^3J_{PC} = 6.4$ Hz, CH=N), 189.1 (d, $^1J_{RhC} = 69.0$, RhCO); $\delta_P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ +117.7 (d, $^1J_{RhP} = 233$ Hz); IR (KBr, $CDCl_3$) 1586 (ν_{CN}), 2000 (ν_{CO}) cm^{-1}.

(2,4,6-Trimethylphenyl)(bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)amine rhodium carbonyl chloride 6c. Using the procedure as described for **5a** with **4c** (0.055 g, 1.2×10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.024 g, 6.2×10^{-5} mol): δ_H NMR (300.13 MHz, $CDCl_3$) 1.27 (d, $^3J_{HH} = 6.6$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.41 (d, $^3J_{HH} = 6.6$ Hz, 12H, $((CH_3)_2CH)_2N$), 2.16 (s, 6H, *o*-$CH_3C_6H_2$), 2.36 (s, 3H, *p*-$CH_3C_6H_2$), 4.45 (dsept, $^3J_{HH} = 6.3$ Hz, $^3J_{PH} = 12.1$ Hz, 4H, $((CH_3)_2CH)_2N$), 6.47 (s, 1H, H^4), 6.84 (s, 2H, *m*-C_6H_2), 6.90 (s, 1H, H^3), 7.57 (s, 1H, H^5), 7.73 (d, $^4J_{PH} = 2.6$ Hz, 1H, CH=N); $\delta_C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) 19.6 (s, *o*-$CH_3C_6H_2$), 21.3 (s, *p*-$CH_3C_6H_2$), 24.2 (d, $^3J_{CP} = 3.2$ Hz, $((CH_3)_2CH)_2N$), 25.1 (d, $^3J_{CP} = 3.2$ Hz, $((CH_3)_2CH)_2N$), 49.8 (d, $^2J_{PC} = 11.1$ Hz, $((CH_3)_2CH)_2N$), 112.4 (s, C^4), 128.6 (s, *m*-C_6H_2), 129.2 (s, C^3), 130.6 (s, *o*-C_6H_2), 130.8 (s, C^5), 135.2 (s, *p*-C_6H_2), 141.8 (s, C^2), 152.3 (s, *i*-C_6H_2), 158.0 (d, $^3J_{PC} = 7.1$ Hz, CH=N), 189.0 (d, $^1J_{RhC} = 69.1$ Hz, RhCO); $\delta_P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) +117.8 (d, $^1J_{RhP} = 236$ Hz); IR (KBr, $CDCl_3$) 1572 (ν_{CN}), 2002 (ν_{CO}) cm^{-1}.

(2,6-Diisopropylphenyl)(bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)amine rhodium carbonyl chloride 6d. Using the procedure as described for **5a** with **4d** (0.054 g, 1.1×10^{-4} mol) and $[Rh(CO)_2Cl]_2$ (0.022 g, 5.7×10^{-5} mol): δ_H NMR (300.13 MHz, $CDCl_3$) 1.06 (d, $^3J_{HH} = 6.7$ Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 1.29 (d, $^3J_{HH} = 6.7$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.35 (d, $^3J_{HH} = 6.7$ Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 1.43 (d, $^3J_{HH} = 6.6$ Hz, 12H, $((CH_3)_2CH)_2N$), 3.13 (sept, $^3J_{HH} = 6.7$ Hz, 2H, *o*-$((CH_3)_2CH)_2C_6H_3$), 4.44 (dsept, $^3J_{HH} = 6.7$ Hz, $^3J_{PH} = 6.7$ Hz, 4H, $((CH_3)_2CH)_2N$), 6.49 (t, $^3J_{HH} = 3.0$ Hz, 1H, H^4), 6.87 (m, 1H, H^3), 7.12 (d, $^3J_{HH} = 1.5$ Hz, 1H, *p*-C_6H_3), 7.15 (s, 2H, *m*-C_6H_3), 7.58 (s, 1H, H^5), 7.81 (d, $^4J_{PH} = 2.7$ Hz, 1H, CH=N); $\delta_C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) 23.3 (d, $^3J_{CP} = 2.4$ Hz, $((CH_3)_2CH)_2N$), 24.1 (d, $^3J_{CP} = 2.4$ Hz, $((CH_3)_2CH)_2N$), 24.7 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 25.0 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 47.8 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 47.9 (s, *o*-$(CH_3)_2CH)_2C_6H_3$), 49.8 (d, $^2J_{PC} = 11.1$ Hz, $((CH_3)_2CH)_2N$), 112.5 (s, C^4), 123.1 (s, *m*-C_6H_3), 126.9 (s, *p*-C_6H_3), 129.2 (s, C^3), 131.0 (s, C^5), 141.2 (s, *o*-C_6H_3), 148.9 (s, C^2), 157.4 (d, $^3J_{PC} = 6.7$ Hz, CH=N), 153.5 (s, *i*-C_6H_3), 189.1 (dd, $^1J_{RhC} = 73.0$, $^2J_{PC} = 15.9$ Hz, RhCO); $\delta_P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +117.5 (d, $^1J_{RhP} = 235$ Hz); IR (KBr, $CDCl_3$) = 1587/1570 (ν_{CN}), 2005 (ν_{CO}) cm^{-1}.

Preparation of (1-diphenylphosphanylselenido-1*H*-pyrrol-2-ylmethylene)phenylamine 7a. A Young's Tap NMR tube was charged with **3a** (0.050 g, 0.1×10^{-3} mol) and grey selenium (0.056 g, 0.7×10^{-3} mol) and sealed under an N_2 atmosphere. $CDCl_3$ (0.6 cm^3) was added and the tube heated to reflux for 1 h, after which time complete conversion of **3a** to **7a** had been achieved according to $^{31}P\{^1H\}$ NMR spectroscopy. No attempt was made to isolate and fully characterise the phosphine selenide **7a**. See Table 2.

Preparation of selenide compounds 7b–d and 8. These compounds were all prepared using a procedure exactly analogous to that used for the preparation of **7a**; each compound was examined by $^{31}P\{^1H\}$ NMR spectroscopy once the reaction had reached completion. See Table 2.

1-Diphenylphosphanylselenido-1*H*-pyrrole 10. 1-Diphenylphosphanyl-1*H*-pyrrole ($0.050 \text{ g}, 0.2 \times 10^{-3}$ mol) was treated with grey selenium (0.048 g, 0.2×10^{-3} mol) in a Young's Tap NMR tube and sealed under an N_2 atmosphere. $CDCl_3$ (0.6 cm^3) was added and the tube heated to reflux for 1 h. δ_P $\{^1H\}$ (162.0 MHz, $CDCl_3$) +58.4 ($^1J_{SeP} = 812$ Hz).

1-Bis(diisopropylamino)phosphanyl-1*H*-pyrrole 11. To a cooled (0 °C) suspension of KH (0.30 g, 7.5×10^{-3} mol) in THF (40 cm^3) was added a solution of pyrrole (0.5 cm^3, 7.5×10^{-3} mol) drop-wise in THF (30 cm^3). The reaction mixture was then allowed to warm to RT during which time it changed colour from a cloudy white, to yellow, to pale green. After 3 h, the reaction vessel was cooled to 0 °C and a solution of $(Pr^i_2N)_2PCl$ (2.00 g, 7.5×10^{-3} mol) in THF (50 cm^3) added. The mixture was then stirred at RT for a period of 12 h. The volatile components were then removed *in vacuo* and the mixture extracted with hexane (3×10 cm^3). Removal of solvent under reduced pressure afforded **11** as an analytically pure pale yellow solid (1.41 g, 63%), (Anal. Calc. for $C_{16}H_{32}N_3P$: C, 64.60, H, 10.86; N, 14.13. Found: C, 64.78; H, 10.81; N, 14.20%); δ_H (499.8 MHz, $CDCl_3$) 1.17 (d, $^3J_{HH} = 6.8$ Hz, 12H, CH_3), 1.28 (d, $^3J_{HH} = 6.8$ Hz, 12H, CH_3), 3.53 (d sept, $^3J_{HH} = 6.8$, $^3J_{PH} = 12.5$ Hz, 4H, $CH_2(CH_3)_2$), 6.25 (m, 2H, $H^3 + H^4$), 6.94 (m, 2H, $H^2 + H^5$); δ_C $\{^1H\}$ (125.7 MHz, $CDCl_3$) 24.0 (d, $^3J_{PC} = 7.5$ Hz, $(CH_3)_2CH$), 24.4 (d, $^3J_{PC} = 7.5$ Hz, $(CH_3)_2CH$), 47.0 (d, $^2J_{PC} = 13.8$ Hz, $(CH_3)_2CH$), 109.2 (d, $^3J_{PC} = 2.3$ Hz, $C^3 + C^4$), 112.7 (d, $^3J_{PC} = 11.9$ Hz, $C^2 + C^5$), δ_P $\{^1H\}$ (161.9 MHz, $CDCl_3$) +89.7 (s); MS (ESI^+): *m*/*z* 298 $(MH)^+$.

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

1-Bis(diisopropylamino)phosphanylselenido-1*H*-pyrrole 12. A sample of **11** (0.050 g, 0.17 × 10^{-3} mol) was treated with grey selenium (0.048 g, 0.2 × 10^{-3} mol) in a Young's Tap NMR tube and sealed under an N_2 atmosphere. $CDCl_3$ (0.6 cm^3) was added and the tube heated to reflux for 1 h, during which time complete conversion of **11** to **12** had been achieved according to $^{31}P\{^1H\}$ NMR spectroscopy. δ_P $\{^1H\}$ (162.0 MHz, $CDCl_3$) +60.4 ($^1J_{SeP}$ = 842 Hz).

(1-Diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)phenylamine palladium dichloride 13a. To a stirred suspension of $[PdCl_2(COD)]$ (0.30 g, 1.0 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **3a** (0.410 g, 1.2 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture allowed to stir for 16 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3) before volatile components were removed under vacuum to afford **13a** (0.40 g, 71%) as a dark yellow crystalline solid (Anal. Calc. for $C_{23}H_{19}N_2PPdCl_2$: C, 51.95; H, 3.61; N, 5.27. Found: C, 52.11; H, 3.50; N, 5.04%). δ_H (300.1 MHz, $CDCl_3$) 6.31 (s, 1H, H^4), 6.48 (m, 1H, H^3), 7.12 (m, 3H, *m*/*p*-C_6H_5), 7.21 (s, 1H, H^5), 7.44 (m, 2H, *o*-C_6H_5), 7.54 (m, 4H, C_6H_5P), 7.72 (m, 6H, C_6H_5P), 8.23 (d, $^4J_{PH}$ = 3.2 Hz, 1H, CH=N); δ_C $\{^1H\}$ (75.5 MHz, $CDCl_3$) 115.0 (s, C^4), 122.0 (s, *m*-C_6H_5), 128.0 (s, *p*-C_6H_5), 128.3 (s, C^3), 128.9 (s, *p*-C_6H_5P), 129.4 (d, $^3J_{PC}$ = 12.1 Hz, *m*-C_6H_5P), 130.0 (s, *o*-C_6H_5), 130.7 (s, C^5), 132.1 (d, $^2J_{PC}$ = 13.2 Hz, *o*-C_6H_5P), 133.0 (d, $^1J_{PC}$ = 12.8 Hz, *i*-C_6H_5P), 137.2 (s, C^2), 150.3 (s, *i*-C_6H_5), 154.5 (d, $^3J_{PC}$ = 7.2 Hz, CH=N); δ_P $\{^1H\}$ (121.5 MHz, $CDCl_3$) +66.5 (s); MS (FAB$^+$) *m*/*z* 495 (M − Cl)$^+$; IR (ATR, neat) 1596 (ν_{CN}).

(3,5-Dimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine palladium dichloride 13b. A Young's NMR tube was charged with $[PdCl_2(MeCN)_2]$ (0.12 g, 0.45 × 10^{-4} mol) and **3a** (0.172 g, 0.45 × 10^{-4} mol). $CDCl_3$ (0.6 cm^3) was added and the tube placed in an ultrasound bath for 10 min. The solution was then filtered to remove undissolved solids and the volatile components removed *in vacuo* to afford **13b** (0.194 g, 77%) as a yellow crystalline solid (Anal. Calc. for $C_{25}H_{23}N_2PPdCl_2$: C, 53.64; H, 4.15; N, 5.01. Found: C, 53.45; H, 4.80; N, 5.18%). Further purification by crystallisation was unsuccessful. δ_H (250.1 MHz, $CDCl_3$) 2.14 (s, 6H, *m*-$CH_3C_6H_3$), 6.45 (s, 1H, H^4), 6.60 (s, 1H, H^3), 6.70 (s, 1H, *p*-C_6H_3), 6.75 (s, 2H, *o*-C_6H_3), 7.22 (s, 1H, H^5), 7.41 (m, 4H, PC_6H_5), 7.51 (m, 6H, PC_6H_5), 7.96 (d, $^4J_{PC}$ = 2.9 Hz, 1H, CH=N); δ_C $\{^1H\}$ (62.9 MHz, $CDCl_3$) 21.0 (s, *m*-$CH_3C_6H_3$), 116.2 (s, C^4), 121.2 (s, *o*-C_6H_3), 127.6 (s, *m*-C_6H_3), 128.6 (s, *p*-C_6H_5P), 129.0 (d, $^3J_{PC}$ = 12.7 Hz, *m*-C_6H_5P), 130.9 (s, C^3), 131.9 (s, C^5), 132.1 (s, *p*-C_6H_3), 132.6 (d, $^2J_{PC}$ = 13.2 Hz, *o*-C_6H_5P), 133.2 (d, $^1J_{PC}$ = 12.6 Hz, *i*-C_6H_5P), 137.5 (s, C^2), 152.5 (s, *i*-C_6H_3), 153.7 (d, $^3J_{PC}$ = 7.0 Hz, CH=N); δ_P $\{^1H\}$ (101.3 MHz, $CDCl_3$) +65.8 (s); MS (FAB$^+$): *m*/*z* 525 (M − Cl$^+$); IR (ATR, neat) 1597 (ν_{CN}).

(2,4,6-Trimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-methylene)amine palladium dichloride 13c. To a stirred solution of $[PdCl_2(COD)]$ (0.31 g, 1.1 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **3c** (0.48 g, 1.2 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture allowed to stir for 19 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3). Elimination of solvent under vacuum afforded **13c** (0.59 g, 94%) as a dark yellow crystalline solid (Anal. Calc. for $C_{26}H_{25}N_2PPdCl_2$: C, 54.42; H, 4.40; N, 4.88. Found: C, 54.22; H, 4.34; N, 4.69%); δ_H (500.1 MHz, $CDCl_3$) 2.11 (s, 6H, *o*-$CH_3C_6H_2$), 2.20 (s, 3H, *p*-$CH_3C_6H_2$), 6.57 (t, 1H, $^3J_{HH}$ = 3.0 Hz, H^4), 6.75 (s, 1H, H^3), 6.78 (s, 2H, *m*-C_6H_2), 7.19 (m, 1H, H^5), 7.49 (m, 4H, PC_6H_5), 7.61 (m, 6H, PC_6H_5), 7.79 (d, $^4J_{PH}$ = 3.0 Hz, 1H, CH=N); δ_C (125.5 MHz, $CDCl_3$) 19.2 (s, *o*-$CH_3C_6H_2$), 21.2 (s, *p*-$CH_3C_6H_2$), 116.6 (s, C^4), 127.9 (s, C^3), 128.4 (s, *m*-C_6H_2), 128.8 (s, *p*-C_6H_5P), 129.5 (d, $^3J_{PC}$ = 12.4 Hz, *m*-C_6H_5P), 130.6 (s, *o*-C_6H_2), 130.9 (s, C^5), 131.7 (s, *p*-C_6H_2), 133.0 (d, $^2J_{PC}$ = 12.9 Hz, *o*-C_6H_5P), 133.4 (d, $^1J_{PC}$ = 12.9 Hz, *i*-C_6H_5P), 136.3 (s, C^2), 149.4 (s, *i*-C_6H_2), 156.7 (d, $^3J_{PC}$ = 7.7 Hz, CH=N); δ_P $\{^1H\}$ (121.5 MHz, $CDCl_3$) +64.4 (s); MS (FAB$^+$) *m*/*z* 539 (M − Cl)$^+$; IR (ATR, neat) 1590 (ν_{CN}).

(2,6-Diisopropylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine palladium dichloride 13d. To a stirred solution of $[PdCl_2(COD)]$ (0.30 g, 1.0 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **3d** (0.500 g, 1.2 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture was allowed to stir for 19 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3). Exposure to vacuum afforded **13d** (0.54 g, 84%) as a dark yellow crystalline solid; prolonged standing of a CH_2Cl_2 solution of **13d** gave rise to yellow cubic crystals suitable for X-ray analysis (Anal. Calc. for $C_{29}H_{31}N_2PPdCl_2$: C, 56.55; H, 5.08; N, 4.55. Found: C, 56.62; H, 4.94; N, 4.47%); δ_H (300.1 MHz, $CDCl_3$) 0.79 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 1.27 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 3.04 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, *o*-$((CH_3)_2CH)_2C_6H_3$), 6.53 (t, $^3J_{HH}$ = 3.3 Hz, 1H, H^4), 6.71 (s, 1H, H^3), 7.04 (m, 3H, *m*/*p*-C_6H_3), 7.19 (m, 1H, H^5), 7.47 (m, 4H, PC_6H_5), 7.57 (m, 6H, PC_6H_5), 7.78 (d, $^4J_{PH}$ = 3.3 Hz, 1H, CH=N); δ_C $\{^1H\}$ (75.5 MHz, $CDCl_3$): δ 23.4 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 24.6 (s, *o*-$((CH_3)_2CH)C_6H_3$), 28.9 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 116.3 (s, C^4), 123.6 (s, *m*-C_6H_3), 127.8 (s, C^3), 127.9 (s, *p*-C_6H_3), 128.6 (s, *o*-C_6H_3), 129.6 (d, $^3J_{PC}$ = 12.5 Hz, *m*-C_6H_5P), 130.4 (s, C^5), 132.1 (d, $^1J_{PC}$ = 12.5 Hz, *i*-C_6H_5P), 133.1 (d, $^2J_{PC}$ = 12.5 Hz, *o*-C_6H_5P), 134.1 (s, *p*-C_6H_5P), 141.3 (s, C^2), 148.6 (s, *i*-C_6H_3), 155.6 (d, $^3J_{PC}$ = 7.9 Hz, CH=N); $\delta_P\{^1H\}$ (121.5 MHz, $CDCl_3$) +65.5 (s); MS (FAB$^+$): *m*/*z* 579 (M − Cl)$^+$; IR (ATR, neat) 1597 (ν_{CN}).

(Bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)-phenylamine palladium chloride 14a. To a stirred solution of $[PdCl_2(COD)]$ (0.30 g, 1.1 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **4a** (0.500 g, 1.2 × 10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture was allowed to stir for 19 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3) and volatiles removed under vacuum to afford **14a** (0.41 g, 69%) as a dark yellow crystalline solid (Anal. Calc. for $C_{23}H_{37}N_4PPdCl_2$: C, 47.80; H, 6.47; N, 9.70. Found: C, 47.60; H, 6.51; N, 9.50); δ_H (300.1 MHz, $CDCl_3$) 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $((CH_3)_2CH)_2N)$), 1.48 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $((CH_3)_2CH)_2N)$), 4.38 (dsept, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 3.0 Hz, 4H, $((CH_3)_2CH)_2N)$), 6.50 (t, $^3J_{HH}$ = 3.3 Hz, 1H, H^4), 7.07 (m, 1H, H^3), 7.21 (m, 2H, *o*-C_6H_5), 7.26 (m, 3H, *m*/*p*-C_6H_5), 7.57 (m, 1H, H^5), 8.01 (d, $^4J_{PH}$ = 3.0 Hz, 1H, CH=N); δ_C $\{^1H\}$ (75.5 MHz, $CDCl_3$) 23.8 (d, $^3J_{CP}$ = 6.0 Hz, $((CH_3)_2CH)_2N)$, 25.1 (d, $^3J_{CP}$ = 6.0 Hz, $((CH_3)_2CH)_2N)$, 51.3 (d, $^2J_{PC}$ = 9.8 Hz, $((CH_3)_2CH)_2N)$, 114.2 (s, C^4), 123.7 (s, *o*-C_6H_5), 127.3 (s, *p*-C_6H_5), 128.8 (s, *m*-C_6H_5), 130.4 (s, C^3), 130.8 (s, C^5), 139.4 (s, C^2), 153.6 (s, *i*-C_6H_5), 154.9 (d, $^3J_{PC}$ = 7.5 Hz, CH=N); δ_P $\{^1H\}$

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

(121.5 MHz, $CDCl_3$) +81.3 (s); MS (FAB^+) m/z 541 $(M - Cl)^+$; IR (ATR, neat) 1601 (ν_{CN}).

(3,5-Dimethylphenyl)(bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)amine palladium dichloride 14b. To a stirred solution of [$PdCl_2$(COD)] (1.22 g, 4.3×10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **4b** (1.665 g, 4.7×10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture was allowed to stir for 19 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3) and solvent removed under vacuum to afford **14b** (0.57 g, 88%) as a dark yellow crystalline solid. Prolonged standing of a CH_2Cl_2 solution of **14b** gave rise to yellow cubic crystals suitable for X-ray analysis (Anal. Calc. for $C_{25}H_{41}N_4PPdCl_2$: C, 49.55; H, 6.83; N, 9.25. Found: C, 49.44; H, 6.92; N, 9.05%). δ_H (300.1 MHz, $CDCl_3$) 1.24 (d, $^3J_{HH} = 5.5$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.54 (d, $^3J_{HH} = 5.5$ Hz, 12H, $((CH_3)_2CH)_2N$), 2.32 (s, 6H, *m*-$CH_3C_6H_3$), 4.44 (d sept, $^3J_{HH} = 5.5$ Hz, $^3J_{PH} = 2.7$ Hz, 4H, $((CH_3)_2CH)_2N$), 6.51 (t, $^3J_{HH} = 3.3$ Hz, 1H, H^4), 6.88 (s, 1H, *p*-C_6H_3), 7.01 (s, 2H, *o*-C_6H_3), 7.08 (s, 1H, H^3), 7.61 (m, 1H, H^5), 8.04 (d, $^4J_{PH} = 3.0$ Hz, 1H, CH=N); δ_C $\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 21.6 (s, *m*-$CH_3C_6H_3$), 23.9 (d, $^3J_{CP} = 5.3$ Hz, $((CH_3)_2CH)_2N$), 25.2 (d, $^3J_{CP} = 5.3$ Hz, $((CH_3)_2CH)_2N$), 51.4 (d, $^2J_{PC} = 9.8$ Hz, $((CH_3)_2CH)_2N$), 114.4 (s, C^4), 121.7 (s, *o*-C_6H_3), 129.4 (s, *p*-C_6H_3), 129.5 (s, *m*-C_6H_3), 130.1 (s, C^3), 130.7 (s, C^5), 138.2 (s, C^2), 153.7 (s, *i*-C_6H_3), 154.8 (d, $^3J_{PC} = 7.6$ Hz, CH=N); δ_P $\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +81.6 (s); MS (FAB^+) m/z 571 $(M - Cl)^+$; IR (ATR, neat) 1600 (ν_{CN}).

(2,4,6-Trimethylphenyl)(bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)amine palladium dichloride 14c. To a stirred solution of [$PdCl_2$(COD)] (0.60 g, 2.1×10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **4c** (1.022 g, 2.3×10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture was allowed to stir for 19 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3) and volatiles removed under vacuum to afford **14c** (0.43 g, 33%) as a dark yellow crystalline solid (Anal. Calc. for $C_{26}H_{43}N_4PPdCl_2$: C, 50.36; H, 7.00; N, 9.04. Found: C, 50.25; H, 7.18; N, 9.22%); δ_H (500.0 MHz, $CDCl_3$) 1.29 (d, $^3J_{HH} = 7.0$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.53 (d, $^3J_{HH} = 7.0$ Hz, 12H, $((CH_3)_2CH)_2N$), 2.27 (s, 3H, *p*-$CH_3C_6H_2$), 2.28 (s, 6H, *o*-$CH_3C_6H_2$), 4.40 (dsept, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 2.1$ Hz, 4H, $((CH_3)_2CH)_2N$)), 6.54 (t, $^3J_{HH} = 3.0$ Hz, 1H, H^4), 6.84 (s, 2H, *m*-C_6H_2), 7.01 (s, 1H, H^3), 7.64 (s, 1H, H^5), 7.76 (d, $^4J_{PH} = 3.8$ Hz, 1H, CH=N); δ_C $\{^1H\}$ (125.5 MHz, $CDCl_3$) 19.4 (s, *o*-$CH_3C_6H_2$), 21.3 (s, *p*-$CH_3C_6H_2$), 24.2 (d, $^3J_{CP} = 4.6$ Hz, $((CH_3)_2CH)_2N$), 25.3 (d, $^3J_{CP} = 4.6$ Hz, $((CH_3)_2CH)_2N$), 51.2 (d, $^2J_{PC} = 9.1$ Hz, $((CH_3)_2CH)_2N$), 114.0 (s, C^4), 128.7 (s, *m*-C_6H_2), 129.0 (s, *p*-C_6H_2), 130.3 (s, C^3), 130.6 (s, *o*-C_6H_2), 131.2 (s, C^5), 132.6 (s, C^2), 150.2 (s, *i*-C_6H_2), 156.4 (d, $^3J_{PC} = 7.3$ Hz, CH=N); δ_P $\{^1H\}$ (162.0 MHz, $CDCl_3$) +81.4 (s); MS (FAB^+) m/z 583 $(M - Cl)^+$; IR (ATR, neat) 1605 (ν_{CN}).

(2,6-Diisopropylphenyl)(bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)amine palladium dichloride 14d. To a stirred solution of [$PdCl_2$(COD)] (0.49 g, 1.7×10^{-3} mol) in CH_2Cl_2 (10 cm^3), a solution of **4d** (0.89 g, 1.8×10^{-3} mol) in CH_2Cl_2 (10 cm^3) was added *via* cannula and the mixture was allowed to stir for 18 h. The volatile components were then removed *in vacuo* and the yellow–orange oil extracted with hexane (20 cm^3) to afford **14d** (0.95 g, 85%) as a dark yellow crystalline solid following removal of volatiles under vacuum (Anal. Calc. for $C_{29}H_{49}N_4PPdCl_2$: C, 52.60, H, 7.47; N, 8.46. Found: C, 52.98; H, 7.34; N, 8.02%); δ_H (250.1 MHz, $CDCl_3$) 1.11 (d, $^3J_{HH} = 6.9$ Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 1.31 (d, $^3J_{HH} = 6.7$ Hz, 12H, $((CH_3)_2CH)_2N$), 1.42 (d, $^3J_{HH} = 6.9$ Hz, 6H, *o*-$((CH_3)_2CH)_2C_6H_3$), 1.47 (d, $^3J_{HH} = 6.7$ Hz, 12H, $((CH_3)_2CH)_2N$), 3.22 (sept, $^3J_{HH} = 6.9$ Hz, 2H, *o*-$((CH_3)_2CH)_2C_6H_3$), 4.47 (dsept, $^3J_{HH} = 6.9$ Hz, $^3J_{PH} = 2.0$ Hz, 4H, $((CH_3)_2CH)_2N$), 6.59 (t, $^3J_{HH} = 3.0$ Hz, 1H, H^4), 7.01 (m, 1H, H^3), 7.12 (s, 1H, *p*-C_6H_3), 7.15 (s, 2H, *m*-C_6H_3), 7.83 (d, $^4J_{PH} = 4.1$ Hz, 1H, CH=N); δ_C $\{^1H\}$ (100.1 MHz, $CDCl_3$) 22.0 (d, $^3J_{PC} = 4.4$ Hz, $((CH_3)_2CH)_2N$), 23.2 (d, $^3J_{PC} = 4.4$ Hz, $((CH_3)_2CH)_2N$), 26.9 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 45.5 (s, *o*-$((CH_3)_2CH)_2C_6H_3$), 49.1 (d, $^2J_{PC} = 9.6$ Hz, $((CH_3)_2CH)_2N$), 113.8 (s, C^4), 122.6 (s, *m*-C_6H_3), 126.9 (s, *p*-C_6H_3), 127.7 (s, *o*-C_6H_3), 130.2 (s, C^3), 131.1 (s, C^5), 140.6 (s, C^2), 149.2 (s, *i*-C_6H_3), 155.4 (d, $^3J_{PC} = 8.8$ Hz, CH=N); δ_P $\{^1H\}$ (121.5 MHz, $CDCl_3$) +80.9 (s); MS (FAB^+): m/z 625 $(M - Cl)^+$; IR (ATR, neat) 1599 (ν_{CN}).

(Phenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine nickel dibromide 15a. To a suspension of [$NiBr_2$(DME)] (0.14 g, 4.7×10^{-4} mol) in CH_3CN (10 cm^3) was added a solution of **3a** (0.29 g, 8.2×10^{-4} mol) in CH_3CN (10 cm^3) *via* cannula and the mixture stirred vigorously for 3 h. The precipitated solid was then isolated by filtration and residual volatile components removed *in vacuo*. The red–brown solid was then washed twice with hexane (2×5 cm^3) to afford **15a** as a brown/green powder following drying under vacuum (0.16 g, 59%) (Anal. Calc. for $C_{23}H_{19}N_2PNiBr_2$: C, 48.22; H, 3.35; N, 4.89. Found: C, 48.41; H, 3.39; N, 4.81%). MS (MALDI) m/z 493 $(M - Br)^+$; IR (ATR, neat) 1596 (ν_{CN}).

(3,5-Dimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine nickel dibromide 15b. To a solution of [$NiBr_2$(DME)] (0.30 g, 9.8×10^{-4} mol) in CH_3CN (10 cm^3) was added a solution of **3b** (0.38 g, 9.8×10^{-4} mol) in CH_3CN (10 cm^3) *via* cannula and then stirred vigorously for 3 h. The brown solid was then isolated by filtration and then washed twice with hexane (2×5 cm^3) to afford **15b** (0.27 g, 47%) as a brown powder following drying under vacuum (Anal. Calc. for $C_{25}H_{23}N_2PNiBr_2$: C, 49.96; H, 3.87; N, 4.67. Found: C, 50.25; H, 3.78; N, 4.55%); MS (ES^+): m/z 521 $(M - Br)^+$; IR (ATR, neat) 1596 (ν_{CN}).

To a solution of [$NiBr_2$(DME)] (0.16 g, 5.3×10^{-4} mol) in CH_3CN (10 cm^3) was added a solution of **3c** (0.21 g, 5.3×10^{-4} mol) in CH_3CN (10 cm^3) *via* cannula and then stirred vigorously for 3 h. Volatile components were then removed *in vacuo* to afford a brown solid that was then washed twice with hexane (2×5 cm^3) to afford **15c** (0.16 g, 50%) as a brown powder following drying under vacuum (Anal. Calc. for $C_{26}H_{25}N_2PNiBr_2$: C, 50.77; H, 4.11; N, 4.56. Found: C, 51.01; H, 4.35; N, 4.39%). MS (MALDI) m/z 535 $(M - Br)^+$; IR (ATR, neat) not assignable.

(2,6-Diisopropylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine nickel dibromide 15d. To a solution of [$NiBr_2$(DME)] (0.14 g, 4.5×10^{-4} mol) in CH_3CN (10 cm^3) was added a solution of **3d** (0.20 g, 4.5×10^{-4} mol) in CH_3CN (10 cm^3) *via* cannula and then stirred vigorously for 3 h. The mixture was then filtered and the volatile components removed *in vacuo*. The

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

brown solid was then washed twice with hexane to afford **15d** (0.21 g, 70%) as a green powder following drying under vacuum (Anal. Calc. for $C_{29}H_{31}N_2PNiBr_2$: C, 52.13; H, 4.85; N, 4.34. Found: C, 51.75; H, 5.03; N, 4.58%). MS (MALDI) m/z 577 $(M - Br)^+$; IR (ATR, neat) not assignable.

Alternative preparation of (3,5-dimethylphenyl)(1-diphenylphosphanyl-1*H*-pyrrol-2-ylmethylene)amine nickel dibromide 15b. To a solution of $[NiBr_2(PPh_3)_2]$ (0.50 g, 0.7×10^{-3} mol) in MeCN (10 cm^3) was added **3b** (0.26 g, 0.7×10^{-3} mol) in MeCN (10 cm^3) and the mixture allowed to stir at RT for 18 h, the solution rapidly changing colour from green to brown. Volatile components were removed *in vacuo* and the brown solid extracted with hexane (3×20 cm^3) and the resulting solid dried under reduced pressure to afford **15b** (0.29 g, 71%) as a dark red/brown powder.

Attempted preparation of (bis(diisopropyl)aminophosphanyl)(1*H*-pyrrol-2-ylmethylene)phenylamine nickel dibromide

This reaction was undertaken using a procedure analogous to that with **3** (above) using $[NiBr_2(DME)]$ (0.30 g, 9.7×10^{-4} mol) and **4b** (0.43 g, 1.1×10^{-3} mol). Following work-up, a green paramagnetic solid was isolated (0.17 g), whose structure could not be elucidated from the available analytical data, together with $Pr^i_2NH_2Br$.

Bis{(2,4,6-trimethylphenyl)(pyrrolato)}nickel 16. To a solution of $[NiBr_2(DME)]$ (0.16 g, 5.3×10^{-4} mol) in CH_2Cl_2 (10 cm^3) was added a solution of **3c** (0.21 g, 5.3×10^{-4} mol) in CH_3CN (10 cm^3) *via* cannula and then stirred vigorously for 3 h to give a clear red solution. Volatile components were then removed *in vacuo* to afford a red solid that was then washed twice with hexane (2×5 cm^3) to afford **16** (0.11 g, 45%) as a brown powder following drying under vacuum (Anal. Calc. for $C_{26}H_{25}N_2PNiBr_2$: C, 69.87; H, 6.30; N, 11.64. Found: C, 69.90; H, 6.30; N, 11.83%). δ_H (300.0 MHz, $CDCl_3$) 2.29 (s, 3H, *p*-ArCH_3), 2.60 (s, 3H, *o*-ArCH_3), 4.75 (s, 1H, H^4), 5.78 (s, 1H, H^3), 6.59 (m, 1H, H^5), 6.89 (s, 2H, *m*-ArH), 7.17 (s, 1H, CH=N); δ_C {^{1}H} (100.6 MHz, $CDCl_3$) 19.4 (s, *o*-ArCH_3), 21.3 (s, *p*-ArCH_3) 112.6 (s, C4), 118.1 (s, C^3), 129.3 (s, *m*-ArC), 133.2 (s, *o*-ArC), 136.2 (s, *p*-ArC), 136.9 (s, C^5), 140.7 (s, *i*-ArC), 144.9 (s, C^2), 162.4 (s, CH=N); MS (MALDI) m/z 482 $(MH)^+$; IR (ATR, neat) 1592 (ν_{CN}).

Ethylene polymerisation testing protocol

Under the conditions described in procedures **1–3** (below) the proinitiators $NiBr_2(PPh_3)_2$ and $PdCl_2(MeCN)_2$ proved inactive.

Procedure 1. In a Schlenk, toluene solutions (100 cm^3) of complexes **13** or **14** (5.0×10^{-5} mol) were treated with 500 equivalents of MAO (10 wt% in toluene) at ambient temperature. This led to an immediate colour change from yellow/orange to brown. The initiator/activator solutions were aged for a period of 10 min under nitrogen. Subsequently, three cycles of vacuum/ethylene (1.0 bar) were applied to the reaction vessel, before it was pressurised with ethylene (1.0 bar) and then stirred rapidly for 0.5 h. The mixture was then quenched by the cautious addition of aqueous 1.0 M HCl and methanol prior to aqueous/organic extraction. GC/MS and ^{1}H NMR spectroscopic analyses of the organic phases were undertaken.

Procedure 2. An autoclave was charged with toluene solutions (20 cm^3) of complexes **13** or **14** (5.0×10^{-5} mol) under nitrogen. Subsequently, 4.5 equivalents of $EtAlCl_2$ (0.1 cm^3, 1.8 M, in toluene) was added under nitrogen and the mixture aged for 20 min. The reactor vessel was then pressurised with ethylene (10 bar) for a period of 3 h at ambient temperature. On releasing the pressure, the resulting mixtures were cautiously hydrolysed by addition of 1.0 M HCl and methanol prior to aqueous/organic extraction. GC/MS and ^{1}H NMR spectroscopic analyses of the organic phases were undertaken.

Procedure 3. A Schlenk was charged with toluene solutions (20 cm^3) of complexes **15** or **16** (5.0×10^{-5} mol) under nitrogen. Subsequently, 4.5 equivalents of $EtAlCl_2$ (0.1 cm^3, 1.8 M, in toluene) was added under nitrogen and the mixture aged for 20 min. The vessel was then pressurised with ethylene (1.0 bar) for a

Table 6 Crystallographic data for complexes **13d**, **14b** and **16**

Compound	**13d**	**14b**	**16**
Formula	$C_{29}H_{31}Cl_2N_2PPd$	$C_{25}H_{41}Cl_2N_4PPd{\cdot}2CH_2Cl_2$	$C_{28}H_{30}N_4Ni$
M	615.83	775.74	481.27
T/K	150(2)	150(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group (no.)	$C2/c$ (15)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a/Å	32.505(4)	13.742(3)	10.031(1)
b/Å	9.9996(11)	17.691(4)	12.921(1)
c/Å	17.8876(19)	14.077(3)	13.951(1)
α/°	90	90	92.56(1)
β/°	102.609(2)	91.965(4)	93.53(1)
γ/°	90	90	91.99(1)
U/Å^3	5673.9(11)	3420.5(12)	1801.7(3)
Z	8	4	3
D_c/g cm^{-3}	1.442	1.506	1.331
μ/mm^{-1}	0.919	1.082	0.83
Crystal size/mm	$0.29 \times 0.21 \times 0.18$	$0.34 \times 0.11 \times 0.04$	$0.37 \times 0.28 \times 0.08$
Reflections collected	21726	26447	24988
Independent reflections	5569	6713	9511
R_{int}	0.0260	0.0643	0.069
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0251, 0.0648	0.0454, 0.0895	0.0385, 0.0881
R Indices (all data)	0.0274, 0.0660	0.0665, 0.0960	0.0565, 0.0943

 This journal is © The Royal Society of Chemistry 2006

View Article Online

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

period of 30 min at ambient temperature. After 5 min, the reaction became extremely exothermic causing the reaction mixture to reach *ca.* 80 °C. At the end of the test period, the pressure was released and nonane (1.00 cm^3) was added and GC/MS analysis of the organic phases undertaken immediately.

Ethylene/carbon monoxide co-polymerisation testing protocol. An autoclave was charged with toluene solutions (50 cm^3) of complexes **13** or **14** (18.0×10^{-5} mol) under nitrogen, followed by addition of methane sulfonic acid (50 μL, 7.2×10^{-4} mol). Subsequently, the reactions were heated to 90 °C under a 1 : 1 $CO–C_2H_4$ atmosphere (40 bar) for periods of 3 h. Upon depressurisation, the contents of the autoclave were filtered and the organic phase subject to GC-MS analysis.

Crystallography

X-Ray diffraction data (Table 6) were collected on Bruker diffractometers equipped with Apex 2 K (for **13d** and **14b**) or SMART 1 K (for **16**) CCD area detectors and Oxford Cryostream N_2 cooling devices, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection and reduction were conducted using the SMART and SAINT programs,[72] respectively. Absorption corrections were applied for **13d** and **14b** by semi-empirical methods,[74] and for **16** by numerical integration based on crystal face-indexing.[73] The structures were solved by Patterson (**13d**, **14b**) or direct (**16**) methods and refined by full-matrix least squares based on F^2, using the SHELXTL package and programs therein.[75] All non-hydrogen atoms were refined anisotropically, then hydrogen atoms included at idealised positions and refined as rigid groups.

CCDC reference numbers 617735–617737.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611652c

Acknowledgements

The Royal Society and The Nuffield Foundation are thanked for grants to P. W. D. Johnson Matthey Plc. is thanked for the generous loan of palladium salts. Financial support from Leicester and Durham Universities (C. E. A. and P. W. D.) is gratefully acknowledged. Mr D. Hunter (Durham University) is thanked for his assistance with high pressure reactions.

References

1 P. J. Guiry and C. P. Saunders, *Adv. Synth. Catal.*, 2004, **346**, 497.
2 P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193–195**, 499.
3 M. S. Rahman, P. D. Prince, J. W. Steed and K. K. Hii, *Organometallics*, 2002, **21**, 4927.
4 S. Naili, A. Mortreux and F. Agbossou, *Tetrahedron: Asymmetry*, 1998, **9**, 3421.
5 F. Speiser and P. Braunstein, *Organometallics*, 2004, **23**, 2625.
6 K. S. Coleman, M. L. H. Green, S. I. Pascu, N. H. Rees, A. R. Cowley and L. H. Rees, *J. Chem. Soc., Dalton Trans.*, 2001, 3384.
7 P. Braunstein, M. D. Fryzuk, M. Le Dall, F. Naud, S. J. Rettig and F. Speiser, *J. Chem. Soc., Dalton Trans.*, 2000, 1067.
8 K. R. Reddy, W.-W. Tsai, K. Surekha, G.-H. Lee, S.-M. Peng, J.-T. Chen and S.-T. Liu, *J. Chem. Soc., Dalton Trans.*, 2002, 1776.
9 A. D. Burrows, M. F. Mahon and M. Varrone, *Dalton Trans.*, 2003, 4718.
10 P. W. Dyer, J. Fawcett and M. J. Hanton, *J. Organomet. Chem.*, 2005, **690**, 5264.
11 E. K. van den Beuken, W. J. J. Smeets, A. L. Spek and B. L. Ferringa, *Chem. Commun.*, 1998, 223.
12 K. R. Reddy, K. Surekha, G.-H. Lee, S.-M. Peng and S.-T. Liu, *Organometallics*, 2000, **19**, 2637.
13 P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680.
14 G. Helmchen and A. Pfaltz, *Acc. Chem. Res.*, 2000, **33**, 336.
15 A. Schnyder, A. Togni and U. Wiesli, *Organometallics*, 1997, **16**, 255.
16 K. N. Gavrilov, O. G. Bondarev, R. V. Lebedev, A. A. Shiryaev, S. E. Lyubimov, A. I. Polosukhin, G. V. Grintselev-Knyazev, K. A. Lyssenko, S. K. Moiseev, N. S. Ikooikov, V. N. Kalinin, V. A. Davankov, A. V. Korostylev and H.-J. Gais, *Eur. J. Inorg. Chem.*, 2002, 1367.
17 E. J. Zijp, J. I. van der Vlugt, D. M. Tooke, A. L. Spek and D. Vogt, *Dalton Trans.*, 2005, 512.
18 J. Ansell and M. Wills, *Chem. Soc. Rev.*, 2002, **31**, 259.
19 M. Alajarín, C. López-Leonardo and P. Llamas-Lorente, *Top. Curr. Chem.*, 2005, **250**, 77.
20 P. W. Dyer, J. Fawcett, M. J. Hanton, R. D. W. Kemmitt, R. Padda and N. Singh, *Dalton Trans.*, 2003, 104.
21 M. L. Clarke, G. L. Holliday, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2002, 1093.
22 M. R. i Zubiri and J. D. Woollins, *Comments Inorg. Chem.*, 2003, **24**, 189.
23 M. L. Clarke, D. J. Cole-Hamilton, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.*, 2000, 2065.
24 K. G. Moloy and J. L. Petersen, *J. Am. Chem. Soc.*, 1995, **117**, 7696.
25 H. Brunner and H. Weber, *Chem. Ber.*, 1985, **118**, 3380.
26 P. G. Cozzi, N. Zimmermann, R. Hilgraf, S. Schaffner and A. Pfaltz, *Adv. Synth. Catal.*, 2001, **343**, 450.
27 S. C. van der Slot, J. Duran, J. Luten, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Organometallics*, 2002, **21**, 3873.
28 A. D. Burrows, R. W. Harrington, M. F. Mahon, M. T. Palmer, F. Senia and M. Varrone, *Dalton Trans.*, 2003, 3717.
29 C. D. Andrews, A. D. Burrows, J. M. Lynam, M. F. Mahon and M. T. Palmer, *New J. Chem.*, 2001, **25**, 824.
30 H. Brunner, B. Reiter and G. Riepl, *Chem. Ber.*, 1984, **117**, 1330.
31 F. Dahan, P. W. Dyer, M. J. Hanton, M. Jones, D. M. P. Mingos, A. J. P. White, D. J. Williams and A.-M. Williamson, *Eur. J. Inorg. Chem.*, 2002, 732.
32 C. E. Anderson, M.Phil. Thesis, University of Leicester, 2003; C. E. Anderson, D. C. Apperley, A. S. Batsanov, P. W. Dyer and J. A. K. Howard, *Dalton Trans.*, 2006, 4134.
33 R. A. Jones, *Aust. J. Chem.*, 1963, **13**, 93.
34 R. Jackstell, H. Klein, M. Beller, K.-D. Wiese and D. Roettger, *Eur. J. Org. Chem.*, 2001, **20**, 3871.
35 *Heterocyclic Chemistry*, ed. J. A. Joule and G. F. Smith, Van Nostrand, New York, 2nd edn, 1978, p. 209.
36 *Spectroscopic Methods in Organic Chemistry*, ed. D. H. Williams and I. Fleming, University Press, Cambridge, UK, 3rd edn, 1995, p. 100.
37 S. Vastag, B. Heil and L. Marko, *J. Mol. Catal.*, 1979, **5**, 189.
38 A. J. Naaktgeboren, R. J. M. Nolte and W. Drenth, *J. Am. Chem. Soc.*, 1980, **102**, 3350.
39 W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1990, 3611.
40 R. D. Kroshefsky, R. Weiss and J. G. Verkade, *Inorg. Chem.*, 1979, **18**, 469.
41 B. Wrackmeyer, *Spectrochim. Acta, Part A*, 1984, **40**, 963.
42 S. Serron, J. Huang and S. P. Nolan, *Organometallics*, 1998, **17**, 534.
43 K. A. Bunten, D. H. Farrar, A. J. Poë and A. Lough, *Organometallics*, 2002, **21**, 3344.
44 N. G. Anderson and B. A. Keay, *Chem. Rev.*, 2001, **101**, 997.
45 D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51.
46 A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 1707.
47 D. B. Grotjahn, S. Van, D. Combs, D. A. Lev, C. Schneider, C. D. Incarvito, K.-C. Lam, G. Rossl, A. L. Rheingold, M. Rideout, C. Meyer, G. Hernandez and L. Mejorado, *Inorg. Chem.*, 2003, **42**, 3347.
48 H. A. Ankersmit, B. H. Loken, H. Kooijman, A. L. Spek, K. Vrieze and G. Van Koten, *Inorg. Chim. Acta*, 1996, **252**, 141.
49 A. J. Blacker, M. L. Clarke, M. S. Loft, M. F. Mahon, M. E. Humphries and J. M. J. Williams, *Chem. Eur. J.*, 2000, **6**, 353.
50 M. Brookhart, L. K. Johnson and C. M. Killian, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
51 M. Brookhart, L. K. Johnson, C. M. Killian and D. J. Tempel, *J. Am. Chem. Soc.*, 1996, **118**, 11664.
52 S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169.

View Article Online

53 M. J. Tenorio, M. C. Puerta, I. Salcedo and P. Valerga, *J. Chem. Soc., Dalton Trans.*, 2001, 653.
54 S. Priya, M. S. Balakrishna and J. T. Mague, *J. Organomet. Chem.*, 2003, **679**, 116.
55 W. J. Birdsall, D. P. Long, S. P. E. Smith, M. E. Kastner, K. Tang and C. Kirk, *Polyhedron*, 1994, **13**, 2055.
56 H. Liang, J. Liu, X. Li and Y. Li, *Polyhedron*, 2004, **23**, 1619.
57 B. de Bruin, P. H. M. Budzelaar, A. W. Gal, J. H. van Lenthe and K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4649.
58 N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3**, 3.
59 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
60 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
61 F. Speiser, P. Braunstein and L. Saussine, *Acc. Chem. Res.*, 2005, **38**, 784, and references therein.
62 H.-P. Chen, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Organometallics*, 2003, **22**, 4893.
63 Z. Guan and W. J. Marshall, *Organometallics*, 2002, **21**, 3580.
64 R. F. de Souza, K. Bernardo-Gusmão, G. A. Cunha, C. Loup, F. Leca and R. Réau, *J. Catal.*, 2004, **226**, 235.
65 F. Speiser, P. Braunstein and L. Saussine, *Dalton Trans.*, 2004, 1539.
66 J. R. Doyle and D. Drew, *Inorg. Synth.*, 1990, **28**, 346.
67 R. B. King and N. D. Sadanani, *Synth. React. Org. Met.-Org. Chem.*, 1985, **15**, 149.
68 *Synthesis of Organometallic Compounds—A Practical Guide*, ed. S. Komiya, Wiley-Interscience, New York, 1998, p. 285.
69 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.
70 W. M. McFarlane and J. A. Nash, *Chem. Commun.*, 1969, 913.
71 V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2002, 4017.
72 *Bruker SMART (v 5.622, 2001) and SAINT-Plus (v 6.02, 1999)*, Bruker AXS Inc., Madison, WI, USA.
73 G. M. Sheldrick, *SHELXTL (v 6.1*, 2000), Bruker AXS Inc., Madison, WI, USA.
74 G. M. Sheldrick, *SADABS, Program for the Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.
75 G. M. Sheldrick, *SHELXTL version 6.14, Bruker AXS*, Madison WI, USA, 2003.

Published on 02 October 2006. Downloaded by Universitat Autonoma de Barcelona on 22/10/2014 14:20:58.

This journal is © The Royal Society of Chemistry 2006