

Cyclometallated complexes of palladium(II) with a C,N,N' terdentate Schiff base donor ligand. Oxidative addition of an aryl–chlorine bond to palladium(0)

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Abstract

Treatment of *N*-(2-chlorobenzylidene)-*N,N'*-dimethylethylenediamine, 2-ClC₆H₄C(H)=NCH₂CH₂NMe₂, with tris(dibenzylideneacetone)dipalladium(0) in chloroform gave the oxidative addition cyclometallated product [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(Cl)] (1) with the palladium atom bonded to a C,N,N' terdentate donor ligand. Treatment of 1 with tertiary monophosphines gave the cyclometallated complexes [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(Cl)(L)] (2: L = PPh₃; 3: L = PEt₃Ph; 4: L = PEt₃; 5: L = PEt₃), where the phosphine ligand is either *trans* to the phenyl carbon atom (2, 3) or *trans* to the imine nitrogen atom (4, 5). Treatment of 1 with silver perchlorate followed by reaction with tertiary monophosphines gave the cyclometallated complexes [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(L)(ClO₄)] (6: L = PPh₃; 7: L = PEt₃Ph; 8: L = PEt₃; 9: L = PEt₃). Reaction of 1 with thallium acetylacetonate gave the cyclometallated complex [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(H₃CCOCHCOCH₃)] (10). Treatment of 1 with ditertiary diphosphines in a complex 1/diphosphine 2:1 molar ratio gave the dinuclear cyclometallated complexes {[Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(Cl)]₂(L-L)] (11: L-L = *trans*-Ph₂PCH=CHP-Ph₂; 12: L-L = Ph₂P(CH₂)₂PPh₂; 13: L-L = Ph₂P(CH₂)₂PPh₂), where the phosphorus atom is *trans* to the phenyl carbon atom. Treatment of 1 with silver perchlorate followed by ditertiary diphosphines in a complex 1/diphosphine 2:1 molar ratio gave the dinuclear cyclometallated complexes {[Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(L-L)(ClO₄)]₂ [14: L-L = *trans*-Ph₂PCH=CHPPh₂; 15: L-L = Ph₂P(CH₂)₂PPh₂; 16: L-L = Ph₂P(CH₂)₂PPh₂]. Reaction of 1 with ditertiary diphosphines in a complex 1/diphosphine 1:1 molar ratio, and silver perchlorate as appropriate, gave the cyclometallated complexes [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(Ph₂P(CH₂)₂PPh₂)(ClO₄)] (17), [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(Ph₂P(CH₂)₂PPh₂)(ClO₄)] (18), [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(*cis*-Ph₂PCH=CHPPh₂)(Cl)] (19) and [Pd(C₆H₄C(H)=NCH₂CH₂NMe₂)(Cl)(Ph₂P(CH₂)₂PPh₂)] (20).

Keywords: Palladium; Cyclometallation; Schiff base; Tertiary phosphine; Oxidative addition

1. Introduction

Cyclometallation is an important part of organometallic chemistry and various reviews covering this area have appeared [1]. Cyclometallated compounds show important applications, such as their use in regioselective organic and organometallic synthesis [2,3] and in insertion reactions [4,5]. Bidentate nitrogen donor ligands which may undergo double cyclometallation to give compounds with two σM–C bonds and with coordi-

ination of each nitrogen atom to one of the metal centers have been reported. To name but a few, *N,N,N',N'*-tetraethyl-*para*-xylene-α,α'-diamines [6], azines [7], diphenylpyrimidines [8], diphenylpyrazines [9], benzylidenehydrazones [10], and bis(*N*-benzylidene)-1,4-phenylenediamines [11] always give doubly cyclometallated complexes; when Schiff bases derived from dialdehydes such as terephthalaldehyde or isophthalaldehyde were used in cyclometallation reactions, mono- or dicyclometallated compounds could be obtained [12,13]. More recently we have become interested in bidentate and terdentate ligands which coordinate to the metal center through two donor atoms simultaneously, giving compounds with two fused five-

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membered rings at palladium or platinum(II) [14]; the synthesis of these complexes is achieved via an oxidative addition process. Oxidative addition by halogenated Schiff bases has been used before as a means to obtain cyclometallated compounds [15–17]. An interesting feature of these compounds is that in the metallation process of the ligands, mononuclear species are produced, as opposed to the dinuclear complexes which are usually obtained when mono- and bidentate Schiff bases are reacted with palladium(II) acetate. In the former case, the cyclopalladated or cycloplatinated starting materials show a greater versatility towards reactions with neutral or anionic ligands, e.g. with Lewis bases such as tertiary phosphines or diphosphines, which may vary their coordination site in the complex, whereas in the latter one, this is more unlikely, probably as a consequence of the dimeric nature of the starting materials. This is one of the features we have encountered upon studying cyclometallation reactions of halogenated organic ligands and the results described in this paper show that the coordination position of the phosphine ligand depends on the synthetic conditions employed. In the present paper we report the intramolecular oxidative addition of *N*-(2-chlorobenzylidene)-*N,N'*-dimethylethylenediamine (this ligand has been used earlier in oxidative addition reactions involving platinum; see Ref. [17]) to tris(dibenzylideneacetone)dipalladium(0) to yield the cyclometallated complex **1** with two fused rings at palladium and subsequent reactions of **1** with phosphine or diphosphine ligands in different reaction conditions. The reaction of **1** with thallium acetylacetonate is also described.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterised by elemental analysis and by IR spectroscopy (data in Section 3) and by ^1H and $^{31}\text{P}\{^1\text{H}\}$ (Table 1) and (in part) ^{13}C NMR spectroscopy (Section 3).

The oxidative addition reaction of *N*-(2-chlorobenzylidene)-*N,N'*-dimethylethylenediamine, $2\text{-ClC}_6\text{H}_4\text{C(H)=NCH}_2\text{CH}_2\text{NMe}_2$, with tris(dibenzylideneacetone)dipalladium(0) in benzene gave the palladium(II) mononuclear cyclometallated complex $[\text{Pd}(\text{C}_6\text{H}_4\text{C(H)=NCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})]$ (**1**), in 60% yield, which was fully characterized. The ^1H NMR spectrum showed well-defined 'virtual triplet' patterns at δ 3.68 and δ 2.89 ppm, for the $=\text{N}-\text{CH}_2$ and CH_2-NMe_2 protons respectively, with $N = 12\text{ Hz}$; a singlet at δ 2.67 ppm (6H) was assigned to the methyl protons. The NMe_2 resonance was shifted to higher frequency, showing palladium coordination to the amine nitrogen atom. A singlet at δ 7.52 was assigned to the

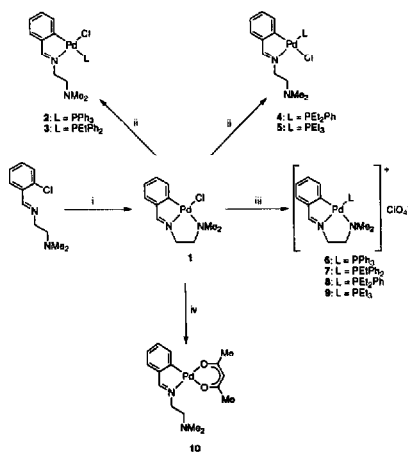
$\text{HC}=\text{N}$ proton, shifted to lower frequency on palladium–nitrogen coordination [18].

The ^{13}C NMR spectrum showed resonances at δ 172.2 (C=N), δ 150.2 (C6), δ 158.0 (C1) and δ 48.3 (NMe_2); the former two were shifted to higher frequency by 13.3 and 26.9 ppm respectively from those for the free ligand, confirming that metallation had taken place [19]. The C1 resonance was also shifted to higher frequency, as expected. The two methylene resonances were separated by ca. 10 ppm, due to coordination of the amine nitrogen to the metal atom (vide infra). There was no noticeable quadrupolar broadening of these resonances with the ^{105}Pd (22% natural abundance, $I = 5/2$) nucleus.

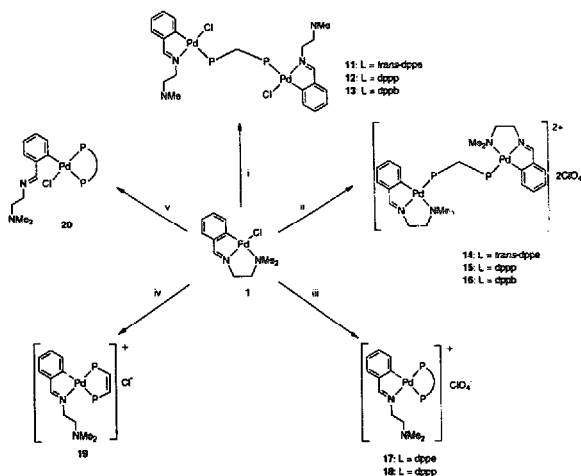
The IR spectrum (see Section 3) showed a band at 1616 cm^{-1} , shifted to lower wavenumbers, consistent with palladium coordination to the nitrogen atom [20,21].

Treatment of $2\text{-ClC}_6\text{H}_4\text{C(H)=NCH}_2\text{CH}_2\text{NMe}_2$ with palladium(II) acetate gave reduction to Pd(0); no oxidative addition of C–Cl bonds to metallic palladium was observed, as has been described before [16]. Reaction of $2\text{-ClC}_6\text{H}_4\text{C(H)=NCH}_2\text{CH}_2\text{NMe}_2$ with $\text{Li}_2[\text{PdCl}_4]$ did not yield any cyclometallated product.

Treatment of **1** with tertiary phosphines gave the mononuclear cyclometallated complexes $[\text{Pd}(\text{C}_6\text{H}_4\text{C(H)=NCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})(\text{L})]$ (**2**: $\text{L} = \text{PPh}_3$; **3**: $\text{L} = \text{PEtPh}_2$; **4**: $\text{L} = \text{PEt}_2\text{Ph}$; **5**: $\text{L} = \text{PEt}_3$) respectively, and treatment of **1** with silver perchlorate, followed by tertiary phosphines, gave the mononuclear cyclometallated complexes $[\text{Pd}(\text{C}_6\text{H}_4\text{C(H)=NCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})(\text{L})]$ (**6**: $\text{L} = \text{PPh}_3$; **7**: $\text{L} = \text{PEtPh}_2$; **8**: $\text{L} = \text{PEt}_2\text{Ph}$; **9**: $\text{L} = \text{PEt}_3$) respectively.



Scheme 1. (i) $1/2 [\text{Pd}_2(\text{dba})_3]$; (ii) 1 equiv. of L ; (iii) AgClO_4 followed by 1 equiv. of L ; (iv) $\text{Tl}(\text{acac})$.



Scheme 2. (i) L; (ii) AgClO₄ followed by L; (iii) AgClO₄ followed by L; (iv) *cis*-dppp in acetone; (v) dppb in acetone.

CH₂NMe₂)(L)ClO₄] (6: L = PPh₃; 7: L = PEtPh₂; 8: L = PEt₂Ph; 9: L = PEt₃) respectively, which were fully characterised (see Section 3 and Table 1). Electric conductivity measurements in dry acetonitrile solution showed complexes 6–9 to be 1:1 electrolytes [22] (see Section 3). In complexes 2 and 3 no coupling of the HC=N and H5 proton resonances to the ³¹P nucleus was observed; also, the =NCH₂ resonance was not coupled to the ³¹P nucleus. However, in complexes 4 and 5 the HC=N, H5 and δ =NCH₂ proton resonances were coupled to the ³¹P nucleus, as corresponds to the phosphine ligand being *cis* to the metallated carbon atom. We and others have observed that, in cyclometallated palladium(II) compounds of Schiff bases with only one tertiary monophosphine coordinated to the metal center, this ligand usually shows a *trans* geometry with respect to the imine nitrogen atom [16, 23–27]; we have also found that the HC=N and H5 proton resonances are always coupled to the ³¹P nucleus, except when the Pd ← N bond was cleaved. Coupling of the H5 resonance to the ³¹P nucleus *trans* to carbon has been observed in complexes with chelating diphosphines; in this case there could be coupling through the carbon chain between the phosphorus atoms [28,29]. However, even in these cases no coupling between the HC=N nucleus to the ³¹P nucleus *trans* to carbon was detected (*vide infra*). In the present case we tentatively attribute these findings to different coordination sites of the phosphine ligand in compounds 2, 3 on the one hand (P *trans* to C), and of compounds 4, 5 on

the other hand (P *trans* to N), in spite of the fact that the ³¹P resonance shows a rather high value in compounds 2 and 3 for phosphorus *trans* to a phenyl carbon atom as compared to values found previously [25] (Table 1). We suggest that the phosphine ligand produces cleavage of the Pd ← NMe₂ bond with coordination of the phosphorus atom to the vacant site at palladium, *trans* to the phenyl carbon atom. This coordination prevails with the less basic phosphines, i.e. PPh₃, PEtPh₂ and the diphosphines *trans*-dppp, dppp and dppb. However, with the more basic phosphines, i.e. PEt₂Ph and PEt₃, palladium coordination is rearranged to give complexes with the phosphine ligand *trans* to the imine nitrogen atom. [This could be related to the π-acceptor properties of the phosphine ligands. We treated compound 1 with 2 mol of PPh₃, and the ¹H and ³¹P NMR results show that the phosphine ligands are mutually *trans* (only one singlet is observed in the ³¹P NMR) as we have observed before [25]; again there is a change in the coordination site of the ligand initially *trans* to the phenyl carbon atom. ¹H NMR data: δ(HC=N) 8.20, δ(H2) 7.25d, δ(H3) 6.87t, δ(H4) 6.51t, δ(H5) 6.42d, δ(NCH₂CH₂) 4.06, 2.82 N = 12.8 Hz, δ(NMe₂) 2.91 ppm. ²J(H2H3) 7.3, ³J(H3H4) 7.4, ³J(H4H5) 7.4 Hz. ³¹P NMR δ 27.3 ppm.] Furthermore, when the chloride ion is removed by the silver salt, this leaves a vacant position at palladium *trans* to the imine nitrogen atom, which renders the phosphine ligand *trans* to nitrogen in all cases (compounds 6–9 and 14–16). The δ Me₂ resonance in the ¹H NMR spectrum for com-

pounds 2–5 lies ca. δ 2.30 ppm as corresponds to the non-coordinated NMe₂ group (cf. δ 2.31 ppm for the free ligand); for compounds 6–9 values close to δ

2.70 ppm would be expected (cf. δ 2.67 ppm for 1), however the δ Me₂ resonance appears in the range δ 2.16–2.02 for compounds 6–8 and at δ 2.74 ppm for

Table 1
³¹P^a and ¹H^b NMR data^{c,d}

	δ (HC=N)	δ (H2)	δ (H3)	δ (H4)	δ (H5)	δ (CH ₂) ^f	δ (NMe ₂)	δ (P) ^g
L	8.73s	8.01d ³ J(H2H3) 7.2		7.36–7.28m		3.78 (13.8)	2.31s	
1	7.52s	7.64d ³ J(H2H3) 7.3		7.09–7.00m		3.68 (12.0)	2.65 2.67s 2.89	
2	8.17s	^c	6.90t ³ J(H3H4) 7.4 ³ J(H2H3) 7.4	6.51t ³ J(H4H5) 7.4	6.36d 2.82	4.06 (12.6)	2.28s	40.86s
3	8.09s	7.23dd ³ J(H2H3) 7.4 ⁴ J(H2H4) 1.4	6.87td ³ J(H3H4) 7.4 ⁴ J(H3H5) 0.7	6.56td ³ J(H4H5) 7.4	6.44d	4.03 (12.8) 2.82	2.32s	34.88s
4	8.07d ⁴ J(PH) 7.5	7.24dd ³ J(H2H3) 7.4 ⁴ J(H2H4) 1.4	6.91t ³ J(H3H4) 7.4	6.68td ³ J(H4H5) 7.4	6.43t ⁴ J(PH5) 7.5	4.03 (12.8) 2.82	2.33s	32.13s
5	8.09d ⁴ J(PH) 7.6	7.31d ³ J(H2H3) 7.5		7.2–7.0m		3.98 (12.8) 2.78	2.31s	27.45s
6	8.41d ⁴ J(PH) 9.5	7.33dd ³ J(H2H3) 7.4 ⁴ J(H2H4) 1.3	6.89t ³ J(H3H4) 7.4	6.48td ³ J(H4H5) 7.4	6.14dd ⁴ J(PH5) 4.6	4.09 (12.2) 3.03	2.02s	36.39s
7	8.35d ⁴ J(PH) 9.0	7.37dd ³ J(H2H3) 7.4 ⁴ J(H2H4) 1.4	7.01t ³ J(H3H4) 7.4	6.75td ³ J(H4H5) 7.4	6.45dd ⁴ J(PH5) 3.8	4.07 (12.2) 3.08	2.16s	31.04s
8	8.28d ⁴ J(PH) 9.3	7.30dd ³ J(H2H3) 7.5 ⁴ J(H2H4) 1.5	6.96t ³ J(H3H4) 7.5	6.80td ³ J(H4H5) 7.5	6.47dd ⁴ J(PH5) 4.0	4.00 (12.0) 3.02	2.11s	23.27s
9	8.29d ⁴ J(PH) 9.5	7.39d ³ J(H2H3) 6.8		7.2–6.9m		4.02 (12.0) 3.03	2.74s	20.45s
10 ^b	7.93s	7.51d ³ J(H2H3) 7.5	7.16td ³ J(H3H4) 7.5 ⁴ J(H3H5) 1.2	7.04t ³ J(H4H5) 7.5	7.24dd	3.73 (13.8) 2.72	2.31s	
11 ⁱ	8.14s ³ J(H2H3) 7.4	7.27dd ³ J(H3H4) 7.4 ⁴ J(H2H4) 1.2	6.91td ³ J(H4H5) 7.4	6.55td	6.45d	4.06 (12.0) 2.81	2.31s	33.68s
12	8.10s	7.22d ³ J(H2H3) 7.5	6.87t ³ J(H3H4) 7.5	6.54t ³ J(H4H5) 7.5	6.35d	3.99	2.26s	30.79s
13	8.09s	7.22d ³ J(H2H3) 7.4	6.87t ³ J(H3H4) 7.4	6.55t ³ J(H4H5) 7.4	6.39d	4.02 (12.2) 2.79	2.31s	31.86s
14 ⁱⁱ	8.53d ⁴ J(PH) 9.3	^c	7.07t ³ J(H2H3) 7.5	6.61t ³ J(H3H4) 7.5	6.46dd ³ J(H4H5) 7.5 ⁴ J(PH5) 4.1	4.08 3.08	^k	37.72s
15 ^l	8.56d ⁴ J(PH) 9.5	^c	7.20t ³ J(H3H4) 7.5 ³ J(H2H3) 7.5	6.96td ³ J(H4H5) 7.5 ⁴ J(H2H4) 1.5	6.73dd ⁴ J(PH5) 4.1	4.03	1.95s	31.78s
16 ^l	8.50d ⁴ J(PH) 9.5	^c	7.08td ³ J(H3H4) 7.5 ³ J(H2H3) 7.5	6.77td ³ J(H4H5) 7.5 ⁴ J(H2H4) 1.5	6.55dd ³ J(H3H5) 0.5 ⁴ J(PH5) 4.3	3.91 2.84	1.95s	32.90s
17 ^m	8.50d ⁴ J(PH) 7.5	^c	6.98td ³ J(H2H3) 7.2 ³ J(H3H4) 7.2	6.71td ³ J(H4H5) 7.2 ⁴ J(H2H4) 1.5	6.59m ³ J(H3H5) 0.5 ⁴ J(PH5) 7.4 ⁴ J(PH5) 5.7	3.29	1.94s	59.09d 41.08d (36.9)
18 ^m	8.32d ⁴ J(PH) 5.8	^c	6.93t ³ J(H2H3) 7.3 ³ J(H3H4) 7.3	6.56m		3.00	1.97s	24.38d – 4.14d (58.3)
19 ^m	8.12d ⁴ J(PH) 6.6	^c	6.86t ³ J(H2H3) 7.2 ³ J(H3H4) 7.2	6.70m		3.34 2.40	1.76s	60.29d 49.09d (55.9)
20 ^m	8.01s	^c	6.69t ³ J(H2H3) 7.4 ³ J(H3H4) 7.4	6.42t ³ J(H4H5) 7.4	6.37d	3.89 (13.2) 2.76	2.07s	32.70d 17.58d (14.6)

compound **9**. We suggest the lower δ value observed for the δ_{Me_2} resonance in **6–8** is due to shielding of a phosphine phenyl ring; as proof, in the compound with triethylphosphine, **9**, the δ_{Me_2} resonance appears at δ 2.74 ppm. The separation of the $\text{N}(\text{CH}_2)_2$ resonances in the ^{13}C NMR spectra of compounds **6–9**, ca. 10–15 ppm, shows coordination of the NMe_2 group to the metal atom, as opposed to compounds **2, 3, 5**, where it is ca. 4–7 ppm.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a singlet resonance for the phosphorus nucleus in **2–5** and **6–9**; substitution of the phosphine phenyl groups for ethyl groups shifts the ^{31}P resonance to lower frequency (Table 1). Comparison of the difference in the ^{31}P chemical shift values for pairs of compounds bearing the same phosphine ligand, $\Delta\delta$, showed the resonances for compounds **6–9** to be at lower frequency than those for **2–5** in all cases (Table 1). However, $\Delta\delta$ is greater when the ^{31}P nucleus is always *trans* to nitrogen [$\Delta\delta(4,8) = 8.86$ ppm; $\Delta\delta(5,9) = 7.0$ ppm] than when the ^{31}P nucleus is *trans* to different atoms in the complexes, i.e. ^{31}P *trans* to carbon or nitrogen [$\Delta\delta(2,6) = 4.47$ ppm; $\Delta\delta(3,7) = 3.84$ ppm].

Treatment of **1** with thallium acetylacetonate gave the soluble complex $[\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{H}_3\text{CCOCHCOCH}_3)_2]$ **10** as an air-stable solid, which was fully characterized (see Section 3 and Table 1). The ^1H NMR spectrum showed singlet resonances at δ 5.37 and 2.03 ppm assigned to the *CH* and to the two *C–Me* groups respectively. The ^{13}C NMR spectrum showed singlets at δ 100.65 and δ 23.03 ppm, assigned to the *CH* and *C–Me* resonances respectively.

Reaction of **1** with ditertiary diphosphines in a complex **1**/diphosphine 2:1 molar ratio gave the dinuclear cyclometallated complexes $[\{\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})_2(\mu\text{-Ph}_2\text{PRPPh}_2)\}]$ [**11**: $\text{R} = \text{trans-CH}=\text{CH}$; **12**: $\text{R} = (\text{CH}_2)_3$; **13**: $\text{R} = (\text{CH}_2)_4$] respectively, and treatment of **1** with silver perchlorate followed by ditertiary diphosphines gave the dinuclear cyclometallated complexes $[\{\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)\}_2(\mu\text{-Ph}_2\text{PR-}$

$\text{PPh}_2)(\text{ClO}_4)_2]$ [**14**: $\text{R} = \text{trans-CH}=\text{CH}$; **15**: $\text{R} = (\text{CH}_2)_3$; **16**: $\text{R} = (\text{CH}_2)_4$] respectively, which were fully characterised (see Section 3 and Table 1). Electric conductivity measurements in dry acetonitrile solution showed complexes **14–16** to be 1:2 electrolytes [22] (see Section 3). In the ^1H NMR spectra of compounds **11–13** singlets were observed for the $\text{HC}=\text{N}$ and H_5 resonances (Table 1); no coupling of the $\delta = \text{NCH}_2$ resonance to the ^{31}P nucleus was observed. In view of this we tentatively assign these compounds the structures depicted in Scheme 2, with the phosphorus atom *trans* to the phenyl carbon atom of the metallated ring. There is only one set of resonances for each cyclopalladated moiety in the ^1H and ^{13}C NMR spectra and only one singlet for the two ^{31}P nuclei in the $^{31}\text{P}\{^1\text{H}\}$ spectrum. This suggests that the compounds are centrosymmetric, as we have shown before in related compounds [30,31]. In the ^1H NMR spectra of complexes **11** and **14**, apparent triplets at δ 6.75 and δ 8.30 ppm respectively were assigned to the $\text{PCH}=\text{CHP}$ resonances ('AA'XX' spin system) with N ca. 41 Hz. In the ^1H NMR spectra of compounds **14–16** the NMe_2 resonance is shifted to lower frequency from the expected position, ca. 2.7 ppm, due to shielding of the phosphine phenyl ring.

Treatment of **1** with ditertiary diphosphines in a complex **1**/diphosphine 1:1 molar ratio, and silver perchlorate gave the mononuclear cyclometallated complexes $[\{\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{Ph}_2\text{PRPPh}_2, P, P)(\text{ClO}_4)_2]$ [**17**: $\text{R} = (\text{CH}_2)_3$; **18**: $\text{R} = (\text{CH}_2)_4$] respectively (see Section 3 and Table 1). Electric conductivity measurements in dry acetonitrile solution showed the complexes to be 1:1 electrolytes [22] (see Section 3). When the reaction was carried out in the absence of the perchlorate salt, an untreatable mixture was obtained. However, when **1** was treated only with *cis*-dppf in a complex **1**/diphosphine 1:1 molar ratio, the mononuclear cyclometallated complex $[\{\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2, P, P)(\text{Cl})]$ (**19**) was obtained, which was fully characterised (see Section 3 and Table 1). Electric

Notes to Table 1:

^a In CDCl_3 . Measured at 100.6 MHz (ca. $\pm 20^\circ\text{C}$); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4 .

^b In CDCl_3 , unless otherwise stated. Measured at 250 MHz (ca. $\pm 20^\circ\text{C}$); chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe_4 .

^c Coupling constants in Hz.

^d s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt, triplet of doublets; m, multiplet.

^e Occluded by the phosphine resonances.

^f The higher value was assigned to the $=\text{NCH}_2$ protons and the lower one to the *CH*, NMe_2 protons; N values in parentheses.

^g For **17–20** $\delta(P\text{-trans-C}) < \delta(P\text{-trans-N})$.

^h acac: $\delta(\text{CH})$ 5.38 ppm; $\delta(\text{Me})$ 2.04 ppm.

ⁱ $\delta(\text{C}=\text{C}H)$: **11**, 6.75 ppm; **14**, 8.30 ppm.

^j Occluded by methylene (phosphine) resonances.

^k Occluded by solvent resonances.

^l In acetone- d_6 .

^m $^J(\text{PP})$ values in parentheses.

conductivity measurements in dry acetonitrile solution showed the complex to be a 1:1 electrolyte (see Section 3). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed two doublets for the two inequivalent phosphorus nuclei. The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom in accordance with the higher *trans* influence of the latter with respect to the C=N nitrogen atom [32]. The HC=N resonance was only coupled to the ^{31}P nucleus *trans* to nitrogen. In compound **17** the H5 proton was coupled to both ^{31}P nuclei with $^3J(\text{P}_{\text{trans-C}}\text{H}) < ^3J(\text{P}_{\text{trans-N}}\text{H})$. This was confirmed by selective decoupling experiments on the ^{31}P atoms. Although the NMe_2 group is not coordinated to the metal atom, the methyl resonance was shifted to lower frequency due to shielding of the phenyl rings on the phosphorus atom *trans* to carbon.

Treatment of **1** with dppe in a complex 1/diphosphine 1:1 molar ratio gave the mononuclear cyclometalated complex $[\{\text{Pd}[\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2-\text{NMe}_2\}(\text{Cl})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\text{-}P, P)]$ (**20**) which was fully characterized (see Section 3 and Table 1). Electric conductivity measurements in dry acetonitrile solution showed the compound to be a non-electrolyte. The Pd(PP)Cl moiety can rotate about the Pd-C vector so that the palladium coordination plane is at 90° to the metallated phenyl ring, eliminating coupling between the ^{31}P atom and the H5 or the HC=N protons [25]; also, no coupling of the =NC H_2 resonance to the ^{31}P nucleus was observed. Both ^{31}P resonances were inequivalently assigned (see above).

Garrou [33] has proposed that the ^{31}P chemical shift is influenced by ring size. The data for compounds **17–19** are summarized in Table 2. We have calculated Δ_R for compounds for both phosphorus atoms *trans* to carbon and *trans* to nitrogen (see Table 2). In the five-membered ring cases (compounds **17, 19**) the absolute value of Δ_R is smaller when the ^{31}P nucleus is

trans to carbon than to nitrogen; the reverse is true for the six-membered ring compound **18**.

3. Experimental details

All reactions were carried out in an atmosphere of dry nitrogen. Solvents were purified by standard methods [34]. Chemicals were reagent grade. Tris(dibenzylideneacetone)dipalladium(0) and thallium acetylacetonate were purchased from Aldrich-Chemie. The diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppe), $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (dppp) and $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (dppb) were purchased from Aldrich-Chemie; *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ (*cis*-1,2-dppe) and *trans*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ (*trans*-1,2-dppe) were prepared according to procedures described elsewhere [35]. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo-Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin-Elmer 1330 and on a Mattson (Servicio de Espectroscopia of the University of Santiago) spectrophotometers. NMR spectra were obtained as CDCl_3 or $(\text{CD}_3)_2\text{CO}$ solutions and referenced to SiMe_4 (^1H , ^{13}C) or 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$) and were recorded on Bruker WM-250, AMX-300 and AC-200 spectrometers. All chemical shifts were reported downfield from the standards.

The synthesis of 2- $\text{ClC}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2$ was performed by heating a chloroform solution of the appropriate quantities of 2-chlorobenzaldehyde and *N,N'*-dimethylethylenediamine in a Dean-Stark apparatus under reflux. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CDCl_3): δ 158.9 (C=N); δ 135.3 (C1); δ 133.3 (C6); δ 131.7, δ 130.0, δ 128.6, δ 127.2 (C2, C3, C4, C5); δ 60.2, δ 60.1 (CH $_2$); δ 46.00 (NMe $_2$).

CAUTION Perchlorate salts of metal complexes are potentially explosive. Extreme caution should be exercised in handling this material.

3.1. Preparation of $[\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})]$ (**1**)

2- $\text{ClC}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2$ (140 mg, 0.67 mmol) and tris(dibenzylideneacetone)dipalladium(0) (300 mg, 0.33 mmol) were added to 25 cm^3 of benzene to give a dark red solution which was heated under reflux for 2 h. After cooling to room temperature the solution was filtered to eliminate the small amount of black palladium formed. The solvent was removed under vacuum to give a yellow solid which was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (1%) afforded the final product as a pale yellow solid after concentration. Yield 60%. Anal. Found: C, 42.0; H, 4.7; N, 8.8.

Table 2
 ^{31}P parameters^a

	P ^b	P _c	Δ_R
17	31.78	59.09	27.31
18	31.78	24.38	-7.40
19	31.78	60.29	28.51
	P ^c	P _b	Δ_R
17	30.79	41.08	10.29
18	30.79	-4.14	-26.65
19	30.79	49.09	18.3
20	30.79	17.58	-13.21

^a P_c phosphorus *trans* to nitrogen. P_b phosphorus *trans* to carbon.

^b Equivalent phosphorus (-PPh $_2$) in a non-chelated analogue (compound **15**).

^c Equivalent phosphorus (-PPh $_2$) in a non-chelated analogue (compound **12**).

$C_{11}H_{15}N_2ClPd$ Calc.: C, 41.7; H, 4.8; N, 8.8%. IR: $\nu(C=N)$ 1616 cm^{-1} ; $\nu(Pd-Cl)$ 349 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 172.2 (C=N); δ 158.0 (C1); δ 150.2 (C6); δ 136.1, δ 130.7, δ 127.6, δ 124.3 (C2, C3, C4, C5); δ 63.5, δ 53.4 (NCH_2CH_2); δ 48.3 (NMe_2).

3.2. Preparation of $[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(Cl)(PPh_3)]$ (2)

PPh_3 (33 mg, 0.13 mmol) was added to a solution of **1** (40 mg, 0.13 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the solvent removed and the product recrystallized from dichloromethane/hexane to give the desired complex as a white solid. Yield 90%. Anal. Found: C, 60.0; H, 5.5; N, 4.6. $C_{25}H_{30}N_2O_2ClPPd$ Calc.: C, 60.1; H, 5.2; N, 4.8%. IR: $\nu(C=N)$ 1628 cm^{-1} ; $\nu(Pd-Cl)$ 310 cm^{-1} . $^{13}C\{^1H\}$ NMR (62.46 MHz, $CDCl_3$): δ 176.4 (C=N); δ 157.1 (C1); δ 148.9 (C6); δ 138.3, δ 136.1, δ 129.9, δ 124.3 (C2, C3, C4, C5); δ 55.1, 53.1 (NCH_2); δ 46.2 (NMe_2). P-phenyl: C_i δ 131.1; C_o δ 135.3d, $J(PC)$ 12.1 Hz; C_m δ 128.3d, $J(PC)$ 11.8 Hz; C_p δ 131.0.

Compounds **3**, **4** and **5** were obtained following a similar procedure as white solids.

3.3. $[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(Cl)(PEtPh_2)]$ (3)

Yield 91%. Anal. Found: C, 56.2; H, 5.7; N, 5.2. $C_{25}H_{30}N_2O_2ClPPd$ Calc.: C, 56.5; H, 5.7; N, 5.3%. IR: $\nu(C=N)$ 1630 cm^{-1} ; $\nu(Pd-Cl)$ 305 cm^{-1} . $^{13}C\{^1H\}$ NMR (62.46 MHz, $CDCl_3$): δ 175.8 (C=N); δ 157.4 (C1); δ 149.8 (C6); δ 137.2, δ 130.0, δ 127.9, δ 123.8 (C2, C3, C4, C5); δ 59.6, 52.8 (NCH_2); δ 45.5 (NMe_2). P-phenyl: C_i δ 129.5d, $J(PC)$ 19.9 Hz; C_o δ 133.6d, $J(PC)$ 21.4 Hz; C_m δ 128.3; C_p δ 131.5.

3.4. $[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(Cl)(PEt_2Ph)]$ (4)

Yield 87%. Anal. Found: C, 52.1; H, 6.5; N, 5.9. $C_{21}H_{30}N_2O_2ClPPd$ Calc.: C, 52.2; H, 6.3; N, 5.8%. IR: $\nu(C=N)$ 1626 cm^{-1} ; $\nu(Pd-Cl)$ 313 cm^{-1} .

3.5. $[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(Cl)(PEt_3)]$ (5)

Yield 77%. Anal. Found: C, 46.7; H, 6.5; N, 6.2. $C_{17}H_{30}N_2ClPPd$ Calc.: C, 46.9; H, 6.9; N, 6.4%. IR: $\nu(C=N)$ 1629 cm^{-1} ; $\nu(Pd-Cl)$ 293 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 174.4 (C=N); δ 156.3 (C1); δ 147.6 (C6); δ 133.8, δ 129.4, δ 127.5, δ 123.3 (C2, C3, C4, C5); δ 58.1, δ 54.7 (NCH_2); δ 44.6

(NMe_2); δ 15.4d, $J(PC)$ 24.4 Hz (CH_2CH_3); δ 7.9 (CH_2CH_3).

3.6. Preparation of

$[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(PPh_3)(ClO_4)]$ (6)

A solution of **1** (40 mg, 0.13 mmol) in acetone (15 cm^3) was treated with silver perchlorate (27 mg) and stirred for 2 h. The solution was filtered through Celite to eliminate the $AgCl$ precipitate. PPh_3 (33 mg, 0.13 mmol) was added to the filtrate and the solution stirred for 4 h, the solvent removed and the product recrystallized from dichloromethane/hexane to give the desired complex as a white solid. Yield 93%. Anal. Found: C, 53.7; H, 4.7; N, 4.1. $C_{25}H_{30}N_2O_2ClPPd$ Calc.: C, 54.1; H, 4.7; N, 4.3%. IR: $\nu(C=N)$ 1639 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 176.1 (C=N); δ 154.3 (C1); δ 150.6 (C6); δ 138.6, δ 130.5, δ 129.6, δ 125.4 (C2, C3, C4, C5); δ 66.4, δ 53.3 (NCH_2CH_2); δ 48.1 (NMe_2). P-phenyl: C_i δ 128.0d, $J(PC)$ 22.6 Hz; C_o δ 135.3d, $J(PC)$ 12.8 Hz; C_m δ 129.0d, $J(PC)$ 10.6 Hz; C_p δ 132.0s. Specific molar conductivity, $\Lambda_m = 169 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

Compounds **7**, **8** and **9** were obtained following a similar procedure as white solids.

3.7. $[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(PEtPh_2)(ClO_4)]$ (7)

Yield 80%. Anal. Found: C, 50.0; H, 5.1; N, 4.6. $C_{25}H_{30}N_2O_2ClPPd$ Calc.: C, 50.4; H, 5.1; N, 4.7%. IR: $\nu(C=N)$ 1637 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 176.0 (C=N); δ 154.3 (C1); δ 150.7 (C6); δ 137.1, δ 131.2, δ 130.1, δ 125.8 (C2, C3, C4, C5); δ 65.8, δ 51.6 (NCH_2); δ 48.3 (NMe_2); δ 21.2d, $J(PC)$ 28.1 Hz (CH_2CH_3); δ 12.4 (CH_2CH_3). P-phenyl: C_i δ 130.6; C_o δ 133.6d, $J(PC)$ 10.6 Hz; C_m δ 129.5d, $J(PC)$ 9.8 Hz; C_p δ 131.9s. Specific molar conductivity, $\Lambda_m = 160 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.8. $[Pd(C_6H_4C(H)=NCH_2CH_2NMe_2)(PEt_2Ph)(ClO_4)]$ (8)

Yield 89%. Anal. Found: C, 45.5; H, 5.9; N, 5.2. $C_{21}H_{30}N_2O_2ClPPd$ Calc.: C, 46.1; H, 5.5; N, 5.1%. IR: $\nu(C=N)$ 1637 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 176.0 (C=N); δ 153.7 (C1); δ 151.2 (C6); δ 135.5, δ 131.0, δ 129.7, δ 125.4 (C2, C3, C4, C5); δ 66.1, δ 51.6 (NCH_2); δ 49.5 (NMe_2); δ 16.6d, $J(PC)$ 27.9 Hz (CH_2CH_3); δ 8.7 (CH_2CH_3). P-phenyl: C_i δ 128.5; C_o δ 132.6d, $J(PC)$ 10.6 Hz; C_m δ 128.9d, $J(PC)$ 9.7 Hz; C_p δ 131.3. Specific molar conductivity, $\Lambda_m = 163 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.9. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}(PEt_3)](ClO_4)$ (9)

Yield 65%. Anal. Found: C, 40.9; H, 6.1; N, 5.7. $C_{49}H_{50}N_4O_4ClPPd$ Calc.: C, 40.9; H, 6.1; N, 5.6%. IR: $\nu(C=N)$ 1639 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 175.1 (C=N); δ 151.8 (C1); δ 150.2 (C6); δ 135.0, δ 131.7, δ 130.5, δ 126.2 (C2, C3, C4, C5); δ 66.7, δ 52.1 (NCH₂); δ 49.3 (NMe₂); δ 14.7, $J(PC)$ 27.9 Hz (CH₂CH₃); δ 8.9 (CH₂CH₃). Specific molar conductivity, $\Lambda_m = 142 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.10. Preparation of $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}(H_3CCOCHCOCH_3)]$ (10)

To a solution of **1** (40 mg, 0.13 mmol) in chloroform (25 cm^3), thallium acetylacetonate (40 mg, 0.13 mmol) was added and the mixture stirred at room temperature for 12 h. The solution was filtered to eliminate the TlCl precipitate and the solvent removed to give the desired complex as a yellow solid which was recrystallized from dichloromethane/hexane. Yield 85%. Anal. Found: C, 50.2; H, 5.9; N, 7.3. $C_{46}H_{42}N_4O_4Pd$ Calc.: C, 50.5; H, 5.8; N, 7.4%. IR: $\nu(C=N)$ 1610 cm^{-1} ; 2,4-pentanedionate: $\nu(C=C)$ 1512 cm^{-1} ; $\nu(C=O)$ 1577.8, 1389 cm^{-1} . $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 176.0 (C=N); δ 157.3 (C1); δ 146.5 (C6); δ 131.0, δ 129.9, δ 126.8, δ 124.5 (C2, C3, C4, C5); δ 100.7 (CH, acac); δ 59.2, δ 56.2 (CH₂); δ 46.0 (NMe₂); δ 28.0 (Me, acac).

3.11. Preparation of $[\overline{Pd[C_5H_2C(H) = NCH_2CH_2NMe_2]}(Cl)]_2(\mu-Ph_2P(CH_2)_4PPh_2)]$ (13)

$Ph_2P(CH_2)_4PPh_2$ (27 mg, 0.06 mmol) was added to a solution of **1** (40 mg, 0.13 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the solvent removed and the product recrystallized from dichloromethane/hexane to give the desired complex as a white solid. Yield 77%. Anal. Found: C, 56.6; H, 5.7; N, 5.3. $C_{50}H_{58}N_4Cl_2P_2Pd_2$ Calc.: C, 56.6; H, 5.5; N, 5.3%. IR: $\nu(C=N)$ 1628 cm^{-1} ; $\nu(Pd-Cl)$ 290 cm^{-1} . $^{13}C\{^1H\}$ NMR (62.46 MHz, $CDCl_3$): δ 175.7 (C=N); δ 157.7 (C1); δ 148.1 (C6); δ 137.3, δ 129.8, δ 127.8, δ 124.0 (C2, C3, C4, C5); δ 59.3, 55.8 (NCH₂); δ 45.8 (NMe₂). P-phenyl: C_i δ 131.5; C_o δ 134.0d, $J(PC)$ 11.5 Hz; C_m δ 128.4, $J(PC)$ 10.4 Hz; C_p δ 130.7.

Compounds **11** and **12** were synthesized following a similar procedure.

3.12. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}(Cl)]_2(\mu-trans-Ph_2PCH = CHPPh_2)]$ (11)

Yield 80%. Anal. Found: C, 56.2; H, 5.0; N, 5.3. $C_{48}H_{52}N_4Cl_2P_2Pd_2$ Calc.: C, 55.9; H, 5.1; N, 5.4%. IR: $\nu(C=N)$ 1631 cm^{-1} ; $\nu(Pd-Cl)$ 300 cm^{-1} .

3.13. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}(Cl)]_2(\mu-Ph_2P(CH_2)_3PPh_2)]$ (12)

Yield 91%. Anal. Found: C, 56.1; H, 4.9; N, 5.0. $C_{49}H_{56}N_4Cl_2P_2Pd_2$ Calc.: C, 56.2; H, 5.4; N, 5.3%. IR: $\nu(C=N)$ 1624 cm^{-1} ; $\nu(Pd-Cl)$ 300 cm^{-1} . $^{13}C\{^1H\}$ NMR (62.46 MHz, $CDCl_3$): δ 175.9 (C=N); δ 157.5 (C1); δ 149.5 (C6); δ 137.4, δ 138.0, δ 127.3, δ 124.2 (C2, C3, C4, C5); δ 59.5, 55.7 (NCH₂); δ 45.8 (NMe₂). P-phenyl: C_i δ 129.9; C_o δ 133.2d, $J(PC)$ 11 Hz; C_m δ 128.5, $J(PC)$ 11 Hz; C_p δ 130.7.

Compounds **14**, **15** and **16** were synthesized following a similar procedure to that for **6** but using a 1/diphosphine 2:1 molar ratio.

3.14. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}]_2(\mu-trans-Ph_2PCH = CHPPh_2)](ClO_4)_2$ (14)

Yield 82%. Anal. Found: C, 49.2; H, 4.6; N, 4.8. $C_{48}H_{52}N_4O_4Cl_2P_2Pd_2$ Calc.: C, 49.8; H, 4.5; N, 4.8%. IR: $\nu(C=N)$ 1639 cm^{-1} . Specific molar conductivity, $\Lambda_m = 320 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.15. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}]_2(\mu-Ph_2P(CH_2)_3PPh_2)](ClO_4)_2$ (15)

Yield 55%. Anal. Found: C, 50.2; H, 4.8; N, 4.8. $C_{49}H_{56}N_4O_4Cl_2P_2Pd_2$ Calc.: C, 50.1; H, 4.8; N, 4.8%. IR: $\nu(C=N)$ 1635 cm^{-1} . Specific molar conductivity, $\Lambda_m = 315 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.16. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}]_2(\mu-Ph_2P(CH_2)_4PPh_2)](ClO_4)_2$ (16)

Yield 83%. Anal. Found: C, 50.5; H, 4.8; N, 4.7. $C_{50}H_{58}N_4O_4Cl_2P_2Pd_2$ Calc.: C, 50.5; H, 4.9; N, 4.7%. IR: $\nu(C=N)$ 1637 cm^{-1} . Specific molar conductivity, $\Lambda_m = 309 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

Complexes **17** and **18** were prepared following a similar procedure to that for **14** using a 1/diphosphine 1:1 molar ratio.

3.17. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}(Ph_2P(CH_2)_2PPh_2-P,P)](ClO_4)_2$ (17)

Yield 63%. Anal. Found: C, 57.2; H, 5.3; N, 3.6. $C_{37}H_{36}N_4O_4ClP_2Pd$ Calc.: C, 57.0; H, 5.0; N, 3.6%. IR: $\nu(C=N)$ 1618 cm^{-1} . Specific molar conductivity, $\Lambda_m = 156 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.18. $[\overline{Pd[C_6H_4C(H) = NCH_2CH_2NMe_2]}(Ph_2P(CH_2)_3PPh_2-P,P)](ClO_4)_2$ (18)

Yield 77%. Anal. Found: C, 57.5; H, 5.0; N, 3.5. $C_{38}H_{41}N_4O_4ClP_2Pd$ Calc.: C, 57.5; H, 5.2; N, 3.5%.

IR: $\nu(\text{C}=\text{N})$ 1620 cm^{-1} . Specific molar conductivity, $\Lambda_m = 153 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

3.19. Preparation of $[\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\text{-P,P})]$ (20)

$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (51 mg, 0.12 mmol) was added to a suspension of **1** (40 mg, 0.13 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h at room temperature, the resulting precipitate was filtered off and recrystallized from dichloromethane/hexane to give the desired product as a pale yellow solid. Yield 87%. Anal. Found: C, 63.0; H, 5.6; N, 3.8. $\text{C}_{39}\text{H}_{33}\text{N}_2\text{Cl}_2\text{Pd}$ Calcd: C, 63.0; H, 5.8; N, 3.8%. IR: $\nu(\text{C}=\text{N})$ 1626 cm^{-1} ; $\nu(\text{Pd}-\text{Cl})$ 301 cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3): δ 182.5 (C=N); δ 149.1 (C6); δ 137.9, δ 132.9, δ 130.1, δ 126.6 (C2, C3, C4, C5); δ 59.3, δ 58.0 (NCH₂); δ 45.5 (NMe₂). P-phenyl: C_i δ 125.7d, 124.3d, J(PC) 44.0 Hz; C_p δ 134.2d, δ 133.5d, J(PC) 13.6 Hz; C_m δ 130.4d, δ 130.4d, J(PC) 9.8 Hz; C_p δ 132.8.

Compound **19** was made using a similar procedure to that of **20**.

3.20. $[\text{Pd}(\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{cis-Ph}_2\text{PCH}=\text{CHPh}_2\text{-P,P})](\text{Cl})$ (19)

Yield 88%. Anal. Found: C, 62.0; H, 5.0; N, 3.8. $\text{C}_{37}\text{H}_{32}\text{N}_2\text{Cl}_2\text{Pd}$ Calcd: C, 62.3; H, 5.2; N, 3.9%. IR: $\nu(\text{C}=\text{N})$ 1618 cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3): δ 174.4 (C=N); δ 157.8 (C1); δ 137.2, δ 131.6, δ 129.7, δ 123.8 (C2, C3, C4, C5); δ 59.1, δ 56.0 (NCH₂); δ 45.4 (NMe₂). P-phenyl: C_i δ 130.5; C_p δ 133.5; C_m δ 128.6, δ 128.2; C_p δ 130.6. Specific molar conductivity, $\Lambda_m = 112 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetonitrile).

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