

Polynuclear cyclometallated palladium (II) complexes derived from potentially hexadentate Schiff base ligands. Crystal structures of  $[(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_2\{C(H)=NCH_2CH_2NMe_2\}-Pd(Cl)]$  and  $[\{(Ph_2PCH_2CH_2)_2PPh-P,P,P\}Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_2\{C(H)=NCH_2CH_2NMe_2\}-Pd\{(Ph_2PCH_2CH_2)_2PPh-P,P,P\}][Cl]_2$

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## Abstract

The oxidative addition reaction of 1,4-(C=N(H)CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub> with tris(dibenzylideneacetone)dipalladium(0) in benzene gave the doubly cyclometallated compound  $[(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_2\{C(H)=NCH_2CH_2NMe_2\}Pd(Cl)]$  (**1**) with each palladium atom *C,N,N'* bonded to the ligand. Treatment of **1** with thallium acetylacetonate gave the dinuclear cyclometallated complex **2** with two chelating acetylacetonate ligands. Reaction of **1** with tertiary monophosphines in a 1–phosphine 1:2 molar ratio gave dinuclear cyclometallated complexes **3–7**, in which the palladium–NMe<sub>2</sub> bond has been broken, whereas treatment of **1** with silver perchlorate, followed by reaction with PPh<sub>3</sub> in a 1–phosphine 1:2 molar ratio gave cyclometallated complex **4** where the ligand remains *C,N,N'* bonded and the chloride ligand has been substituted by triphenylphosphine. Treatment of **1** with tertiary diphosphines leads to dinuclear compounds **8**, **10** and **11**, whilst previous treatment of **1** with silver perchlorate followed by the diphosphine 1,4-bis(diphenylphosphino)butane (dppb) in a 1–diphosphine 1:1 molar ratio yielded the tetranuclear complex **9**. Reaction of **1** with the tertiary triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine in 1:2 molar ratio gave the complex  $[\{(Ph_2PCH_2CH_2)_2PPh-P,P,P\}Pd\{Me_2NCH_2CH_2N=(H)C\}-C_6H_2\{C(H)=NCH_2CH_2NMe_2\}Pd\{(Ph_2PCH_2CH_2)_2PPh-P,P,P\}][Cl]_2$  (**12**) in which both palladium atoms are pentacoordinated. The crystal structures of **1** and **12** are described. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Palladium; Cyclometallation; Schiff base; Dinuclear complexes; Oxidative addition; Phosphine complexes

## 1. Introduction

Cyclometallated compounds have been much studied over the last three decades [1–5], showing numerous applications in organic and organometallic synthesis [6], in insertion reactions [7], in the synthesis of new metal

mesogenic compounds [8], biologically active compounds [9] and in catalytic materials [10]. By far, the most widely studied examples are five-membered palladacycles with nitrogen donors. Generally, such compounds are prepared by reaction of an organic ligand with either palladium acetate or a tetrachloropalladate salt. Where the synthesis using palladium(II) salts as starting materials does not yield the expected cyclometallated complexes, synthesis via oxidative addition to halogenated ligands has shown to be an adequate method to achieve metallation [11,12].

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In previous work we have shown that potentially terdentate ligands such as Schiff bases **I** [11,13], semicarbazones **II** [14,15] and thiosemicarbazones **III** [16,17] undergo facile metallation with palladium(II), palladium(0) and platinum(II) to give mononuclear compounds with two five-membered fused rings at the metal centre (Fig. 1).

When [C, N, O] and [C, N, N] derivatives are treated with neutral ligands such as tertiary phosphines cleavage of the oxygen–metal or of the nitrogen–metal bonds occurs prior to ring-opening of the five-membered metallacycle upon continued reaction with the corresponding phosphine. If the cyclometallated compound has been treated previously with a silver(I) salt, the chloride ligand is removed as silver chloride and the vacant coordination site is occupied by the phosphine.

Doubly cyclometallated complexes, containing two metallated phenyl rings are frequent [18] but relatively few are known with two metallated sites on the same phenyl ring [19], or where each metal atom coordinates to the ligand through three donor atoms [20]. Less common are those in which both metal atoms coordinate to the same phenyl ring [13,21].

As part of our interest in the study of complexes derived from potentially terdentate ligands, in the present paper we report the synthesis via oxidative addition reaction of a new doubly cyclometallated palladium(II) complex derived from the hexadentate ligand 1,4-(C=N(H)CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub>. The X-ray crystal structure of this complex is reported, this being one of the few examples in which a cyclometallated complex derived from a doubly terdentate ligand is described [22]. We also give an account of its reactivity with tertiary mono and diphosphines. Recently, we have become interested in the reactivity of cyclometallated complexes with terdentate phosphines in order to obtain unusual coordination numbers and modification of the geometry at the metal centre. The reaction of the cyclometallated halide-bridged complexes with bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) has proved to be a novel route in promoting pentacoordination in palladium(II) [23]. Following our studies in this area we report the results of the reaction between **1** and the terdentate ligand. The crystal structure of this complex is also presented.

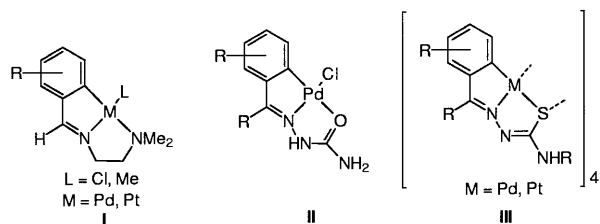


Fig. 1.

## 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 characterized by elemental analyses, IR spectroscopy (data in Section 3), <sup>1</sup>H-, <sup>31</sup>P-<sup>1</sup>H}- (see Table 1) and, in part, by <sup>13</sup>C-<sup>1</sup>H}-NMR (Section 3).

The oxidative addition reaction of 1,4-(C=N(H)-CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub> with tris(dibenzylideneacetone)dipalladium(0) in benzene gave the dicyclopalladated compound [(Cl)Pd{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N=(H)C}C<sub>6</sub>H<sub>2</sub>{C(H)=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Pd(Cl)] (**1**), which was fully characterized. The <sup>1</sup>H-NMR spectrum showed well-defined 'virtual triplet' patterns at δ 3.89 and δ 2.93 ppm for the C=NCH<sub>2</sub> and CH<sub>2</sub>NMe<sub>2</sub> protons, respectively, with *N*=11.8 Hz; a singlet at δ 2.30 ppm was assigned to the NMe<sub>2</sub> methyl protons, which was shifted to higher frequency as compared to the free ligand showing palladium coordination to the amine nitrogen atom. The singlet resonance at δ 7.94 ppm was assigned to the HC=N protons shifted to lower frequency confirming palladium–nitrogen coordination [24]. The <sup>13</sup>C-<sup>1</sup>H} spectrum showed resonances at δ 173.4 ppm (C=N) and δ 151.4 (C2, C5) ppm downfield shifted (related to the free ligand) as a consequence of cyclometallated ring formation [25,11]. The signal assigned to the NMe<sub>2</sub> carbon atoms was also shifted to higher frequency upon coordination to the amino nitrogen atom. The palladium–nitrogen bond formation was confirmed by the separation of the two methylene resonances (ca. 10 ppm; cf. 0 ppm for the non-coordinated ligand) [11].

The IR spectrum showed a band at 1600 cm<sup>-1</sup> shifted to lower wavenumbers, consistent with palladium coordination to the imino nitrogen atom [26,27], and a band at 350 cm<sup>-1</sup> assigned to the ν(Pd–Cl) vibration.

The structure has been confirmed by the X-ray crystal structure determination of **1**.

1,4-(C=N(H)CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub> was treated with Pd(OAc)<sub>2</sub> and Li<sub>2</sub>[PdCl<sub>4</sub>], but no cyclometallated compound was isolated. Reduction of the Pd(II) salts to Pd(0) was observed. No reaction with the C–Cl bonds took place, as has been described before [28].

Treatment of **1** with thallium acetylacetonate gave the dinuclear complex [(H<sub>3</sub>CCOCHCOCH<sub>3</sub>)Pd{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N=(H)C}C<sub>6</sub>H<sub>2</sub>{C(H)=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Pd-(H<sub>3</sub>CCOCHCOCH<sub>3</sub>)] (**2**) as an air-stable solid which was fully characterized. The <sup>1</sup>H-NMR spectrum showed the characteristic signals corresponding to the metallated ligand as well as the resonances corresponding to the coordinated acac ligand (δ (CH) 5.35s ppm, δ (Me) 2.01s ppm). The singlet at 2.30 ppm was assigned to the NMe<sub>2</sub> group (the same shift was observed for the uncoordinated ligand) showing the cleavage of

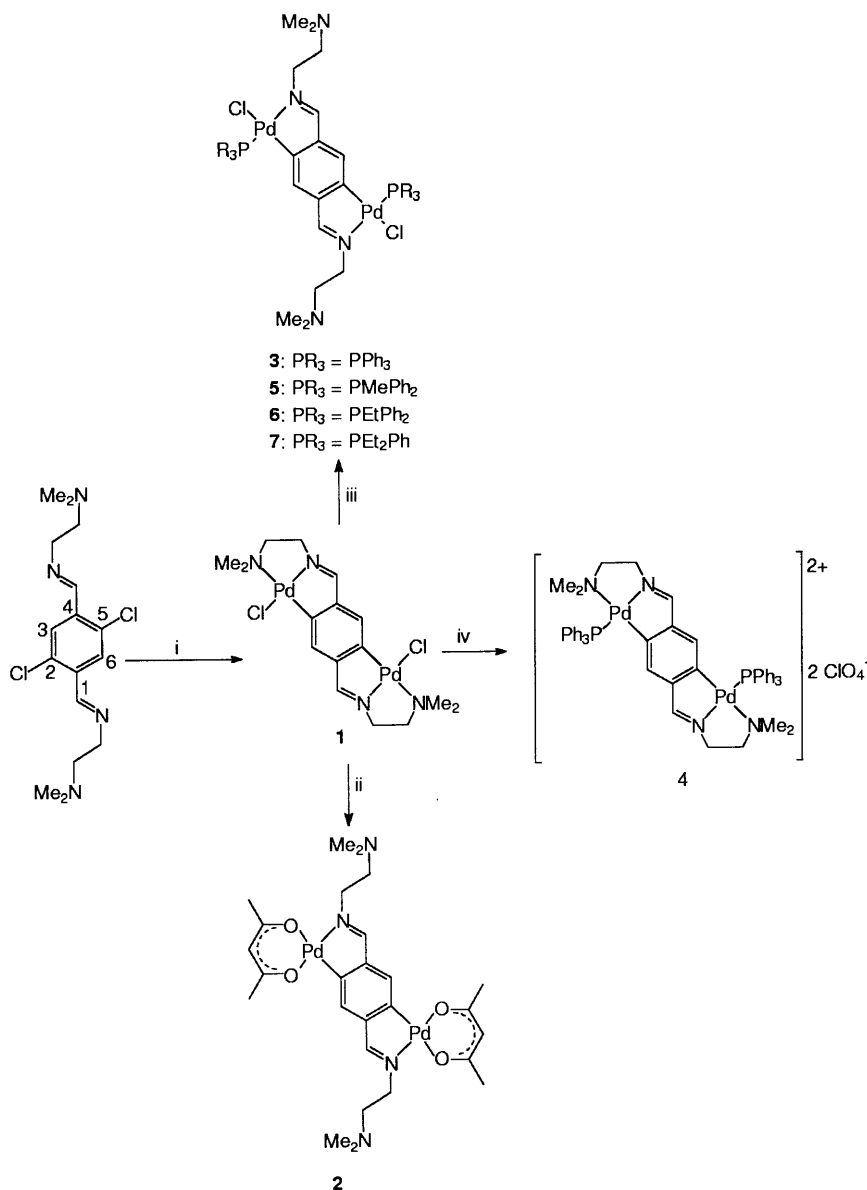
the Pd–NMe<sub>2</sub> bond. In the <sup>13</sup>C-<sup>1</sup>H} spectrum the separation of the two methylene resonances was ca. 3 ppm, confirming cleavage of the Pd–NMe<sub>2</sub> bond. The <sup>13</sup>C-<sup>1</sup>H} spectrum showed singlets at δ 100.17 and δ 27.48 ppm for the CH and C–Me carbons, respectively.

Reaction of **1** with tertiary monophosphines afforded the binuclear cyclometallated complexes [(L)(Cl)Pd{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N=(H)C}C<sub>6</sub>H<sub>2</sub>{C(H)=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Pd(Cl)(L)] (L = PPh<sub>3</sub>, **3**; L = PMePh<sub>2</sub>, **5**; L = PEtPh<sub>2</sub>, **6**; L = PEt<sub>2</sub>Ph, **7**) as pure air-stable solids which were fully characterized (see Table 1 and Section 3). The <sup>1</sup>H-NMR spectra of the complexes showed the singlet resonance assigned to the NMe<sub>2</sub> protons at ca. δ 2.25 ppm as corresponds to a non-coordinated amine nitrogen. The HC=N resonance appeared at ca. δ 7.2 ppm, high field shifted as compared to complexes **1** and

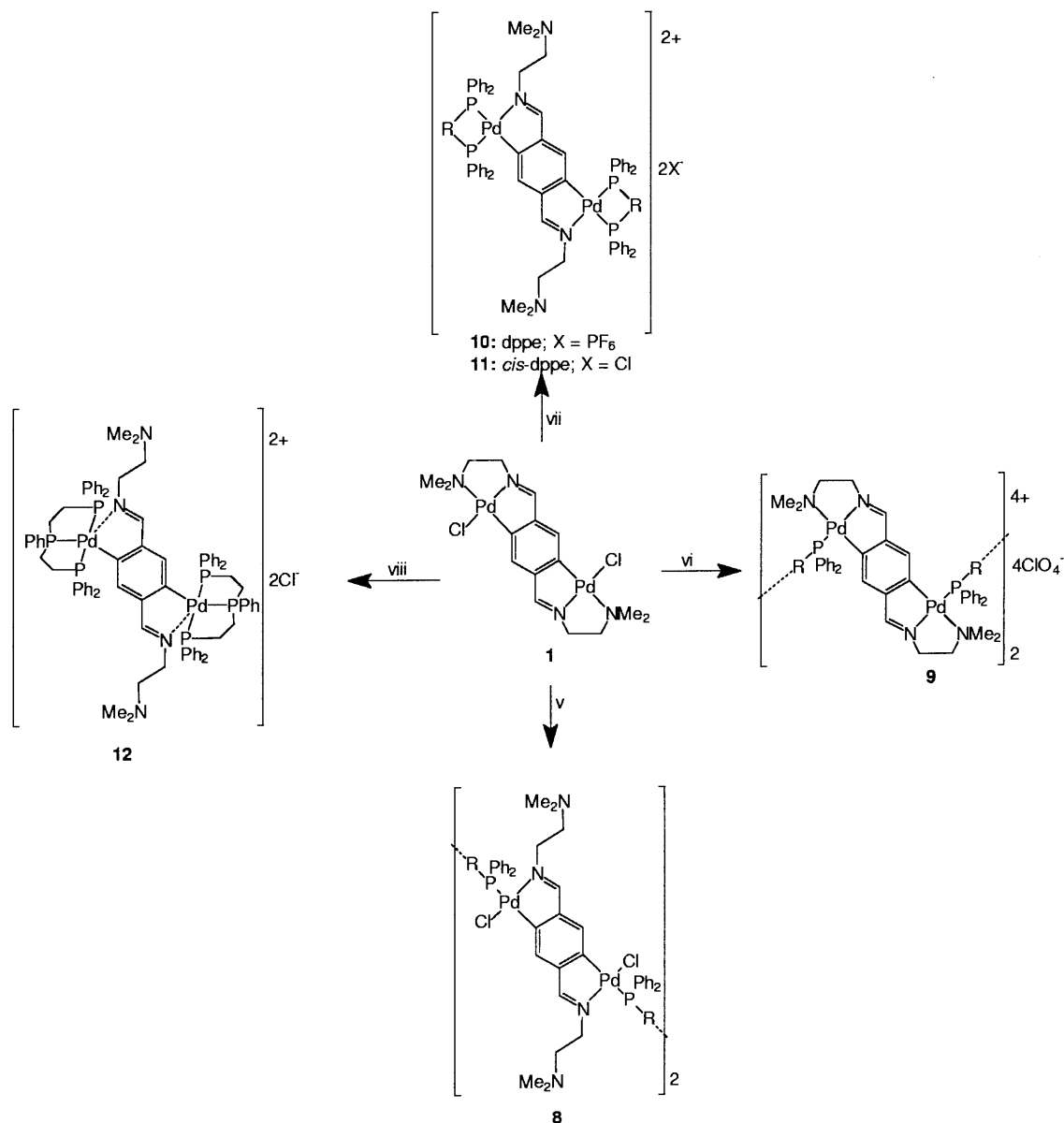
**2**. This shift has not been observed in mononuclear analogue complexes derived from terdentate Schiff bases [11]. We attribute this finding to the shielding effect of a phosphine phenyl ring that lies close to the HC=N as a consequence of the binuclear structure of the complex.

The IR spectra showed the ν(Pd–Cl) band in the range 281–301 cm<sup>-1</sup> confirming the presence of the chlorine atom in the coordination sphere of palladium.

Treatment of **1** with silver perchlorate followed by reaction with triphenylphosphine in 1–diphosphine 1:2 molar ratio yielded the doubly cyclometallated complex [(PPh<sub>3</sub>)Pd{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N=(H)C}C<sub>6</sub>H<sub>2</sub>{C(H)=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Pd(PPh<sub>3</sub>)] [ClO<sub>4</sub>]<sub>2</sub> (**4**) which was fully characterized (see Section 3 and Table 1). Electric conductivity measurements in dry acetonitrile solution showed



Scheme 1. (i) [Pd<sub>2</sub>(dba)<sub>3</sub>]-benzene; (ii) Tl(acac)-chloroform; (iii) PR<sub>3</sub>-acetone; (iv) AgClO<sub>4</sub> followed by PPh<sub>3</sub>-acetone.



Scheme 2. (v) dppp one equivalent–acetone; (vi) AgClO<sub>4</sub> followed by dppb one equivalent–acetone; (vii) diphosphine two equivalents–acetone; (viii) triphos–acetone.

the complex to be 1:2 electrolyte [29]. In the IR spectrum, the absence of the  $\nu(\text{Pd}-\text{Cl})$  band showed chloride abstraction as AgCl. The coupling constant  $J(\text{PH})$  to H3, H6 (4.2 Hz) in the <sup>1</sup>H spectrum, as well as the phosphorus chemical shift ( $\delta$  39.7 ppm) showed the palladium *trans* to phosphorus and *cis* to carbon disposition. Therefore, the phosphine ligand occupies the coordination site that was left vacant after removal of the chlorine atom. The  $\delta$  NMe<sub>2</sub> resonances were occluded by the NMR solvent (DMSO) resonances ca.  $\delta$  2.2 ppm; a value close to that observed for compound **1** ( $\delta$  2.70 ppm) would be expected. We suggest the lower  $\delta$  value is due to shielding of the phosphine phenyl rings [11].

Treatment of **1** with the tertiary diphosphine 1,3-bis(diphenylphosphino)propane (dppp) in a complex of **1**–phosphine with a 1:1 molar ratio gave the cyclometallated complex  $\{[\mu\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2](\text{Cl})\text{Pd}\{[\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{H}]\text{C}_6\text{H}_4\{[\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2](\text{Cl})\text{Pd}\{[\mu\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]\}_2\}$  (**8**). The  $\delta$  NMe<sub>2</sub> resonance appeared as a singlet at  $\delta$  2.24 ppm showing Pd–NMe<sub>2</sub> bond cleavage. The H3, H6 resonances showed  $J_{\text{PH}}$  coupling ( $J_{\text{PH}} = 3.8$  Hz). The phosphorus resonance appeared as a singlet at  $\delta$  30.6 ppm in the <sup>31</sup>P–{<sup>1</sup>H} NMR showing the high symmetry of the complex. The mass (FAB) spectrum for **8** showed peaks at 1005 [ $1/2\text{M} + \text{Cl}$ ] and 933 [ $1/2\text{M} - \text{Cl}$ ], but no peak was found for the tetranuclear ion, nevertheless similar-

ity with related complexes derived from doubly cyclometallated Schiff bases points towards a tetranuclear structure [30]. The relatively large solubility of the complex in the usual organic solvents sustains this conjecture.

Treatment of **1** with silver perchlorate followed by reaction with the tertiary diphosphine 1,4-bis(diphenylphosphino)butane (dppb) in a 1–diphosphine 1:1 molar ratio yielded the tetranuclear complex  $[\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}\text{-Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{(H)C}\}\text{-C}_6\text{H}_5\text{-}\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{-Pd}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}\text{-}]_2\text{-}[\text{ClO}_4]_4$  (**9**). The  $^1\text{H}$ -NMR spectrum of the complex is similar to the one for **4** with the  $\text{HC}=\text{N}$  and H3, H6 resonances coupled to the  $^{31}\text{P}$  nuclei. This was confirmed by the shift of the  $^{31}\text{P}$  resonance in the  $^{31}\text{P}\text{-}\{^1\text{H}\}$ -

NMR spectrum, which appeared as a singlet at  $\delta$  28.43 ppm [31]. Conductivity measurements carried out in dry acetonitrile showed higher values than expected for 2:1 electrolytes and smaller than for 4:1 electrolytes. We were unable to obtain a clear mass spectrum of **9**, therefore we tentatively assign a tetranuclear structure for the complex.

Reaction of **1** with the tertiary diphosphines 1,2-bis(diphenylphosphino)ethane (dppe) and *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-dppe), followed by treatment with ammonium hexafluorophosphate in the latter case, in a complex of 1–diphosphine 1:2 molar ratio, yielded the binuclear cyclometallated complexes  $[\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\text{-}P,P\}\text{-Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{(H)C}\}\text{-C}_6\text{H}_5\text{-}\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{-Pd}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\text{-}$

Table 1  
 $^{31}\text{P}$ - and  $^1\text{H}$ -NMR data <sup>a,b,c,d</sup>

	$\delta(\text{H}_7\text{C}=\text{N})$	$\delta(\text{H}3, \text{H}6)$	$\delta(\text{CH}_2)^i$	$\delta(\text{NMe}_2)$	$\delta(\text{P})^j$
<b>L</b>	8.65t $^4J(\text{HiCH}_2)$ 1.3	8.05s	3.78(13.6) 2.65	2.30s	
<b>1</b>	7.94s	7.55s	3.89(11.8) 2.93	2.70s	
<b>2<sup>k</sup></b>	7.96s	7.38s	3.72(13.4) 2.69	2.30s	
<b>3</b>	7.20s	6.07br	3.85 2.72	2.24s	38.5s
<b>4<sup>e,l</sup></b>	f	6.10d $^4J(\text{PH})$ 4.2	3.81 2.87	<sup>g</sup>	39.7s
<b>5</b>	7.13s	5.99s	3.83(12.2) 2.65	2.24s	20.9s
<b>6</b>	7.16s	6.09s	3.85 2.68	2.26s	33.9s
<b>7</b>	7.29d $^4J(\text{PHi})$ 6.6	6.12d $^4J(\text{PH})$ 4.3	3.88 2.70	2.28s	31.9s
<b>8</b>	f	5.97d $^4J(\text{PH})$ 3.8	<sup>h</sup>	2.24s	30.6s
<b>9</b>	7.87d $^4J(\text{PHi})$ 9.9	6.45d $^4J(\text{PH})$ 5.0	<sup>h</sup>	2.04s	28.4s
<b>10<sup>m</sup></b>	7.36d $^4J(\text{PHi})$ 8.9	6.54m	3.16 <sup>h</sup>	1.86s	58.5d 40.9d $J(\text{PP})$ 41.8
<b>11</b>	7.39d $^4J(\text{PHi})$ 7.8	6.94d $^4J(\text{PH})$ 12.5 $^4J(\text{PH})$ 7.5	3.35(12.2) 1.80	1.93s	56.9br 48.9br
<b>12</b>	f	6.94d $^4J(\text{PH})$ 5.7	<sup>h</sup>	1.97s	90.4t 44.5d $J(\text{PP})$ 26.4

<sup>a</sup> In  $\text{CDCl}_3$  unless otherwise stated. Measured at 100.6 MHz (ca.  $\pm 20^\circ\text{C}$ ); chemical shifts ( $\delta$ ) in ppm ( $\pm 0.1$ ) to high frequency of 85%  $\text{H}_3\text{PO}_4$ .

<sup>b</sup> In  $\text{CDCl}_3$  unless otherwise stated. Measured at 250 or 300 MHz; chemical shifts ( $\delta$ ) in ppm ( $\pm 0.01$ ) to high frequency of  $\text{SiMe}_4$ .

<sup>c</sup> Coupling constants in Hz.

<sup>d</sup> s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

<sup>e</sup> In  $\text{DMSO-}d^6$ .

<sup>f</sup> Occluded by phenyl (phosphine) resonances.

<sup>g</sup> Occluded by solvent resonances.

<sup>h</sup> Occluded by methylene (phosphine) resonances.

<sup>i</sup> The higher value was assigned to the  $\text{C}=\text{NCH}_2$  protons and the lower one to the  $\text{CH}_2\text{NMe}_2$  protons;  $N$  values in parentheses.

<sup>j</sup> For **10** and **11**  $\delta(\text{P-trans-C}) < \delta(\text{P-trans-N})$  and for **12**  $\delta(\text{P-trans-C}) > \delta(\text{P-trans-P})$ .

<sup>k</sup> acac:  $\delta(\text{CH})$  5.35s ppm,  $\delta(\text{Me})$  2.01s ppm.

<sup>l</sup> Phosphine:  $\delta(\text{MeP}) = 2.22\text{d}$ .  $^2J(\text{PMe}) = 10.4$  Hz.

<sup>m</sup>  $\delta(\text{PF}_6) = 146.1\text{m}$  ppm.

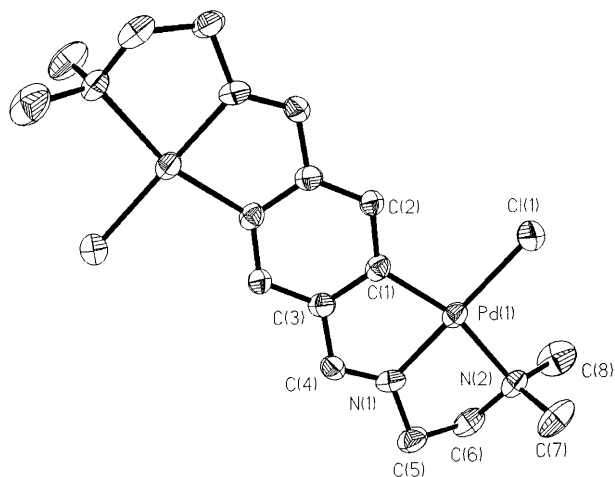


Fig. 2. Molecular structure of complex  $[(\text{Cl})\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=(\text{H})\text{C}\}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}(\text{Cl})]$ , **1**, with labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 2  
Crystal and structure refinement data

	<b>1</b>	<b>12</b>
Formula	$\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{N}_4\text{Pd}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$	$[\text{C}_{84}\text{H}_{92}\text{N}_4\text{P}_4\text{Pd}_2] 2\text{Cl} \cdot \text{CHCl}_3 \cdot \text{H}_2\text{O}$
$M_r$	598.55	1762.50
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Cell dimensions		
$a$ (Å)	11.989(1)	17.409(5)
$b$ (Å)	12.914(1)	23.699(11)
$c$ (Å)	17.014(1)	21.977(6)
$\beta$ (°)	110.146(1)	90.68(1)
$V$ (Å <sup>3</sup> )	2473.1(2)	9067(6)
$Z$	4	4
$\mu$ (mm <sup>-1</sup> )	1.608	0.693
Crystal size (mm)	0.05 × 0.20 × 0.50	0.73 × 0.24 × 0.24
$2\theta_{\text{max}}$ (°)	56.6	45.2
Reflections collected	16 744	13 958
Reflections unique	6128 ( $R_{\text{int}} = 0.05$ )	11 846 ( $R_{\text{int}} = 0.08$ )
Transmissions	0.92, 0.47	no abs. corr.
Number of parameters	257	959
Number of restraints	88	15
$S$	1.025	1.002
$R$ [ $F$ , $I > 2\sigma(I)$ ]	0.0662	0.0968
$wR$ [ $F^2$ , all data]	0.1951	0.2916
Max $\Delta/\sigma$	0.000	0.001
Max $\rho$ (e Å <sup>-3</sup> )	1.581	1.148

$P,P$ ]/[PF<sub>6</sub>]<sub>2</sub> (**10**) and  $[(\text{cis-Ph}_2\text{PCH}=\text{CHPh}_2P,P)\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=(\text{H})\text{C}\}_6\text{H}_2\{\text{C}(\text{H})=\text{N}/\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}(\text{cis-Ph}_2\text{PCH}=\text{CHPh}_2P,P)]\text{[Cl]}_2$  (**11**) as air-stable solids which were fully characterized (see Section 3 and Table 1). Electric conductivity measurements showed the complexes to be 1:2 electrolytes. The <sup>31</sup>P-<sup>1</sup>H-NMR spectra showed two doublets for **10** ( $J_{\text{PP}} = 41.8$  Hz) and two broad signals for **11**, 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]. In the <sup>1</sup>H-NMR, the HC=N resonance was coupled only to the <sup>31</sup>P nucleus *trans* to nitrogen, and the H3, H6 resonances were coupled to both phosphorus nuclei. The  $\delta$  NMe<sub>2</sub> resonance was shifted to a lower frequency as a consequence of the Pd–NMe<sub>2</sub> bond cleavage.

Treatment of **1** with the tertiary triphosphine bis(2-diphenylphosphinoethyl)-phenylphosphine in 1:2 molar ratio gave the complex  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh-}P,P,P\text{-Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=(\text{H})\text{C}\}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}/\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh-}P,P,P\}\text{[Cl]}_2$  (**12**). The compound was a 1:2 electrolyte as shown by the conductivity measurement in dry acetonitrile. The phosphorus resonances in the <sup>31</sup>P-<sup>1</sup>H-NMR spectra were downfield shifted from their values in the free phosphine suggesting coordination of all the phosphorus atoms to the metal center. A triplet signal was assigned to the central <sup>31</sup>P nucleus, which was *trans* to the phenyl carbon atom, and a doublet was assigned to the two equivalent mutually *trans* phosphorus nuclei, which appeared at lower frequency in accordance with the high *trans* influence of the phosphine ligand [32]. The H3 and H6 proton resonances were only coupled to the central phosphorus nucleus with  $J(\text{PH5})$  5.7 Hz; no coupling was observed between H3, H6 and the terminal phosphorus nuclei in accordance with the ca. 90° angle between the metallated phenyl ring and the plane defined by the metallated carbon, the terminal phosphorus and the palladium atom. These observations are in agreement with coordination of the palladium atom to the carbon atom and to three phosphorus atoms, with subsequent Pd–NMe<sub>2</sub> and Pd–Cl bond cleavage, as shown by the high-field shift of the resonance corresponding to the NMe<sub>2</sub> protons related to **1**, as well as the absence of a  $\nu(\text{Pd-Cl})$  band in the IR spectrum. The HC=N resonances were occluded by the signals of the phosphine protons. These findings were confirmed by the resolution of the X-ray crystal structure of compound **12**.

### 2.1. Crystal structure of $[(\text{Cl})\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=(\text{H})\text{C}\}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}(\text{Cl})]$ (**1**)

Suitable crystals of the title compound were grown by slowly evaporating a dichloromethane solution. The

Table 3  
Selected bond Lengths (Å) and angles (°) for **1**

Pd(1)–N(1)	1.969(6)	Pd(2)–N(3)	1.973(6)
Pd(1)–C(1)	2.001(6)	Pd(2)–C(11)	1.969(7)
Pd(1)–N(2)	2.169(6)	Pd(2)–N(4)	2.187(7)
Pd(1)–Cl(1)	2.304(2)	Pd(2)–Cl(2)	2.303(2)
C(1)–C(3)	1.401(10)	C(11)–C(13)	1.418(9)
C(3)–C(4)	1.435(9)	C(13)–C(14)	1.497(10)
C(4)–N(1)	1.278(9)	C(14)–N(3)	1.242(9)
C(1)–Pd(1)–N(1)	80.7(3)	C(11)–Pd(2)–N(3)	81.9(3)
C(1)–Pd(1)–N(2)	163.3(3)	C(11)–Pd(2)–N(4)	163.6(3)
N(1)–Pd(1)–N(2)	82.7(2)	N(4)–Pd(2)–N(3)	82.0(3)
C(1)–Pd(1)–Cl(1)	98.3(2)	C(11)–Pd(2)–Cl(2)	96.7(2)
N(2)–Pd(1)–Cl(1)	98.4(1)	N(4)–Pd(2)–Cl(2)	99.4(2)

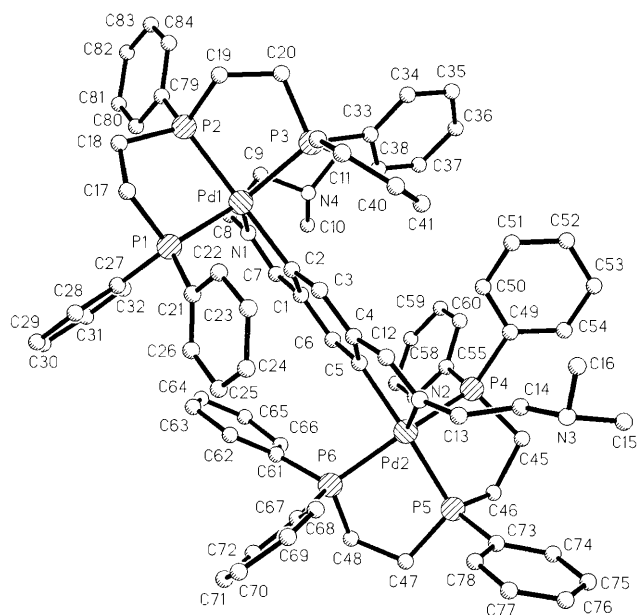


Fig. 3. Molecular structure of complex  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}-P,P,P]\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{(H)C}\}\text{C}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}-P,P,P\}[\text{Cl}]_2$ , **12**, with labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 4  
Selected bond Lengths (Å) and angles (°) for **12**

Pd(1)–C(2)	2.086(14)	Pd(2)–C(5)	2.067(14)
Pd(1)–P(1)	2.323(4)	Pd(2)–P(6)	2.303(4)
Pd(1)–P(3)	2.327(4)	Pd(2)–P(5)	2.306(4)
Pd(1)–P(2)	2.329(4)	Pd(2)–P(4)	2.318(5)
Pd(1)–N(1)	2.429(13)	Pd(2)–N(2)	2.415(13)
P(1)–Pd(1)–P(3)	133.80(16)	P(6)–Pd(2)–P(4)	143.48(17)
P(1)–Pd(1)–N(1)	112.3(4)	P(6)–Pd(2)–N(2)	112.4(3)
P(3)–Pd(1)–N(1)	113.5(3)	P(4)–Pd(2)–N(2)	103.9(3)
C(2)–Pd(1)–N(1)	76.6(5)	C(5)–Pd(2)–N(2)	75.8(5)
C(2)–Pd(1)–P(1)	92.3(4)	C(5)–Pd(2)–P(4)	93.0(4)
C(2)–Pd(1)–P(3)	92.4(4)	C(5)–Pd(2)–P(6)	91.8(4)
P(1)–Pd(1)–P(2)	84.50(15)	P(5)–Pd(2)–P(4)	85.80(17)
P(3)–Pd(1)–P(2)	85.71(15)	P(6)–Pd(2)–P(5)	84.93(16)
P(2)–Pd(1)–N(1)	110.0(3)	P(5)–Pd(2)–N(2)	111.6(3)
C(2)–Pd(1)–P(2)	173.4(5)	C(5)–Pd(2)–P(5)	172.6(5)

molecular structure is illustrated in Fig. 2. Crystal data are given in the Table 2 and selected bond distances and angles with estimated standard deviations are shown in Table 3.

The structure of **1** comprises a centrosymmetric molecule of  $[(\text{Cl})\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{(H)C}\}\text{C}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}(\text{Cl})]$  (two similar half molecules per asymmetric unit) and one 50% occupancy dichloromethane solvent molecule.

Each palladium is bonded in a slightly distorted square-planar geometry to a carbon atom of the phenyl ring, the imine and amine nitrogen atoms and to the chlorine atom. The mean deviations from the coordination planes are 0.0218 and 0.0203 Å. The angles between adjacent atoms in the coordination sphere of palladium are in the range 80.7(3)–99.4(2)°. The angles C–Pd–N<sub>imine</sub> and N<sub>imine</sub>–Pd–N<sub>amine</sub> are less than 90° (in the range 80.7(3)–82.7(2) for C(1)–Pd(1)–N(1) and N(1)–Pd(1)–N(2) angles, respectively) and the angles C–Pd–Cl and N<sub>amine</sub>–Pd–Cl are thus >90° (in the range 96.7(2)–99.4(2)° for the angles C(11)–Pd(2)–Cl(2) and N(4)–Pd(2)–Cl(2), respectively).

The Pd–N<sub>imine</sub> (1.969(6) and 1.973(6) Å) and Pd–N<sub>amine</sub> (2.169(6) and 2.187(7) Å) bond distances are similar to others reported for related compounds, [14,16,33]. The Pd–N(2) bond length, longer than the Pd–N(1) distance, shows the strong *trans* influence of the donor ligand.

The Pd(1)–C(1) and Pd(2)–C(11) bond distances of 2.001(6) and 1.969(7) Å, respectively, are somewhat shorter than the values predicted from their covalent radii [34], but similar to values found earlier [14,16]. The Pd–Cl bond distances (2.304(2), 2.303(2) Å) are in accordance with the values found early in similar cyclometallated compounds [35–37].

## 2.2. Crystal structure of $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}-P,P,P]\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{(H)C}\}\text{C}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}-P,P,P\}[\text{Cl}]_2$ (**12**)

Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The molecular structure is illustrated in Fig. 3. Crystal data are given in the Table 2 and selected bond distances and angles with estimated standard deviations are shown in Table 4.

The structure of **10** comprises the  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}-P,P,P]\text{Pd}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{(H)C}\}\text{C}_6\text{H}_2\{\text{C}(\text{H})=\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Pd}\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}-P,P,P\}]^{2+}$  cation, two chloride anions, two half-occupancy chloroform and two half-occupancy water solvent molecules. Each palladium is bonded to three phosphorus atoms from the terdentate bis(2-diphenylphosphinoethyl)phenylphosphine and to an *ortho* carbon atom of the Schiff base phenyl ring. An additional fifth bond constituted by a weak interaction

between the imino nitrogen atoms and their respective palladium atoms is observed (Pd(1)–N(1) and Pd(2)–N(2) distances of 2.429(13) and 2.415(13) Å, respectively). The geometry around the palladium atoms may be considered as being distorted by pyramidal trigonal. The equatorial plane is formed by the palladium atom, the imino nitrogen atom and the terminal phosphorus atoms (Pd(1), N(1), P(1), P(3) plane 1; Pd(2), N(2), P(4), P(6), plane 2). The metallated carbon and the central phosphorus complete the coordination sphere. The most noticeable distortions correspond to the enlarged P(1)–Pd(1)–P(3) and P(6)–Pd(2)–P(4) bond angles of 133.80(16) and 143.48(17)°, and the reduced P(4)–Pd(2)–N(2) angle of 103.9(3)°. The bond angles C(2)–Pd(1)–N(1) and C(5)–Pd(2)–N(2) of 76.6(5) and 75.8(5)° are also smaller than the expected 90° consequent upon chelation.

The Pd–N bond lengths are longer than the Pd–N bond length of 2.23(2) Å in an authentic five-coordinate Pd(II) complex [38]. Nevertheless, some five-coordinated palladium(II) compounds with the Pd–N bond length in the range 2.359(4)–2.805(5) Å have been described by us [15,23] and others before [39]. The Pd(1)–C(2) and Pd(2)–C(5) bond lengths of 2.086(14) and 2.067(15) Å are similar to those found in related cyclometallated complexes [15,23], with C *trans* to phosphorus but longer than Pd–C distances found in cyclometallated complexes with carbon *trans* to nitrogen or chlorine supporting a phosphine ligand in the *trans* position. The Pd–P bond lengths (Pd(1)–P(1), 2.323(4); Pd(1)–P(2), 2.329(4); Pd(1)–P(3), 2.327(4); Pd(2)–P(4), 2.318(5); Pd(2)–P(5), 2.306(4); Pd(1)–P(3), 2.303(4) Å) are similar to those found in related Pd(II) complexes [15,23,40] and suggest that a slightly partial double bond between the palladium and phosphorus atoms may exist [41].

### 3. Experimental

All reactions were carried out in an atmosphere of dry nitrogen. Solvents were purified by standard methods [42]. Chemicals were reagent grade. Tris(dibenzylideneacetone)dipalladium(0), thallium acetylacetonate and silver perchlorate were purchased from Aldrich-Chemie. The diphosphines Ph<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Ph<sub>2</sub> (dppe), Ph<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Ph<sub>2</sub> (dppp), Ph<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>Ph<sub>2</sub> (dppb) and the triphosphine (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh (triphos), were purchased from Aldrich-Chemie; *cis*-PPh<sub>2</sub>CH=CHPPh<sub>2</sub> (*cis*-1,2-dppe) was prepared according to procedures described elsewhere [43]. Microanalyses were carried out using a Carlo-Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spec-

trophotometer. NMR spectra were obtained as CDCl<sub>3</sub> or (CD<sub>3</sub>)<sub>2</sub>SO solutions and referenced to SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P-<sup>1</sup>H}) and were recorded on Bruker WM-250 and AMX-300 spectrometers. All chemical shifts were reported downfield from standards.

The synthesis of 1,4-(C=N(H)CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub> was performed by heating a chloroform solution of the appropriate quantities of 2,5-dichloroterephthaldehyde and *N,N*-dimethylethylenediamine in a Dean–Stark apparatus under reflux. <sup>13</sup>C-<sup>1</sup>H-NMR (75.48 MHz, CDCl<sub>3</sub>): δ 152.0 (C=N); δ 133.4 (C1, C4); δ 128.4 (C2, C5); δ 124.1 (C3, C6); δ 54.6 (CH<sub>2</sub>); δ 46.0 (NMe<sub>2</sub>). IR: ν(C=N), 1627s cm<sup>-1</sup>.

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

#### 3.1. Preparation of [(Cl)Pd{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N=(H)C}C<sub>6</sub>H<sub>2</sub>{C(H)=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Pd(Cl)] (1)

1,4-(C=N(H)CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub> (112 mg, 0.33 mmol) and tris(dibenzylideneacetone)dipalladium(0) (300 mg, 0.33 mmol) were added to 25 cm<sup>3</sup> of benzene to give a dark red solution which was heated under reflux for 2 h. After cooling to r.t. the solvent was removed under vacuum to give a dark yellow solid which was chromatographed on a column packed with silica gel. Elution with dichloromethane–ethanol (1%) afforded the final product as a yellow solid after concentration. Yield 65%. Anal. Found: C, 34.7; H, 4.2; N, 9.8. C<sub>16</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>Pd<sub>2</sub> Calc.: C, 34.5; H, 4.3; N, 10.1%. IR: ν(C=N), 1600s cm<sup>-1</sup>; ν(Pd–Cl), 350m cm<sup>-1</sup>. <sup>13</sup>C-<sup>1</sup>H-NMR (75.48 MHz, CDCl<sub>3</sub>): δ 173.4 (C=N); δ 151.4 (C2, C5); δ 134.0 (C3, C6); δ 62.9, 53.2 (CH<sub>2</sub>); δ 47.4 (NMe<sub>2</sub>).

#### 3.2. Preparation of [(H<sub>3</sub>CCOCHCOCH<sub>3</sub>)Pd{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N=(H)C}C<sub>6</sub>H<sub>2</sub>{C(H)=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Pd(H<sub>3</sub>CCOCHCOCH<sub>3</sub>)] (2)

To a suspension of **1** (40 mg, 0.07 mmol) in chloroform (25 cm<sup>3</sup>), thallium acetylacetonate (44 mg, 0.14 mmol) was added and the mixture stirred at r.t. 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 78%. Anal. Found: C, 45.2; H, 6.6; N, 8.0. C<sub>26</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>Pd<sub>2</sub> Calc.: C, 45.3; H, 6.4; N, 8.1%. ν(C=N), 1604s cm<sup>-1</sup>; 2,4-Pentanedionate: ν(C=C), 1512s cm<sup>-1</sup>; IR: ν(C=O), 1577s, 1389s cm<sup>-1</sup>. <sup>13</sup>C-<sup>1</sup>H-NMR (75.48 MHz CDCl<sub>3</sub>): δ 175.0 (C=N); δ 151.5 (C2, C5); δ 146.6 (C1, C4); δ 128.5 (C3, C6); δ 100.17 (CH, acac); δ 58.7, 55.8 (CH<sub>2</sub>); δ 45.7 (NMe<sub>2</sub>); δ 27.48 (Me, acac).



3.3. Preparation of  $[(PPh_3)(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd(Cl)(PPh_3)]$  (**3**)

$PPh_3$  (38 mg, 0.14 mmol) was added to a suspension of **1** (40 mg, 0.072 mmol) in acetone (15 cm<sup>3</sup>). The mixture was stirred for 4 h at r.t., the resulting yellow solid was filtered off and recrystallized from dichloromethane–hexane. Yield 85%. Anal. Found: C, 57.5; H, 5.0; N, 5.5.  $C_{52}H_{54}Cl_2N_4P_2Pd_2$  Calc.: C, 57.8; H, 5.0; N, 5.2%. IR:  $\nu(C=N)$ , 1618s cm<sup>-1</sup>;  $\nu(Pd-Cl)$ , 286w cm<sup>-1</sup>.

Compounds **5**, **6** and **7** were obtained following a similar procedure as white solids.

3.4.  $[(PMePh_2)(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd(Cl)(PMePh_2)]$  (**5**)

Yield 77%. Anal. Found: C, 52.7; H, 5.2; N, 5.8.  $C_{42}H_{50}Cl_2N_4P_2Pd_2$  Calc.: C, 52.7; H, 5.3; N, 5.9%. IR:  $\nu(C=N)$ , 1620s cm<sup>-1</sup>;  $\nu(Pd-Cl)$ , 301w cm<sup>-1</sup>.

3.5.  $[(PEtPh_2)(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd(Cl)(PEtPh_2)]$  (**6**)

Yield 68%. Anal. Found: C, 54.0; H, 5.5; N, 5.4.  $C_{44}H_{54}Cl_2N_4P_2Pd_2$  Calc.: C, 53.7; H, 5.5; N, 5.7%. IR:  $\nu(C=N)$ , 1615s cm<sup>-1</sup>;  $\nu(Pd-Cl)$ , 281m cm<sup>-1</sup>.

3.6.  $[(PEt_2Ph)(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd(Cl)(PEt_2Ph)]$  (**7**)

Yield 93%. Anal. Found: C, 48.0; H, 6.1; N, 6.3.  $C_{36}H_{54}Cl_2N_4P_2Pd_2$  Calc.: C, 48.7; H, 6.1; N, 6.3%. IR:  $\nu(C=N)$ , 1611s cm<sup>-1</sup>;  $\nu(Pd-Cl)$ , 293m cm<sup>-1</sup>.

3.7. Preparation of  $[(PPh_3)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd(PPh_3)]ClO_4$  (**4**)

A suspension of **1** (40 mg, 0.072 mmol) in acetone (15 cm<sup>3</sup>) was treated with silver perchlorate (30 mg) and stirred for 4 h.  $PPh_3$  (38 mg, 0.14 mmol) was added and the resulting mixture stirred for 12 h. The solution was filtered through Cellite to eliminate the  $AgCl$  precipitate. The solvent was removed and the product recrystallized from dichloromethane–hexane to give the desired complex as a yellow solid. Yield 87%. Anal. Found: C, 52.0; H, 4.8; N, 4.9.  $C_{52}H_{54}Cl_2N_4O_8P_2Pd_2$  Calc.: C, 51.7; H, 4.5; N, 4.6%. IR:  $\nu(C=N)$ , 1618m cm<sup>-1</sup>.  $A_M = 250$  ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile).

3.8. Preparation of  $[\{\mu-Ph_2P(CH_2)_3PPh_2\}(Cl)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=N-CH_2CH_2NMe_2\}(Cl)Pd\{\mu-Ph_2P(CH_2)_3PPh_2\}_2]$  (**8**)

$Ph_2P(CH_2)_3PPh_2$  (30 mg, 0.073 mmol) was added to a suspension of **1** (40 mg, 0.072 mmol) in acetone (15 cm<sup>3</sup>). The mixture was stirred for 4 h and the resulting

yellow precipitate was filtered and dried in vacuo. Yield 87%. Anal. Found: C, 53.3; H, 5.1; N, 5.7.  $C_{43}H_{50}Cl_2N_4P_2Pd_2$  Calc.: C, 53.3; H, 5.2; N, 5.8%. IR:  $\nu(C=N)$ , 1611s cm<sup>-1</sup>;  $\nu(Pd-Cl)$ , 272m cm<sup>-1</sup>.

Compound **9** was synthesised following a similar procedure to that for **4** but using a 1–diphosphine 1:1 molar ratio.

3.9.  $[\{\mu-Ph_2P(CH_2)_4PPh_2\}Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd\{\mu-Ph_2P(CH_2)_4PPh_2\}_2]ClO_4$  (**9**)

Yield 75%. Anal. Found: C, 47.7; H, 4.8; N, 5.0.  $C_{44}H_{52}N_4O_8Cl_2P_2Pd_2$  requires: C, 47.6; H, 4.7; N, 5.0. IR:  $\nu(C=N)$ , 1637s cm<sup>-1</sup>.  $A_M = 320$  ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile).

3.10. Preparation of  $[\{Ph_2P(CH_2)_2PPh_2-P,P\}Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=N-CH_2CH_2NMe_2\}-Pd\{Ph_2P(CH_2)_2PPh_2-P,P\}]PF_6$  (**10**)

$Ph_2P(CH_2)_2PPh_2$  (57 mg, 0.14 mmol) was added to a suspension of **1** (40 mg, 0.072 mmol) in acetone (15 cm<sup>3</sup>). The mixture was stirred for 4 h, after which ammonium hexafluorophosphate was added. The complex was precipitated out by addition of water, filtered off and dried in vacuo. Recrystallization from chloroform–hexane gave the final compound as a yellow solid.

Yield 96%. Anal. Found: C, 54.0; H, 4.7; N, 3.9.  $C_{68}H_{72}F_{12}N_4P_4Pd_2$  Calc.: C, 54.1; H, 4.8; N, 3.7%. IR:  $\nu(C=N)$ , 1609m cm<sup>-1</sup>.  $A_M = 300$  ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile).

Compound **11** was obtained as a white solid following a similar procedure to that for **8** but using a 1–diphosphine 1:2 molar ratio.

3.11.  $[(cis-Ph_2PCH=CHPPh_2-P,P)Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}-Pd(cis-Ph_2PCH=CHPPh_2-P,P)]Cl_2$  (**11**)

Yield 82%. Anal. Found: C, 60.2; H, 5.3; N, 4.1.  $C_{68}H_{68}Cl_2N_4P_4Pd_2$  Calc.: C, 60.5; H, 5.0; N, 4.1%. IR:  $\nu(C=N)$ , 1608m cm<sup>-1</sup>.  $A_M = 285$  ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile).

Compound **12** was obtained as a yellow solid following a similar procedure to that for **8** using a 1–trifos 1:2 molar ratio.

3.12.  $[\{(Ph_2PCH_2CH_2)_2PPh-P,P,P\}Pd\{Me_2NCH_2CH_2N=(H)C\}C_6H_5\{C(H)=NCH_2CH_2NMe_2\}Pd-\{(Ph_2PCH_2CH_2)_2PPh-P,P,P\}]Cl_2$  (**12**)

Yield 76%. Anal. Found: C, 60.2; H, 5.4; N, 2.9.  $C_{84}H_{90}Cl_2N_4P_6Pd_2$  Calc.: C, 62.1; H, 5.6; N, 3.4%. IR:  $\nu(C=N)$ , 1611s cm<sup>-1</sup>.  $A_M = 263$  ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile).

### 3.13. Single-crystal X-ray diffraction analysis

For complex **1** three-dimensional X-ray data were collected at r.t. in the range  $3.62 < 2\theta < 56.66^\circ$  on a Siemens Smart CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of collected data, of frames each covering  $0.3^\circ$  in omega. Of the 16 744 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 3440 independent reflections exceeded the significance level  $|F|/\sigma(|F|) > 4.0$ . The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  with allowance for thermal anisotropy of all non-hydrogen atoms (except the disordered dichloromethane solvent molecule). Hydrogen atoms were included in calculated positions and refined in riding mode. One of the  $\text{CH}_2\text{NMe}_2$  groups was disordered with the carbon atoms occupying two positions (C16, C16a, C17, C17a and C18, C18a). The occupancies of the two pairs of positions were tied to give an overall value of 1.0 and then refined giving values of 0.5 for each component. PLATON/SQUEEZE [44] was used to remove the effects of two ill defined dichloromethane solvent molecules from the data. Two solvent voids were found (potential solvent area of  $192 \text{ \AA}^3$ , 7.8% of the cell volume, 68 electrons in the voids). The largest residual peaks were adjacent to the palladium atoms. The structure solution and refinement were carried out using the program package SHELX-97 [45].

For complex **12** three-dimensional, r.t. X-ray data were collected in the range  $3.7 < 2\theta < 45.2^\circ$  on a Siemens P4 diffractometer by the omega scan method. Of the 13 958 reflections measured, all of which were corrected for Lorentz and polarisation effects, 5906 independent reflections exceeded the significance level  $|F|/\sigma(|F|) > 4.0$ . The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$ . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final  $R = 0.0968$  ( $wR_2 = 0.2916$  for all 11 846 unique data, 959 parameters, mean and maximum  $\delta/\sigma$  0.000, 0.001), with allowance for the thermal anisotropy of all non-hydrogen atoms. Geometric constraints were used in all chloroform solvent molecules. The minimum and maximum final electron densities were  $-0.875$  and  $1.148 \text{ e \AA}^{-3}$ . Complex scattering factors were taken from the program package SHELXL-97 [45].

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data

Centre, CCDC Nos. 142880 and 142881 for compounds **1** and **12**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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