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FULL PAPER

Palladium(II) complexes with the bidentate iminophosphine ligand [$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$]

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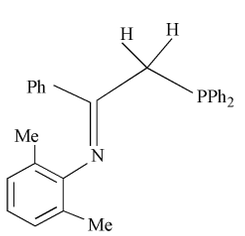
A new iminophosphine ligand, [$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$] (HL), and the complexes [PdX_2(HL)], where X = Cl (**1**) and Br (**2**), [PdMeX(HL)], X = Cl (**3**) and Br (**4**), and [$PdMe_2$(HL)] (**5**) have been prepared and characterised. Reaction of **2** with MeLi or KH leads to deprotonation of the neutral ligand to give [$Pd_2(\mu\text{-}Br)_2(L^-)_2$], (**6**), where L^- is [Ph_2PCH=$C(Ph)N(2,6\text{-}Me_2C_6H_3)]^-$. Similarly, reaction of **3** with KH and triphenylphosphine affords the neutral complex [$PdMe(PPh_3)(L^-)$] (**7**). Insertion of CO into the Pd–Me bond has been investigated, as well as the catalytic properties of [PdClMe(HL)] towards CO/ethylene copolymerisation. The crystal structures of HL, **1**–**3** and **5**–**7** have been determined.

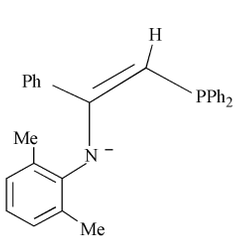
Introduction

Transition metal complexes of hybrid ligands containing P and N or O donor atoms are of interest[1] since, with group 10 metals, such heteroditopic ligands can exhibit hemi-labile character. Such behaviour has been exploited in homogeneous catalysis and in the activation of small molecules, as the formation and stabilisation of intermediate species is often facilitated.[2,3] Ni complexes of P/O ligands have been investigated as promising catalysts for the oligomerisation of olefins, as in the Shell higher olefin process (SHOP).[4,5] Similarly, group 10 transition metals with P- and N-based donor ligands have been found to be active catalysts for polymerisation of ethene and propene, giving rise to a new generation of polymers.[6] Although a variety of N/P ligand systems have been studied,[7] only a small number of bidentate $N(sp^2)$–$P(sp^3)$ ligands, mainly oxazoline and imidazolyl based, and transition metal complexes thereof have been described.[8–19] The synthesis and reactivity of new N/P ligands and their coordination to late transition metals continues to attract intrest owing to the possibility of tailoring the steric and electronic properties of the different donor groups. Recently, oxazoline-based N/P ligands, when coordinated to Pd(II) centres, have shown some activity in the copolymerisation of carbon monoxide and olefins, a reaction typically confined to bidentate phosphine and imine systems.[13]

Herein, we describe the synthesis and reactivity of a novel iminophosphine ligand with a flexible backbone, HL, and the preparation of the corresponding Pd(II) complexes. The activity of the Pd(II) complexes toward the copolymerisation of CO and ethylene is discussed.



HL



L^-

Results and discussion

Synthesis and characterisation of the ligand [$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$] HL

The iminophosphine ligand [$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$], HL, was prepared in a two-step process, as shown in Scheme 1. The arylimine [$MeC(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$] was reacted with lithium diisopropylamide (LDA) at −78 °C and, after stirring for 1 h, a pre-cooled solution of Ph_2PCl was added to afford ligand HL as a white solid. HL was characterised by elemental analysis, mass spectrometry (FAB^+) and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy using COSY, HSQC, HMBC, NOESY and $^1H\{^{31}P\}$ experiments. NMR spectroscopy indicated the presence of two species in solution, Tables 1 and 2. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) exhibits two signals, both singlets, at δ −14.4 and −19.8, in the ratio 85 : 15. This can be attributed to the presence of the *E* and *Z* isomers. Although no exchange broadening was detected in the room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra, the presence of exchange peaks in the room temperature NOESY spectrum showed that the two species were in slow exchange. The effects of exchange were eliminated by cooling to −40 °C. From particular diagnostic nOes, the major species was assigned to the *E* isomer (correlations were observed between the signal for $Me_2C_6H_4N$ and each of the signals for CH_2 and PPh_2-*o*) and the minor species to the *Z* isomer (a correlation was observed between the $Me_2C_6H_4N$ and Ph-*o* signals). Imines, and particularly *N*-aryl imines, are known to isomerise in solution *via* a lateral shift mechanism. This involves the shift of the substituent attached to nitrogen from one side of the molecule to the other through a linear transition state.[20] The rate of *E*–*Z* isomerisation was determined from variable temperature $^{31}P\{^1H\}$ NMR selective inversion transfer experiments,[21] and from the Eyring plot the barrier to isomerisation was calculated to be 62.8 kJ mol^{-1} (Fig. 1). This was further confirmed by line shape analysis.

Molecular structure of ligand HL

Crystals of HL, [$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$], suitable for single-crystal X-ray diffraction were obtained by slowly cooling a toluene solution of the compound. An ORTEP view of the

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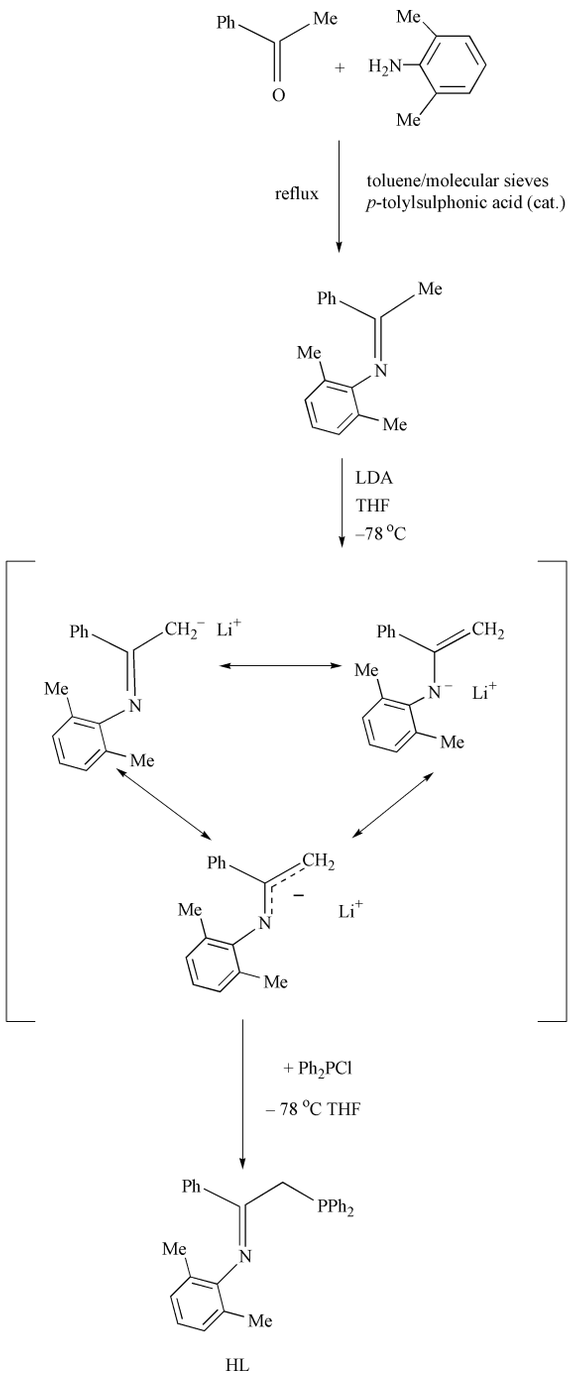


Scheme 1 Synthesis of the neutral N/P ligand [(2,6-$Me_2C_6H_3$)N=C(Ph)CH_2PPh_2], HL.

molecular structure of HL is shown in Fig. 2, with selected bond lengths and angles listed in Table 3. The C(1)–N(1) bond is 1.273(2) Å, consistent with significant double bond character and the bond angles at both C(1) and N(1) atoms are indicative of sp^2 centres. The C(1)–C(2) bond of the backbone is 1.504(2) Å, indicating a typical carbon–carbon single bond. The phosphorus–phenyl P–C bond lengths are 1.818(2) and 1.829(2) Å and the phosphorus–CH_2 P–C bond length is 1.862(2) Å, as expected for free tertiary phosphines. In the solid state, ligand HL adopts the *E* isomer configuration. The *E* isomer is presumably the energetically favoured isomer for steric reasons, this was supported by simple molecular mechanics calculations using the CAChe software package.[22] Similarly, *E* was the major isomer in solution, as detected by NMR spectroscopy.

Palladium(II) complexes

The metal complexes [PdX_2(HL)], where X = Cl (**1**) and Br (**2**)

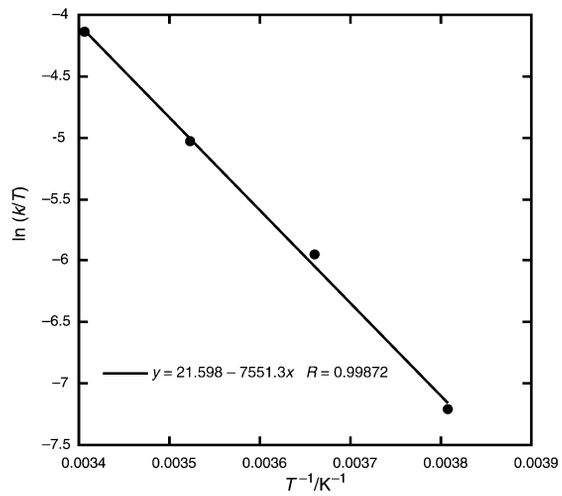


Fig. 1 Estimation of the isomerisation barrier *E*/*Z* of ligand HL by an Eyring plot: $\Delta H^{\#} = 62.8$ kJ mol^{-1}; $\Delta S^{\#} = -17.9 \times 10^{-3}$ kJ mol^{-1} K^{-1} and $\Delta G^{\#}$ (273 K) = 67.68 kJ mol^{-1}. [Eyring plot: $\ln(K/T) = -\Delta H^{\#}/RT + \Delta S^{\#}/R + 23.76$.]

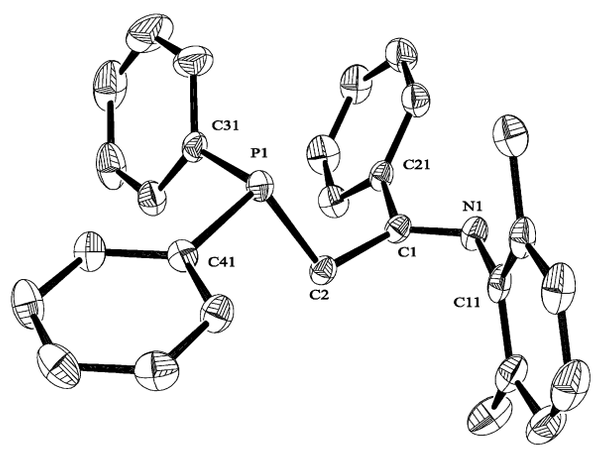
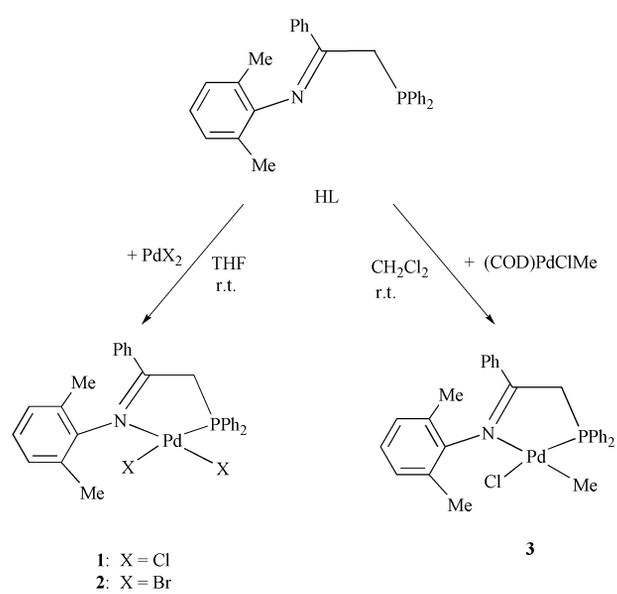


Fig. 2 ORTEP diagram of the molecular structure of HL (major isomer *E*).



Scheme 2 Synthesis of compounds **1**–**3**.

were prepared from the reaction of PdX_2, where X = Cl and Br, respectively, with 1 molar equivalent of ligand HL, as shown in Scheme 2. Similarly, the neutral complex [PdMeCl(HL)] **3**, where HL = [$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)] was prepared by reacting [PdMeCl(COD)] with HL in CH_2Cl_2 at room

Table 1 ^{1}H and $^{31}P\{^{1}H\}$ NMR data (CD_2Cl_2) of neutral ligand HL and complexes thereof (chemical shifts in ppm and coupling constants in Hz)[a]

		HL(major)	HL(minor)	**1**	**2**	**3**	**4**	**5**[b]	**8**[c]	**9**
	X	—	—	Cl	Br	Cl	Br	Me	MeCN	Cl
	Y	—	—	Cl	Br	Me	Me	Me	Me	MeC=O
$^{31}P\{^{1}H\}$		−14.4	−19.8	43.8	43	40.9	40.3	21.3	42.5	22.3
^{1}H										
$Me_2C_6H_3N$	*o*-Me	1.95	1.78	2.11	2.02	2.02	2.03	2.02	2.08	2.03
	m-H	7.02	6.82	6.90	6.81	6.90	6.88	6.77	7.03	6.90
	p-H	6.96	6.75	6.99	6.89	6.90	6.88	6.77	7.03	6.90
Ph	*o*-H	7.84	7.12	7.03	6.95	7.03	7.02	6.74	7.16	7.01
	m-H	7.38	7.22	7.23	7.13	7.20	7.19	6.74	7.27	7.21
	p-H	7.45	7.27	7.34	7.27	7.31	7.30	6.80	7.40	7.31
CH_2–P		3.43	3.81	4.27	4.24	4.15	4.16	3.47	4.37	4.13
PPh_2	*o*-H	7.16	7.56	7.93	7.84	7.56	7.75	7.64	7.75	7.81
	m-H	7.16	7.37	7.59	7.49	7.78	7.55	7.11	7.62	7.56
	p-H	7.30	7.27	7.69	7.59	7.61	7.59	7.11	7.68	7.61
X	Me							0.28	2.09	
Y	Me					0.66	0.78	1.20	0.56	2.26
$^{2}J_{P–CH_2}$		2.6	1.1	12.8	12.9	11.2	11.1	7.5	11.6	10.8
$^{3}J_{P–Ph\text{-}o}$		7.5	7.5	13.2	12.9	12.2	13.3	11.7	12.7	12.3
$^{4}J_{P–Ph\text{-}m}$		1.6		3.0	3.0	1.5	2.7		2.7	2.1
$^{5}J_{P–Ph\text{-}p}$		0.9		2.1	2.3	2.2	2.1		2.3	2.3
$^{3}J_{P–Pd–Me}$	*trans*							7.6		
	cis					2.9	3.3	8.7	1.9	
$^{4}J_{P–Pd–C–Me}$										1.3

[a] Assignments assisted by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectroscopy, using COSY, HSQC, HMBC (HL, **1**–**5**, **8**, **9**), as well as NOESY and $^{1}H\{^{31}P\}$ experiments (HL major and minor); ROESY (**1**–**5**), nOe difference experiments (**3**, **5**, **9**). [b] NMR data recorded in d^8-toluene. [c] ^{11}B NMR: δ −0.66, ^{19}F NMR: δ −153.15.

Table 2 $^{13}C\{^{1}H\}$ NMR data (CD_2Cl_2) of neutral ligand HL and complexes thereof (chemical shifts in ppm and coupling constants in Hz)[a]

		HL(major)	HL(minor)	**1**	**2**	**3**	**4**	**5**[b]	**8**	**9**
	X	—	—	Cl	Br	Cl	Br	Me	MeCN	Cl
	Y	—	—	Cl	Br	Me	Me	Me	Me	MeC=O
$Me_2C_6D_6N$										
	i	148.80	148.73	146.19	146.82	146.15	146.46	146.70	145.59	145.57
	o	126.47	126.15	130.55	130.37	129.07	129.03		128.82	129.06
	o-Me	18.41	18.43	19.03	19.29	18.95	19.15	18.77	18.60	19.04
	m-H	128.39	127.90	128.05	127.88	127.75	127.68		127.52	127.85
	p-H	123.31	126.75	127.46	127.22	125.63	125.60		126.62	125.61
N=C		166.26	167.24	182.16	181.37	174.94	174.97	174.94	176.88	174.68
Ph	*i*	139.17	138.66	133.17	133.00	135.47	135.41	134.02	133.78	135.55
	o-H	128.30	127.17	127.29	127.21	127.03	126.94		128.64	127.01
	m-H	128.49	—	128.84	128.65	128.57	128.49	129.83	128.98	128.62
	p-H	130.54	129.40	131.99	131.75	130.90	130.80		132.06	131.04
CH_2–P		32.28	41.72	48.11	48.94	47.61	47.60	45.12	47.92	45.75
PPh_2	*i*	138.26	139.03	126.39	126.71	129.31	128.81		127.01	127.67
	o-H	133.07	133.28	133.47	133.43	133.44	133.34	133.20	133.42	133.18
	m-H	128.86	—	129.77	129.50	129.54	129.49	130.12	129.97	129.65
	p-H	129.27	—	133.16	132.92	131.96	131.91		132.87	131.93
X	Me *trans*							9.43	2.24	
	CN								119.42	
Y	Me *cis*					−4.73	−6.15	−9.19	−3.90	19.00
	CO									225.58
$^{2}J_{(P–C=N)}$		14	9	8	8	6	8	11	4	5
$^{1}J_{(P–CH_2)}$		22	15	29	28	29	28	17	31	29
$^{3}J_{(P–Ph\text{-}i)}$				10	10	8	8	22	8	5
$^{1}J_{(P–Ph\text{-}i)}$		16	15	58	58	50	61		57	55
$^{2}J_{(P–Ph\text{-}o)}$		20	20	12	11	13	13	14	12	11
$^{3}J_{(P–Ph\text{-}m)}$		7		12	12	11	11		12	13
$^{4}J_{(P–Ph\text{-}p)}$		<1		3	3	<1	3		<1	<1
$^{2}J_{(P–Pd–Me\ cis)}$								7		
$^{2}J_{(P–Pd–Me\ trans)}$								115		
$^{2}J_{(P–Pd–C=O)}$										8

[a] Assignments assisted by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectroscopy, using COSY, HSQC, HMBC (HL, **1**–**5**, **8**, **9**), as well as NOESY and $^{1}H\{^{31}P\}$ experiments (HL major and minor); ROESY (**1**–**5**), nOe difference experiments (**3**, **5**, **9**). [b] NMR data recorded in d^8-toluene.

temperature. The complexes **1**–**3** have been characterised by mass spectrometry (FAB^+), elemental analysis and ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectroscopy using COSY, HSQC, HMBC, ROESY, nOe difference and $^{1}H\{^{31}P\}$ experiments. Full assignment of the NMR data is presented in Tables 1 and 2. In the ^{1}H NMR spectrum of complex **3** recorded in CD_2Cl_2, the resonances of the Pd–Me protons were found at δ 0.66 as a doublet with the coupling constant $^{3}J_{P–Pd–Me}$ = 2.9 Hz. In **3**, the strong methyl to PPh_2-*ortho* nOe indicates that the methyl is coordinated to the palladium *cis* to the phosphorus atom, which was further confirmed by X-ray crystallography. Although ligand HL predominantly exists as the *E* isomer, a conformation

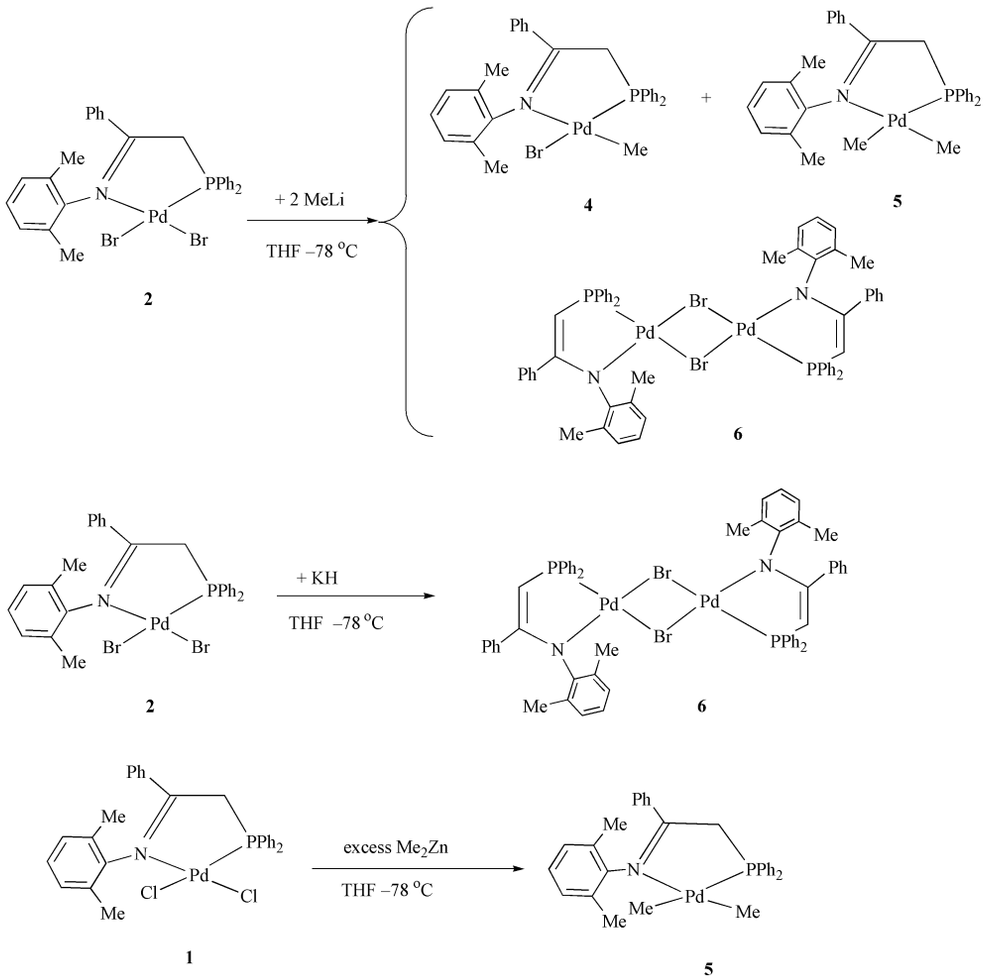
Table 3 Selected bond lengths (Å) and angles (°) for compounds HL, **1**–**3** and **5**–**7**

Compounds	Bond lengths		Bond angles	
HL	N(1)–C(11)	1.414(2)	C(1)–N(1)–C(11)	121.1(2)
	P(1)–C(41)	1.829(2)	C(31)–P(1)–C(2)	101.67(9)
	N(1)–C(1)	1.273(2)	C(31)–P(1)–C(41)	103.64(8)
	P(1)–C(31)	1.818(2)	C(41)–P(1)–C(2)	100.60(8)
	P(1)–C(2)	1.862(2)	N(1)–C(1)–C(2)	125.0(2)
	C(1)–C(2)	1.504(2)	C(1)–C(2)–P(1)	108.62(13)
1	Pd(1)–N(1)	2.049(4)	N(1)–Pd(1)–P(1)	83.63(10)
	Pd(1)–Cl(2)	2.2881(12)	P(1)–Pd(1)–Cl(2)	88.76(5)
	N(1)–C(1)	1.288(5)	P(1)–Pd(1)–Cl(1)	173.57(5)
	C(1)–C(2)	1.489(6)	N(1)–Pd(1)–Cl(2)	170.53(10)
	C(2)–P(1)	1.834(5)	N(1)–Pd(1)–Cl(1)	94.92(10)
	P(1)–C(31)	1.801(5)	Cl(2)–Pd(1)–Cl(1)	93.26(4)
	Pd(1)–P(1)	2.1845(12)		
	Pd(1)–Cl(1)	2.3505(12)		
	N(1)–C(11)	1.445(6)		
	P(1)–C(41)	1.796(5)		
2	Pd(1)–N(1)	2.081(2)	N(1)–Pd(1)–Br(2)	170.51(6)
	Pd(1)–Br(2)	2.4169(5)	N(1)–Pd(1)–Br(1)	94.99(6)
	N(1)–C(1)	1.292(3)	Br(2)–Pd(1)–Br(1)	93.68(2)
	C(2)–P(1)	1.831(3)	N(1)–Pd(1)–P(1)	82.91(6)
	P(1)–C(31)	1.809(3)	P(1)–Pd(1)–Br(2)	88.98(3)
	Pd(1)–P(1)	2.2020(8)	P(1)–Pd(1)–Br(1)	172.40(2)
	Pd(1)–Br(1)	2.4894(5)		
	N(1)–C(11)	1.451(3)		
	C(1)–C(2)	1.502(3)		
	P(1)–C(41)	1.800(3)		
3	Pd(1)–Cl(1)	2.3798(9)	Cl(1)–Pd(1)–P(1)	176.46(4)
	Pd(1)–N(1)	2.169(3)	P(1)–Pd(1)–N(1)	82.91(8)
	P(1)–C(31)	1.815(3)	P(1)–Pd(1)–C(1)	90.8(1)
	P(1)–C(3)	1.834(3)	Cl(1)–Pd(1)–N(1)	94.88(8)
	C(2)–N(1)	1.297(4)	Cl(1)–Pd(1)–C(1)	91.5(1)
	N(1)–C(11)	1.444(4)	N(1)–Pd(1)–C(1)	173.54(14)
	Pd(1)–P(1)	2.1925(9)		
	Pd(1)–C(1)	2.062(4)		
	P(1)–C(41)	1.818(3)		
	C(3)–C(2)	1.509(5)		
5	Pd(1)–P(2)	2.273(3)	P(2)–Pd(1)–N(17)	80.2(2)
	Pd(1)–N(17)	2.185(8)	P(2)–Pd(1)–C(32)	174.3(3)
	Pd(1)–C(32)	2.09(1)	N(17)–Pd(1)–C(32)	95.5(4)
	Pd(1)–C(33)	2.045(11)	P(2)–Pd(1)–C(33)	96.6(3)
	P(2)–C(3)	1.81(1)	N(17)–Pd(1)–C(33)	175.8(4)
	P(2)–C(9)	1.84(1)	C(32)–Pd(1)–C(33)	87.8(5)
	P(2)–C(15)	1.84(1)		
	C(15)–C(16)	1.510(12)		
	C(16)–N(17)	1.300(11)		
	N(17)–C(18)	1.451(11)		
6	Pd(1)–Br(1)	2.4629(4)	Br(1)–Pd(1)–Br(1)′	84.937(14)
	Pd(1)–Br(1)′	2.5655(4)	Br(1)–Pd(1)–P(1)	93.77(2)
	Pd(1)–P(1)	2.2123(8)	Br(1)′–Pd(1)–P(1)	176.87(3)
	Pd(1)–N(1)	2.039(3)	Br(1)–Pd(1)–N(1)	173.09(8)
	P(1)–C(1)	1.738(4)	Br(1)′–Pd(1)–N(1)	97.98(7)
	P(1)–C(17)	1.820(4)	P(1)–Pd(1)–N(1)	83.62(8)
	P(1)–C(23)	1.814(4)	Pd(1)–Br(1)–Pd(1)′	84.981(13)
	C(1)–C(2)	1.379(4)	Pd(1)–P(1)–C(1)	102.03(11)
	C(2)–N(1)	1.351(4)	Pd(1)–N(1)–C(2)	117.5(2)
	C(3)–N(1)	1.424(4)	Pd(1)–N(1)–C(3)	116.9(2)
7	Pd(1)–P(2)	2.3276(7)	P(2)–Pd(1)–N(11)	82.42(6)
	Pd(1)–N(11)	2.097(2)	P(2)–Pd(1)–P(32)	102.48(3)
	Pd(1)–P(32)	2.2420(7)	N(11)–Pd(1)–P(32)	174.86(7)
	Pd(1)–C(51)	2.143(3)	P(2)–Pd(1)–C(51)	167.37(7)
	P(2)–C(3)	1.821(3)	N(11)–Pd(1)–C(51)	90.95(9)
	P(2)–C(9)	1.756(2)	P(32)–Pd(1)–C(51)	83.95(7)
	P(2)–C(26)	1.825(3)		
	C(9)–C(10)	1.363(4)		
	C(10)–N(11)	1.380(3)		
	N(11)–C(12)	1.410(3)		
	P(32)–C(33)	1.827(3)		
	P(32)–C(39)	1.836(3)		
	P(32)–C(45)	1.833(3)		

sterically unfavourable to chelation in a bidentate manner, the metal complexes **1**–**3** are readily formed in high yield (*ca.* 70%). The *E* and *Z* isomers are in equilibrium and addition of palladium halides leads to the formation of $[PdX_2(HL)]$ product, probably with kinetic control. The structures of complexes **1**–**3** were determined by single crystal X-ray diffraction.

Reactivity

Reaction of the PdX_2 compounds **1** and **2** with methyllithium failed to afford the desired dimethyl complex cleanly (Scheme 3). For the case of the reaction of **2** with MeLi, three major species were identified in the reaction mixture, the mono-



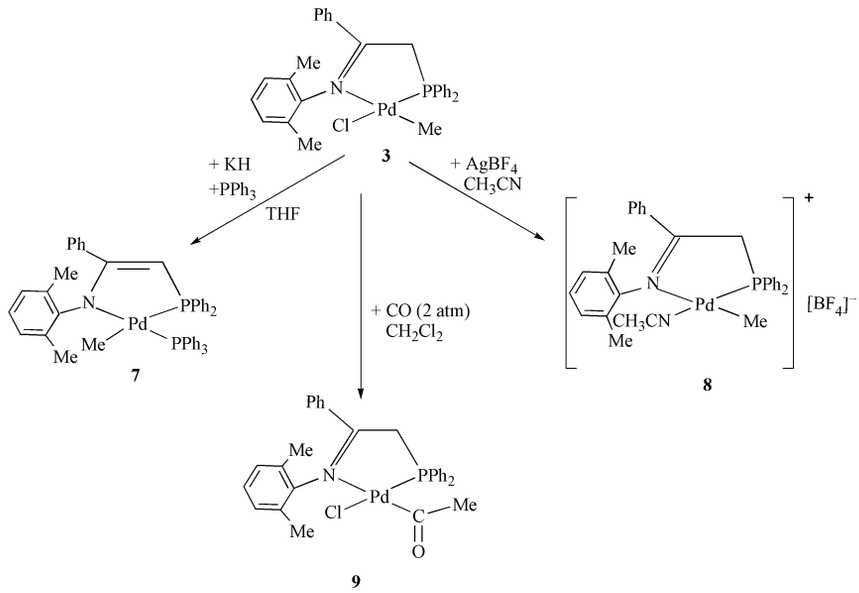
Scheme 3 Formation of complexes **4**–**6**.

methyl, [PdMeBr(HL)] complex **4**, the dimethyl complex [$PdMe_2$(HL)] **5** and the dimeric species [$Pd_2(\mu\text{-}Br)_2(L^-)_2$] **6**. Separation of **4** from the mixture of reaction products proceeded in very low yield, due to similar solubility in common solvents with complexes **5** and **6**. Compound [PdMeBr(HL)] **4**, was characterised by mass spectrometry (FAB^+), elemental analysis and NMR spectroscopy (Tables 1 and 2). As observed for [PdMeCl(HL)] **3**, the ^{1}H NMR spectrum of complex **4** (recorded in CD_2Cl_2) exhibits a doublet ($^3J_{P\text{–}Pd\text{–}Me}$ = 3.3 Hz) assignable to the Pd–Me protons *cis* to PPh_2 at δ 0.78. The presence in the $^{31}P\{^1H\}$ NMR spectrum, of a singlet at δ 40.3, close to that observed in the corresponding spectrum of complex **3**, indicates the expected structural analogy between these two mono-methyl derivatives of the neutral ligand [$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)].

Complex [$PdMe_2$(HL)] **5** was isolated by reacting [$PdCl_2$(HL)] with excess Me_2Zn at −78 °C (Scheme 3), as a highly air and moisture sensitive compound, both in solution and the solid state. In the presence of chlorinated solvents such as CD_2Cl_2, formation of [PdMeCl(HL)] occurs rapidly, as the Me group *trans* to PPh_2 can be readily exchanged to form the more stable mono-methylated derivative. It was previously found that the mutual *trans* position of carbon and phosphorous ligands in Pd(II) complexes leads to the weakening of the corresponding Pd–C and Pd–P bonds.[23] This could be responsible for the instability of **5** towards formation of a mono-methylated species. This could also occur as a consequence of the steric hindrance between the xylyl group and the Me group *cis* to the imine moiety. For **5**, the ^{1}H NMR spectrum (in d^8-toluene) exhibits a doublet at δ 0.28 ($^3J_{P\text{–}Pd\text{–}Me}$ = 7.6 Hz) assignable to the protons of the Me group *trans* to phosphorus and a doublet at δ 1.20 ($^3J_{P\text{–}Pd\text{–}Me}$ = 8.7 Hz) which was assigned to the Me group *cis* to PPh_2. This assignment was based on the strong methyl to PPh_2-*ortho* nOe, and confirms that this particular methyl group is co-ordinated to the palladium *cis* to the phosphorus atom (Tables 1 and 2).

The formation of the complex [$Pd_2(\mu\text{-}Br)_2(L^-)_2$] **6** (where L^- is [Ph_2PCH=C(Ph)N(2,6-$Me_2C_6H_3$)]$^-$), as indicated by mass spectrometry (FAB^+), elemental analysis and NMR spectroscopy, by reacting [$PdBr_2$(HL)] **2** with 2 equivalents of MeLi, clearly shows that the deprotonation of the CH_2 of the ligand backbone in **2** is favoured over the mono- or di-methylation of the Pd(II) centre. Furthermore, the reaction of **2** with KH in THF at −78 °C similarly forms the dimer [$Pd_2(\mu\text{-}Br)_2(L^-)_2$] **6** in high yield.

The acidity of the backbone CH_2 can be exploited to produce the neutral complex [$PdMe(PPh_3)(L^-)$] **7**, by addition of KH to the PdMeCl complex **3** in the presence of PPh_3, as shown in Scheme 4. This template reaction is, to the best of our knowledge, unprecedented. The deprotonation of the co-ordinated ligand backbone was confirmed by ^{1}H NMR spectroscopy, which showed a single (by integration) olefinic proton at δ 3.67 and the loss of the CH_2 backbone resonance. Interestingly, the ROESY spectrum shown in Fig. 3, indicates that ligand redistribution has occurred and the methyl group is now positioned *cis* to the nitrogen atom in the N/P ligand. This is confirmed by the small coupling constant of 26 Hz between the two phosphorus nuclei (Table 4). The proton resonances of the Pd–Me group appear as a double-doublet at δ −0.57 with $^3J_{P\text{–}Pd\text{–}Me}$ = 3.9 Hz (coupling with PPh_3) and $^3J_{P\text{–}Pd\text{–}Me}$ = 6.7 Hz (coupling with PPh_2). The molecular structure of complex **7** was determined by single crystal X-ray diffraction. The geometry of **7** is



Scheme 4 Reactions of the neutral complex **3**, [PdMeCl(L)].

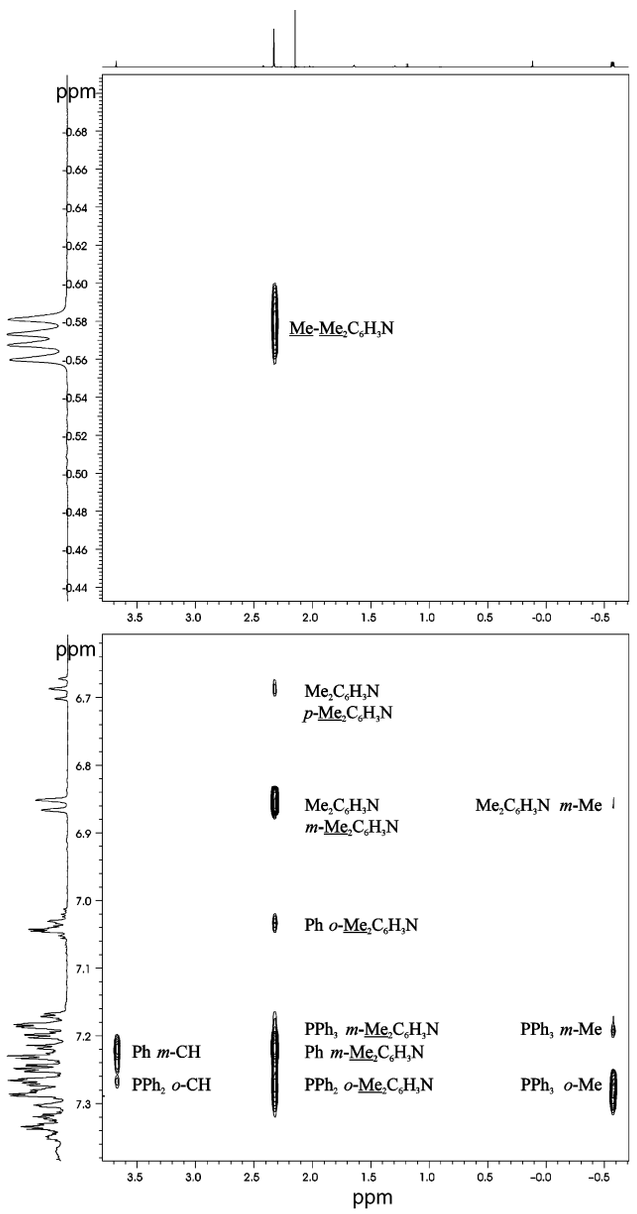


Fig. 3 500 MHz ROESY spectrum of complex **7** in CD_2Cl_2 (mixing time = 250 ms).

unexpected due to the predicted preference of alkyl groups to be placed *cis* to the phosphine unit of the chelating ligand.[23] A possible explanation for the preferred geometry of **7**, with the metal-bound methyl group placed *trans* to PPh_2 both in solution and solid state, could be the steric hindrance between PPh_3 and the xylyl group of the imine moiety.

Complex [PdMeCl(HL)] **3** was also found to undergo reactions with $AgBF_4$ to give the cationic complex [PdMe(MeCN)(HL)][BF_4] **8**, shown in Scheme 4. This complex was characterised by elemental analysis, mass spectrometry (FAB^+) and NMR spectroscopy (Tables 1 and 2). NMR studies indicated that the methyl group is positioned *cis* to the P atom.

The potential for inserting CO into the Pd–Me bond, the first step in the CO/ethylene copolymerisation reaction, was tested for the case of complexes **3** and **7** by NMR-scale reactions performed in CD_2Cl_2 at room temperature, using *ca.* 2 bar CO.

In the case of [PdMe(PPh_3)(L^-)] **7**, rapid CO insertion was observed and the reaction proceeded to full conversion after 15 min. ^{1}H NMR spectra of the reaction mixture showed a new doublet assignable to Pd–CO–Me resonances at δ 2.34 with a coupling constant $^4J_{P–Pd–C–Me}$ = 4.9 Hz. Also, the simultaneous disappearance of the double-doublet at δ −0.57 corresponding to the Pd–Me protons (*trans* to the ligand PPh_2 and *cis* to PPh_3) was observed. $^{31}P\{^1H\}$ NMR spectroscopy confirmed complete conversion of the starting material and formation of a mixture of products. The absence of a signal assignable to the coordinated PPh_3 in the $^{31}P\{^1H\}$ NMR spectrum also suggests that this ligand was displaced. However, decomposition to Pd metal occurred after 2 h at room temperature, halting further investigations and characterisation. By treating the complex **3**, [PdMeCl(HL)], with *ca.* 2 bar CO in an NMR tube at room temperature, CO insertion into the Pd–Me bond *cis* to PPh_2 occurred leading to the formation of the new complex, [Pd(CO)MeCl(HL)] **9**. ^{1}H NMR spectroscopy of the reaction mixture showed a doublet assignable to Pd–CO–Me protons at δ 2.26 with coupling constant $^4J_{P–Pd–C–Me}$ = 1.3 Hz (Table 2). Partial conversion (estimated by integration of the ^{1}H NMR spectrum to be *ca.* 70%) of the starting material was observed after 24 h at room temperature. NMR experiments and solution IR confirmed the proposed structure for complex **9** (Scheme 4). Full assignments of the NMR spectra for complexes **1**–**9** are presented in Tables 1, 2 and 4.

Molecular structures of the Pd(II) complexes

Crystals of **1**–**3** and **6** suitable for single-crystal X-ray structural

Table 4 ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR data (CD_2Cl_2) of complexes **6** and **7** (chemical shifts in ppm and coupling constants in Hz)[a]

	6				**7**			
Y	Br				Ph_3P			
X	$PdBrL^-$				Me			
	$^{31}P\{^{1}H\}$				$^{31}P\{^{1}H\}$ $^{2}J_{P-P} = 26$			
PPh_2	54.4				26.6			
X					39.9			
	^{1}H		$^{13}C\{^{1}H\}$		^{1}H		$^{13}C\{^{1}H\}$	
$Me_2C_6D_6N$			*i*	150.73			*i*	150.69
	o-H	2.15	*o*	136.47	*o-H*	2.32	*o*	135.57
			o-Me	19.88			*o-Me*	19.85
	m-H	6.70	*m*-H	127.50	*m*-H	6.85	*m*-H	127.17
	p-H	6.70	*p*-H	124.94	*p*-H	6.68	*p*-H	122.62
N–C=				178.87				177.23
Ph	*i*			137.53	*i*			142.09
	o-H	7.12	*o*-H	127.32	*o*-H	7.04	*o*-H	126.86
	m-H	7.02	*m*-H	128.07	*m*-H	7.21	*m*-H	127.89
	p-H	7.07	*p*-H	128.21	*p*-H	7.02	*p*-H	126.86
CH–P		3.54		72.64		3.67		77.50
PPh_2			*i*	133.58			*i*	136.56
	o-H	7.77	*o*-H	133.18	*o*-H	7.25	*o*-H	132.43
	m-H	7.43	*m*-H	128.73	*m*-H	7.24	*m*-H	128.34
	p-H	7.53	*p*-H	131.22	*p*-H	7.33	*p*-H	129.04
			i					133.96
Y	*o*-H		*o*-H			7.28		134.52
	m-H		*m*-H			7.18		128.29
	p-H		*p*-H			7.33		130.17
X					Me	−0.57	Me	17.25
$^{2}J_{(P-CH)}$	8.6	$^{2}J_{(P-C-N)}$	21	^{2}J(P–CH)	PPh_2	0.7	^{2}J(P–C–N)	30
$^{3}J_{(P-Ph-o)}$	12.8	$^{1}J_{(P-CH)}$	65	^{3}J(P–Ph-*o*)	PPh_2	8.9	^{1}J(P–CH)	50
$^{4}J_{(P-Ph-m)}$	2.5	$^{3}J_{(P-Ph-i)}$	25	^{4}J(P–Ph-*m*)	PPh_2	1.8	^{3}J(P–Ph-*i*)	22
$^{5}J_{(P-Ph-p)}$	2.1	$^{1}J_{(P-Ph-i)}$	45	^{5}J(P–Ph-*p*)	PPh_2	1.9	^{1}J(P–Ph-*i*)	39
		$^{2}J_{(P-Ph-o)}$	11	^{3}J(P–PdMe)	PPh_2	6.7	^{2}J(P–Ph-*o*)	13
		$^{3}J_{(P-Ph-m)}$	12				^{3}J(P–Ph-*m*)	10
		$^{4}J_{(P-Ph-p)}$	1				^{4}J(P–Ph-*p*)	2
							^{2}J(P–PdMe)	86
				^{3}J(P–CH)	X	0.7	^{1}J(P–Ph-*i*)	49
				^{3}J(P–Ph-*o*)	X	8.3	^{2}J(P–Ph-*o*)	8
				^{4}J(P–Ph-*m*)	X	2.2	^{3}J(P–Ph-*m*)	2
				^{5}J(P–Ph-*p*)	X	1.9	^{4}J(P–Ph-*p*)	2
				^{3}J(P–PdMe)	X	3.9	^{2}J(P–PdMe)	10

[a] Assignments assisted by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectroscopy, using COSY, HSQC, HMBC (**6** and **7**) as well as NOESY and $^{1}H\{^{31}P\}$ experiments (**7**).

determination were obtained by slowly cooling a CH_2Cl_2 solution of each complex, whereas crystals of **5** and **7** were grown from toluene and pentane, respectively. ORTEP diagrams for HL and compounds **1**–**3** and **5**–**7** are presented in Fig. 4–8 and their significant molecular parameters listed in Table 3. Molecular structural determinations confirm that the studied Pd(II) complexes exhibit the same structures in the solid state and in solution.

Complex $[PdCl_2(HL)]$ **1**, with the ORTEP view shown in Fig. 4, is isostructural with complexes $[PdBr_2(HL)]$ **2**, and [PdMeCl(HL)] **3** (Fig. 5). In the solid state, all complexes are of pseudo square planar geometry around the metal centre. For **1**–**3** and **5**, the N–Pd–P bite angles are 83.63(10), 82.91(6), 82.91(8) and 80.2(2)°, respectively. The palladium–halogen bond lengths are as expected for Pd(II) complexes, with the longer metal–halogen bond *trans* to the phosphorus atom.[11,13] In complex **3** (Fig. 5), the Pd–Me separation is 2.062(4) Å with the methyl group located *cis* to the phosphorus atom, as predicted by NMR for the solution species. In the case of $[PdMe_2(HL)]$ **5**, the Pd–C bond length for the methyl group situated *trans* to phosphorus is 2.09(1) Å (Fig. 6). This is somewhat longer than the Pd–C distance *cis* to PPh_2 [2.045(11) Å], which we attribute to the greater *trans*-influence of PPh_2 compared to the aryl imine donor functionality. In general, little variation in the bond lengths of the structure of $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ is observed upon chelation to Pd(II), although the carbon–nitrogen separation C=N does increase from 1.273(2) (in the free ligand) to

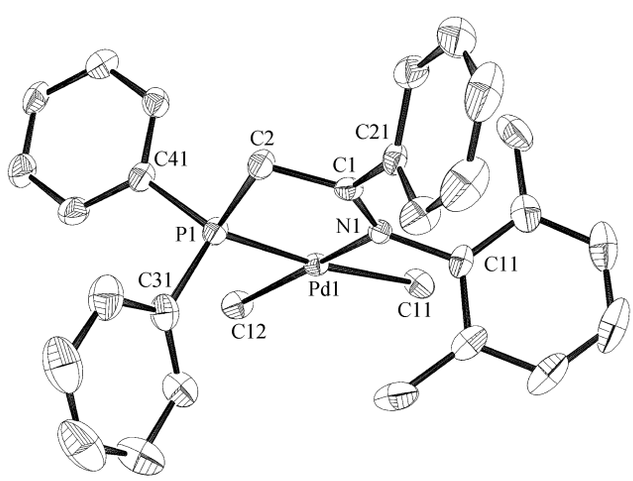


Fig. 4 ORTEP diagram of the molecular structure of complex **1** (isostructural with complex **2**).

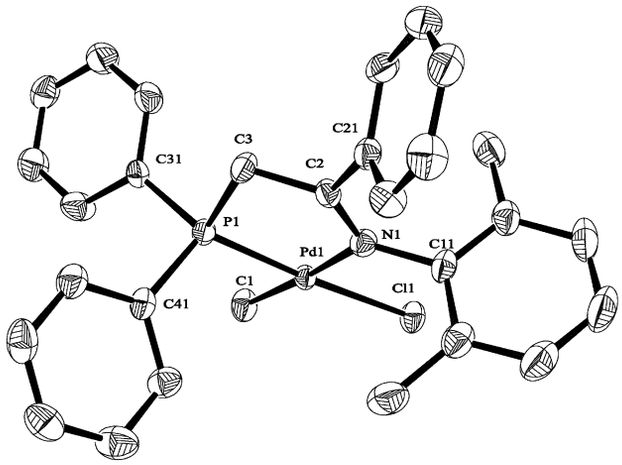


Fig. 5 ORTEP diagram of the molecular structure of complex **3**.

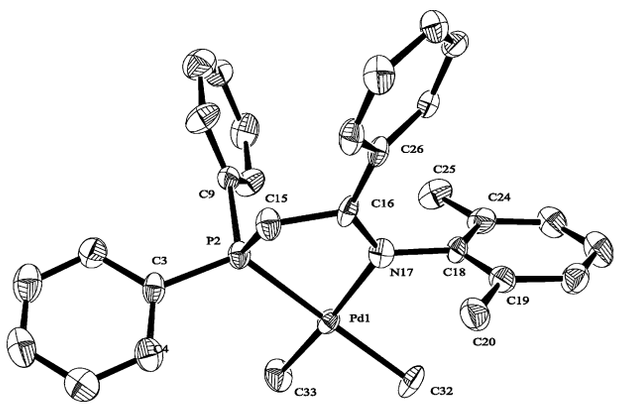


Fig. 6 ORTEP diagram of the molecular structure of complex **5**.

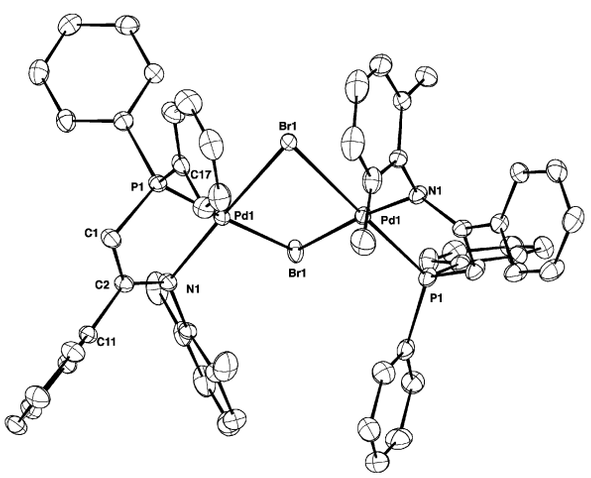


Fig. 7 ORTEP diagram of the molecular structure of complex **6**. The molecule crystallises with two molecules of CH_2Cl_2 (not shown).

1.288(5) in **1**, 1.292(3) in **2**, 1.297(4) in **3**, and to 1.300(11) Å in **5**.

Molecular structures of **6** and **7**, where the ligand is $[Ph_2PCH{=}C(Ph)N(2,6\text{-}Me_2C_6H_3)]^-$, were determined by single crystal X-ray diffraction and their ORTEP diagrams are shown in Fig. 7 and 8, respectively. Changes in the structure of the ligand are reflected in the molecular parameters of the complexes. The bond lengths determined for the C–C backbone in **6** and **7** were found to be considerably shorter than the corresponding bonds determined in the neutral (free or coordinated) ligand. For $[Pd_2(\mu\text{-}Br)_2(L^-)_2]$, **6**, the C–C distance of the backbone is 1.379(4) Å, close to the corresponding carbon–carbon

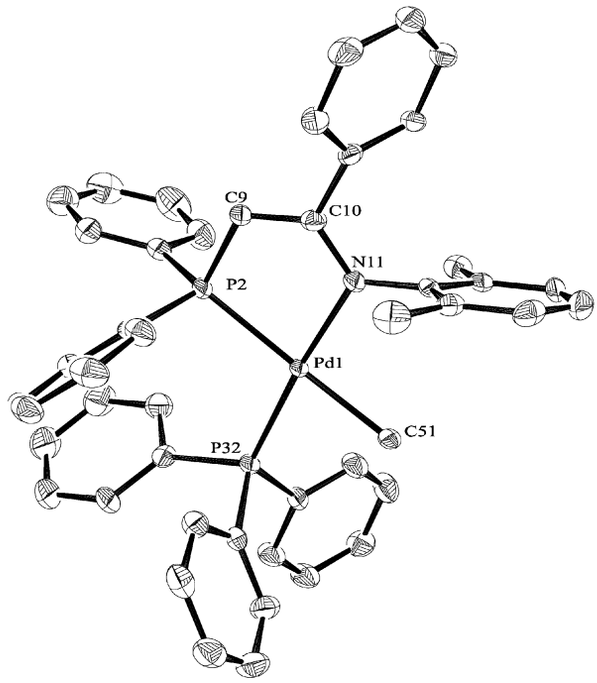


Fig. 8 ORTEP diagram of the molecular structure of complex **7**. The molecule crystallises with one molecule of toluene (not shown).

separation in $[PdMe(PPh_3)(L^-)]$ **7**, of 1.363(4) Å. For complexes **1**–**3** and **5**, these distances were found to be 1.489(6), 1.502(3), 1.509(5) and 1.510(12) Å, respectively, close to the value determined for the non-coordinated neutral ligand [1.504(2) Å]. The shorter carbon–carbon bond of the ligand backbone in compounds **6** and **7** is consistent with the formation of a double bond as a result of the deprotonation of the coordinated neutral ligand in the presence of a base. In addition, the carbon(backbone)–nitrogen distances are significantly greater in **6** [1.351(4) Å] and **7** [1.380(5) Å] than those found in the free and coordinated neutral ligand $[Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)]$. This is consistent with a decrease in the C–N bond order as a result of deprotonation and imine–enamine tautomerisation.

In the structure of **6**, the Pd–Br distances *trans* to phosphorus are 2.5655(4) Å, somewhat longer than the corresponding bonds *cis* to phosphorus of 2.4629(4) Å. The palladium and bromine atoms form inorganic four-membered rings, distorted from planarity, with a dihedral angle Pd1–Br1–Pd1′–Br1′ of 130.08°. It was noted that the P–Pd–N bite angle found for **6**, 83.62(8)°, is slightly larger than that found in complex **2**, $[PdBr_2(HL)]$, with the neutral ligand HL, 82.91(6)°. The geometries around the palladium centres are essentially square-planar in **6**, and the molecule is folded and forms a 'cavity', which accommodates the two molecules of CH_2Cl_2.

In the case of complex $[PdMe(PPh_3)(L^-)]$ **7** containing the anionic ligand $[Ph_2PCH{=}C(Ph)N(2,6\text{-}Me_2C_6H_3)]^-$, the Pd–$P(Ph_2)$ bond [2.2420(7) Å] was found to be longer than that in the neutral ligand $[Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)]$ complexes **1**–**3** and **5**. The Pd–C separation in **7** is 2.143(3) Å, with the methyl group *trans* to the PPh_2 moiety, which is larger than the Pd–C bond in **3** [2.062(4) Å], where the Pd–Me group is *cis* to phosphorus atom of the chelating ligand. This may account for the greater reactivity of compound **7** towards CO insertion into the Pd–C bond compared to compound **3**.

Copolymerisation tests

Complexes $[PdMeCl(HL)]$ **3** and $[PdMe(PPh_3)(L^-)]$ **7** were tested for their ability to catalyse the copolymerisation of ethylene and CO. Solutions of the compounds were stirred for 12 h in CH_2Cl_2 at 90 °C in the presence of 40 bar 1 : 1 ethylene : CO

in a sealed Parr autoclave. No significant reduction in pressure of the autoclave was observed during any of the runs.

The activity of **3** in the catalysis of CO/ethylene copolymerisation was tested using $AgBF_4$ or $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ as co-catalysts. In both cases, grey solids were isolated, with productivities of 634 g polymer (mol Pd)$^{-1}$ h^{-1} (335 mg yield of copolymer) and 358 g polymer (mol Pd)$^{-1}$ h^{-1} (215 mg yield of copolymer), respectively. The resultant products were characterised by solution IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopies in a 1 : 1 mixture of 1,1,1,3,3,3-hexafluoroisopropanol and C_6D_6. The ^{1}H NMR spectra of the copolymers contained a single band of resonances in the region δ 2.39–2.41 which can be assigned to the methylene protons $-[CH_2\text{–}CH_2\text{–}CO]_n-$. The $^{13}C\{^1H\}$ NMR spectra showed singlet resonances for the methylene and carbonyl carbons at δ 35.3 and 212, respectively. The presence of end-groups could not be unambiguously detected by ^{1}H or $^{13}C\{^1H\}$ NMR and the melting points of the resulting copolymers were 249–259 °C, which suggests that $n >$ 400.[24,25] Notably, the NMR spectra of the resulting copolymers did not show any detectable signals in the region expected for a double insertion fault of ethylene into the copolymer. Spectroscopic data suggest the formation of a perfectly alternating copolymer, probably with the formula $CH_3CH_2C(O)[CH_2CH_2\text{-}C(O)]_nCH_2CH_2C(O)CH_3$.[24,25] As a consequence of the poor solubility of the copolymer in common organic solvents, accurate molecular weight determinations were not obtained.

When $[PdMe(PPh_3)(L^-)]$ was used as catalyst, a very small amount of black powder was formed, whose infrared spectra did not contain a carbonyl stretch characteristic of poly(C_2H_4-*alt*-CO) at 1692 cm^{-1}. Elemental analysis confirmed that mainly Pd metal was isolated.

A probable reason for the inactivity of complex **7** is that the PPh_3 ligand is too strong a σ donor and therefore not displaced by ethylene. Ligand displacement is regarded as a crucial step before ethylene insertion into the initial Pd–acyl bond and, hence, copolymerisation can occur.[25]

Conclusions

A novel route for the synthesis of a family of ligands with bulky substituents at the N-donor and flexible backbone has been demonstrated by the isolation and characterisation of the neutral N/P ligand $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$.

Several group 10 metal halide and alkyl complexes of this ligand have been prepared and fully characterised showing the ability of the ligand to coordinate in a chelating bidentate fashion. An initial study of the reactivity of the complexes, and of their catalytic properties towards CO/ethylene copolymerisation is described and further detailed studies are in progress.

Experimental

General

All manipulations of air and/or moisture sensitive materials were performed under an inert atmosphere of pure Ar or dry N_2 using standard Schlenk line techniques or in an inert atmosphere dry box. Inert gases were purified firstly by passage through columns filled with activated molecular sieves (4 Å) and then either manganese(II) oxide suspended on vermiculite, for the Schlenk line, or BASF catalyst, for the dry box. Celite filtration aid was purchased from Fluka Chemie and oven-dried at 150 °C prior to use. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from Na–K alloy (light petroleum ether b.p. 40–60 °C, diethyl ether, pentane), from sodium (toluene), from potassium (THF), or from calcium hydride (dichloromethane), under N_2. Deuterated NMR solvents (Aldrich, Goss Scientific) were refluxed and distilled from potassium metal (d^8-toluene) or from calcium hydride (CD_2Cl_2), distilled and degassed prior to use. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford and FAB^+ mass spectra by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, UK.

The reagents ^{n}BuLi, MeLi, KH, $[(COD)PdCl_2]$, $PdBr_2$ were purchased from Aldrich and used as received. Ph_2PCl, $^iPr_2NH$ and $2,6\text{-}Me_2C_6H_3$ were purchased from Strem and purified by vacuum distillation before use. The imine $[MeC(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ was prepared as described below, and [(COD)PdMeCl] was prepared as previously described.[26]

NMR

NMR spectra were recorded using either a Varian Mercury 300 (^{1}H 300, ^{13}C 75.5, ^{19}F 282.3, ^{31}P 121.6 MHz) or a Varian UNITY*plus* (^{1}H 500, ^{11}B 160.4, ^{13}C 125.7, ^{31}P 202.4 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances relative to tetramethylsilane (^{1}H, ^{13}C, $\delta = 0$) or externally to $BF_3{\cdot}Et_2O$ (^{11}B, $\delta = 0$), H_3PO_3 (^{31}P, $\delta = 0$) or $CFCl_3$ (^{19}F, $\delta = 0$). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz.

A solution of HL in d^8-toluene was used for ^{31}P selective inversion transfer experiments. The temperature was calibrated using a 100% methanol (<300 K) or ethylene glycol (>300 K) sample. Data was acquired using a ($180_{selective}\text{–}\tau\text{–}90_{non\text{-}selective}$–acquire) pulse sequence with proton decoupling during the $180_{selective}$ pulse and the acquisition. The selective 180 pulse was achieved using a Dante sequence and the choice of values of τ was optimised to give the most points over the initial build up of transferred saturation. A non-selective inversion recovery experiment was used to estimate the spin–lattice relaxation rates. The exchange rates were extracted from the data using the program CIFIT[21] and are summarised in the Eyring plot (Fig. 1).

Preparations

$[MeC(Ph)=N(2,6\text{-}Me_2C_6H_3)]$. A mixture of acetophenone (25.75 g, 21.45 mmol), 2,6-dimethylphenylamine (25.96 g, 21.45 mmol) and *p*-tolylsulfonic acid (1.37 g) in a round-bottom flask fitted with a Soxhlet extractor containing about 20 g anhydrous $CaSO_4$ was refluxed in 200 mL toluene over three days. During the reaction, the water was removed using activated molecular sieves (4 Å). After removal of volatiles, the brown residue was distilled under vacuum (10^{-3} bar), the unreacted starting materials distilled up to 60 °C and the imine distilled between 160–166 °C as a yellow oil which solidified at room temperature giving a yellow oily powder (21 g, overall yield 44%). Elemental analysis (%) found (calculated): C 85.6 (86.0), H 7.5 (7.6), N 6.2 (6.3); IR (CsI): ν_{CN} = 1640s cm^{-1}.

$[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$, HL. To a pre-cooled solution of dry $^iPr_2NH$ (2.26 g, 22.42 mmol) in 50 mL THF, a 1.6 M solution of ^{n}BuLi in hexanes (1.43 g, 22.42 mmol) was added dropwise at −78 °C. The mixture was allowed to warm up to room temperature and stirred for 30 min for completing the formation of LDA. A cold solution of dry imine $[MeC(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (5 g, 22.42 mmol) in 25 mL THF was added dropwise at −78 °C under stirring. The mixture was stirred for 2 h at −78 °C and the formation of the lithium salt of the imine as a bright-yellow precipitate was observed, however no isolation attempts have been made. A cold mixture of the freshy distilled Ph_2PCl (4.94 g, 22.42 mmol) and 25 mL THF was transferred dropwise. After addition of Ph_2PCl, the yellow precipitate gradually disappeared and the solution colour turned a lighter yellow. The mixture was stirred for 12 h at room temperature followed by the removal of volatiles under reduced pressure. The white residue was washed with 50 mL toluene and the LiCl formed removed by filtration over Celite. The toluene was removed under reduced pressure and the remaining solid

washed three times with 20 mL of cold pentane. White crystals of HL (5.5 g, crude yield 60%) were formed from a 1 : 4 mixture of toluene and pentane after storing at −20 °C overnight. Elemental analysis (%) found (calculated): C 82.2 (82.5), H 6.6 (6.4), N 3.4 (3.4); IR (CsI): ν_{CN} = 1634s; FAB$^+$: 407 (40) $[M]^+$, 208 (100) $[M - (Ph_2PCH_2)]^+$.

[PdCl$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], 1. The ligand HL (1 g, 2.457 mmol) in 50 mL THF was added to a suspension of $PdCl_2$ (434 mg, 2.457 mmol) in 50 mL THF. The mixture was stirred at room temperature overnight and 1.14 g (80% crude yield) of **1** was formed (as a fine yellow powder). The product was separated by filtration and recrystallised from a 1 : 4 mixture of CH_2Cl_2 and pentane to give yellow crystals of **1** in near quantitative yield. Elemental analysis (%) found (calculated): C 56.7 (57.5), H 4.5 (4.5), N 2.3 (2.4); IR (CsI): ν_{CN} = 1600 cm^{-1}; FAB$^+$: 548.1 (100) $[M - Cl]^+$, 513.1 (15) $[M - 2Cl]^+$.

[PdBr$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], 2. The ligand HL (765.5 mg, 0.5 mmol) in 50 mL THF was added dropwise to a suspension of $PdBr_2$ (500.3 mg, 0.5 mmol) in 50 mL THF. The mixture was stirred at room temperature for 48 h. The orange precipitate formed was separated by filtration, washed with 20 mL pentane and dried in vacuum to afford 0.89 g product in a 70% yield. Needle-like orange crystals were grown by the slow diffusion of pentane at room temperature onto a concentrated CH_2Cl_2 solution of **2** in a crystallisation bridge. Elemental analysis (%) found (calculated): C 50.0 (49.9), H 4.0 (3.9), N 2.0 (2.1), Pd 15.6 (15.7); IR (CsI): ν_{CN} = 1584 cm^{-1}; FAB$^+$: 594 (100) $[M - Br]^+$, 513 (15) $[M - 2Br]^+$, 672 (15) $[M - H]^+$.

[PdMeCl{Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], 3. To a mixture of the ligand HL (387 mg, 0.945 mmol) and (COD)PdMeCl (250 mg, 0.945 mmol) 100 mL toluene was added, whilst stirring. The reaction mixture was stirred for 6 h at room temperature. The resulting white solid was isolated by filtration, washed with 20 mL cold pentane and the residual volatiles removed under reduced pressure; 0.5 g product was isolated (yield = 89%). Light yellow block-shaped crystals were obtained after recrystallisation of the product from a 1 : 4 mixture of CH_2Cl_2 and pentane at −20 °C. Elemental analysis (%) found (calculated): C 61.2 (61.7), H 5.2 (5.2), N 2.5 (2.5); IR (CsI): ν_{CN} = 1612 cm^{-1}; FAB$^+$: 563.9 (10) $[M]^+$, 549.9 (80) $[M - CH_3]^+$, 527.9 (100) $[M - Cl]^+$.

Reaction of [PdBr$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}] with MeLi. To a suspension of **2**, [PdBr$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], (950 mg, 1.41 mmol) in 100 mL Et_2O at −78 °C, a cold solution of MeLi 1.57 M in Et_2O (62.1 mg, 2.82 mmol) was added dropwise. The reaction mixture was stirred for 15 min at −78 °C and left to reach room temperature over 1 h. The volatiles were removed under reduced pressure and the residue washed with 100 mL warm petroleum ether (b.p. 40–60 °C) to yield a red–brown solution (fraction 1) and a dark precipitate. This precipitate was further washed with 50 mL CH_2Cl_2 to give a purple solution (fraction 2) and LiBr, which was discarded.

Fraction 1. The volatiles were removed to give a small amount of a brown solid which was recrystallised from toluene to give a mixture of compounds **4**, [PdMeBr{Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], and **5**, [PdMe$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], in a ratio of 2 : 3 by integration of the ^{1}H NMR spectrum thereof. Attempts to isolate either **4** or **5** from the mixture were unsuccessful. These complexes were characterised by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy (Tables 1 and 2).

Fraction 2. The CH_2Cl_2 solution was concentrated to about 10 mL and stored at −20 °C. After 48 h green crystals of complex **6**, [Pd$_2$(μ-Br)$_2${Ph$_2$PCH=C(Ph)N(2,6-Me$_2$C$_6$H$_3$)}$_2$] with two molecules of CH_2Cl_2, were formed and isolated by filtration (210 mg, 0.177 mmol, 50% yield).

***4* and *5*.** Elemental analysis (%) found (calculated for **4**): C 56.8 (57.2), H 5.2 (4.8), N 2.1 (2.3); FAB$^+$: 594.9 (40) $[M - Me]^+$; 513 (25) $[M - Br - Me]^+$; 609 (100) $[M]^+$. **6**·CH_2Cl_2. Elemental analysis (%) found (calculated): C 53.8 (53.9), H 4.1 (3.9), N 2.1 (2.2); FAB$^+$: 1186 (20) $[M]^+$, 594 (85) $[M/2]^+$.

Reaction of [PdBr$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}] with KH. The solids **2** [PdBr$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}] (100 mg, 1.5 mmol) and KH (5.94 mg, 1.5 mmol) were mixed in a Schlenk tube and 50 mL cold THF was added at −78 °C under stirring. The reaction mixture was left to reach room temperature over 12 h. The volatiles were removed under reduced pressure and the residue washed with 100 mL of pentane to yield a dark grey solid. This compound was extracted into 50 mL CH_2Cl_2 to give a purple solution and the insoluble materials discarded. Removal of volatiles from the purple solution yielded 75 mg of **6** as a purple solid (85% yield). Recrystallisation from CH_2Cl_2 at −20 °C yielded plate-like green crystals of compound **6**, [Pd$_2$(μ-Br)$_2${Ph$_2$PCH=C(Ph)-N(2,6-Me$_2$C$_6$H$_3$)}$_2$], crystallised with two molecules of CH_2Cl_2.

[PdMe$_2${Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], 5. A solution of Me_2Zn (190 mg, 2 mmol, 2 M in THF) cooled to −78 °C was added dropwise to a cold solution (−78 °C) of **1**, [PdCl$_2$-{Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], (100 mg, 0.17 mmol) in 50 mL THF. The mixture was left to reach room temperature overnight, and a colour change from light yellow to brown was observed. Volatiles were removed under reduced pressure and a brown oily residue was obtained. This was extracted with 20 mL cold toluene which was then concentrated under reduced pressure to 2 mL and layered with pentane (*ca.* 8 mL). Air and thermally sensitive yellow crystals of complex **5**, [PdMe$_2$-{Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], (50 mg, 0.092 mmol, yield = 54%) formed after storing the mixture at −20 °C for 48 h and were isolated by filtration. Elemental analysis (%) found (calculated): C 65.3 (66.2), H 5.6 (5.9), N 2.0 (2.5); FAB$^+$: 528.1 (70) $[M - Me]^+$, 513.1 (55) $[M - 2Me]^+$, 406.1 (30) $[M - Pd - 2Me]^+$.

[PdMe(PPh$_3$){Ph$_2$PCH=C(Ph)N(2,6-Me$_2$C$_6$H$_3$)}], 7. The solids **3**, [PdMeCl{Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}] (100 mg, 0.177 mmol), KH (7.093 mg, 0.177 mmol) and PPh_3 (46.46 mg, 0.177 mmol) were mixed in a Schlenk tube and 50 mL of THF was added. The mixture was stirred at room temperature under N_2 for 12 h. A colour change from light yellow to orange was observed. The solvent was removed under reduced pressure and the resulting orange solid was washed with 20 mL of cold pentane. Recrystallisation from a mixture of toluene and pentane at 0 °C gave 90 mg (0.114 mmol, 64% yield) of orange crystals of complex **7**, [PdMe(PPh$_3$){Ph$_2$PCH=C(Ph)N(2,6-Me$_2$C$_6$H$_3$)}]. Elemental analysis (%) found (calculated): C 71.8 (71.4), H 5.4 (5.5), N 1.8 (1.8); FAB$^+$: 789.6 (70) $[M]^+$, 774.5 (25) $[M - Me]^+$, 527.7 (98) $[M - PPh_3]$.

[PdMe(CH$_3$CN){Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}][BF$_4$], 8. The complex **3**, [PdMeCl{Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}], (120 mg, 0.454 mmol) and $AgBF_4$ (88.47 mg, 0.454 mmol) were mixed together in a Schlenk tube and 50 mL CH_3CN added. The mixture was stirred for 12 h in darkness at room temperature. AgCl was removed by filtration over Celite and the volatiles removed under reduced pressure to give 0.1 g (62% crude yield) of white–yellow powder [PdMe(CH$_3$CN){Ph$_2$PCH$_2$-C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)}][BF$_4$] **8**. The solid was washed with pentane and recrystallised from CH_2Cl_2 and pentane to give **8** as a light-yellow microcrystalline powder. Elemental analysis (%) found (calculated): C 56.0 (56.7), H 5.3 (4.9), N 4.2 (4.3), B 2.1 (1.7); IR (CsI): ν_{CN} = 1600 cm^{-1}, ν_{BF} = 1100–1299 cm^{-1} (broad); FAB$^+$: 530.3 (100) $[M - CH_3CH - BF_4]^+$.

Table 5 Crystallographic data for compounds HL, **1**–**3** and **5**–**7**

	HL	**1**	**2**	**3**	**5**	**6**[a]	**7**[b]
Chemical formula	$C_{28}H_{26}NP$	$C_{28}H_{26}Cl_2NPPd$	$C_{28}H_{26}Br_2NPPd$	$C_{29}H_{29}ClNPPd$	$C_{30}H_{27}NPPd$	$C_{29}H_{27}BrCl_2NPPd$	$C_{54}H_{51}NP_2Pd$
Formula weight	407.47	584.77	673.69	564.38	537.92	677.72	882.35
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	Cc	$P\bar{1}$	$C2/c$	$P\bar{1}$
Unit cell dimensions							
a/Å	13.402(5)	11.182(1)	9.037(2)	20.307(6)	7.8590(7)	28.0025(4)	11.0390(9)
α/°	90	90	90	90	89.044(6)	90	99.511(5)
b/Å	9.595(5)	22.663(1)	13.944(3)	10.905(5)	9.2000(13)	11.62482(2)	12.1030(7)
β/°	92.423(5)	117.47(2)	97.06(3)	130.49(2)	84.199(8)	121.2300(6)	106.438(4)
c/Å	17.249(5)	11.314(1)	20.419(4)	15.256(7)	18.778(3)	19.8002(4)	17.4530(14)
γ/°	90	90	90	90	70.296(7)	90	90.095(5)
Volume/Å^3	2216.1(16)	2544.0	2553.5(9)	2569.3(6)	1271.4	5513.1	2201.5
Temperature/K	150	150	150	150	150	150	190
Z	4	4	4	4	2	8	2
Absorption coefficient/mm^{-1}	0.139	1.019	3.936	0.91	0.81	2.39	0.53
Reflections collected	27212	29609	28729	13025	11841	42409	20284
Independent reflections	3906	4207	5084	2594	4630	5914	6812
R(int)	0.027	0.048	0.060	0.03	0.08	0.04	0.03
Final R indices							
$R1$	0.0476	0.0563	0.0246	0.0308	0.0868	0.0354	0.0564
$wR2$	0.1049[c]	0.0915[c]	0.0642[c]	0.0161[d]	0.0704[e]	0.0415[d]	0.0264[d]

[a] Crystallises with two molecules of CH_2Cl_2. [b] Crystallises with one molecule of $CH_3C_6H_5$. [c] $[I > 2\sigma(I)]$. [d] $[I > 3\sigma(I)]$. [e] $[I > 4\sigma(I)]$.

NMR-scale reaction between [PdMeCl{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}] and CO. A yellow CD_2Cl_2 solution (0.55 mL) of complex **3**, [PdMeCl{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}], (10 mg, 0.0177 mmol) maintained at −78 °C was degassed and CO (<2 atm) admitted into an NMR tube fitted with a Teflon valve before sealing. The mixture was allowed to warm to room temperature and the ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded after 5 min, which showed 20% conversion of **3** to **9**. Further ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 2 h showed 50% conversion. After 24 h at room temperature, 70% conversion was estimated by integration of the ^{1}H NMR spectrum. However, no significant reaction progress occurred after one week at room temperature. The maximum conversion of **3** to **9** was therefore estimated to be 70%. Compound **9** was characterised by solution IR recorded in CD_2Cl_2 (ν_{CO} = 1752 cm^{-1}, $\nu_{C=N}$ = 1696 cm^{-1}, ν_{N-Ar} = 1604 cm^{-1}) and by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopies (Tables 1 and 2).

NMR-scale reaction between [PdMe(PPh_3){Ph_2PCH=C(Ph)-N(2,6-$Me_2C_6H_3$)}] and CO. A red CD_2Cl_2 solution (0.55 mL) of **7**, [PdMe(PPh_3){Ph_2PCH=C(Ph)N(2,6-$Me_2C_6H_3$)}], (10 mg, 0.01266 mmol) maintained at −78 °C was degassed and CO (<2 atm) admitted into an NMR tube fitted with a Teflon valve before sealing. The mixture was allowed to warm to room temperature and ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 15 min to show complete insertion of CO in the Pd–Me bond. ^{1}H NMR spectroscopy showed a signal (a doublet at δ 2.35, with $^4J_{P-Pd-C-Me}$ = 4.95 Hz) which was assigned to acyl proton resonances. In the ^{31}P NMR spectra, the occurrence of a major signal, a singlet at δ 28.3, was observed. No traces of starting material were observed. Decomposition to Pd metal occurred after 2 h at room temperature.

Copolymerisation tests

A mixture of Pd pre-catalyst, compound **3** [PdMeCl{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}], (25 mg, 0.044 mmol) and the co-catalyst $AgBF_4$ (8.64 mg, 0.044 mmol) in 50 mL CH_2Cl_2 was transferred using a glove box into a dried 200 mL Parr autoclave fitted with a Teflon liner and equipped with a stirrer bar. The autoclave was charged with 40 bar 1 : 1 C_2H_4 : CO mixture, sealed, and allowed to reach 90 °C. The mixture was stirred at this temperature for a further 12 h. Subsequently, the autoclave was allowed to cool to room temperature before the remaining C_2H_4–CO mixture was vented. The grey precipitate obtained was separated by filtration, washed with methanol and dried under vacuum [yield poly(C_2H_4-*alt*-CO) 335 mg, 634 g product (mol Pd)$^{-1}$ h^{-1}]. The same procedure was employed using 28 mg (0.05 mmol) of **3**, [PdMeCl{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}] and Na[B{3,5-$(CF_2)_2C_6H_3$}$_4$] (12.35 mg, 0.05 mmol) to generate the catalyst [yield poly(C_2H_4-*alt*-CO) 215 mg, 358 g product (mol Pd)$^{-1}$ h^{-1}] was isolated as a grey solid.

Infrared spectroscopy of the products showed the characteristic carbonyl stretch of poly(C_2H_4-*alt*-CO) at 1692 cm^{-1}. Furthermore, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy of the products are similar to those reported for catalysts based on Pd(II) complexes of chelating diphosphines.[24]

The method described above was also applied using compound **7** (10 mg, 0.0127 mmol) as the catalyst. In this case, 3 mg of a black solid was formed whose IR spectra contained no CO stretch characteristic of poly(C_2H_4-*alt*-CO) and was shown by elemental analysis to contain mainly Pd metal.

Crystal structure determination

Sample preparation. Crystals of HL were grown by diffusion of pentane into a toluene solution at −20 °C. Crystals of compound **1** were grown from a 1 : 4 mixture of CH_2Cl_2 and pentane at −20 °C. Crystals of compounds **2** and **3** were grown by slow diffusion of pentane into concentrated CH_2Cl_2 solutions (ratio pentane : CH_2Cl_2 *ca.* 1 : 1) at room temperature. Crystals of **5** and **7** were formed in a 1 : 4 mixture of toluene and pentane at −20 and 0 °C, respectively. Crystals of **6** were formed in a concentrated CH_2Cl_2 solution stored at −20 °C. In all cases, the crystals were isolated by filtration, and a specimen crystal selected under an inert atmosphere, covered with polyfluoroether, and mounted on the end of a glass fibre. Crystal data are summarised in Table 5.

Data collection and processing. All data were collected at 150 K except for compound **7**, data for which were collected at 190 K, on an Enraf-Nonius DIP2000, except **6**, data for which were collected on a Nonius KappaCCD, with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), as summarised in Table 5. The images were processed with the DENZO and SCALEPACK programs.[27]

Structure solution and refinement. The crystal structures were solved by direct methods using the programs SIR92[28] (for compounds HL, **1**, **2** and **5**–**7**) and SIR97[29] (compound **3**).

The structures of compounds HL, **1** and **2** were refined using full-matrix least squares on all F^2 data using SHELXL-93;[30] all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions with isotropic thermal parameters *ca.* 1.2 × (aromatic CH) or 1.5 × (Me) the equivalent isotropic thermal parameters of their parent carbon atoms, and allowed to 'ride' on their parent atoms during refinement.

In the case of compounds **3** and **5**–**7**, the refinement and graphical calculations were performed using the CRYSTALS[31] and CAMERON[32] software packages. The structures were refined by full-matrix least squares procedures on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated positions with isotropic thermal parameters, with the exception of those on $PdMe_2$ in **5**, where they could not be located in a Fourier map or positioned geometrically with confidence. A Chebychev weighting scheme with the parameters 1.36, −1.45 and 0.870 was applied for compound **3**, 1.70, −1.44 and 0.855 for compound **5**, 1.94, −0.180 and 1.21 for **6** and 1.94, −1.82 and 1.38 for compound **7**, as well as empirical absorption corrections.[33]

CCDC reference numbers 171176–171182.

See http://www.rsc.org/suppdata/dt/b1/b102476k/ for crystallographic data in CIF or other electronic format.

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