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Novel structures of cyclometallated complexes of palladium(II) derived from terdentate ligands. Crystal and molecular structure of $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(X)]$ (X = Cl, Br, I)

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Abstract

Treatment of *N*-(2-chlorobenzylidene)-*N*,*N*-dimethyl-1,3-propanediamine (**1**) and *N*-(2-bromo-3,4-$(MeO)_2$-benzylidene)-*N*,*N*-dimethyl-1,3-propanediamine (**20**) with tris(dibenzylideneacetone)dipalladium(0) in toluene gave the mononuclear cyclometallated complexes $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(Cl)]$ (**2**) and $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2CH_2NMe_2\}(Br)]$ (**21**), respectively, via oxidative addition reaction with the ligand as a *C*,*N*,*N* terdentate ligand. Reaction of **2** with sodium bromide or iodide in an acetone–water mixture gave the cyclometallated analogues of **2**, $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(Br)]$ (**3**) and $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(I)]$ (**4**), by halogen exchange. The X-ray crystal structures of **2**, **3** and **4** were determined and discussed. Treatment of **2**, **3**, **4** and **21** with tertiary monophosphines in acetone gave the mononuclear cyclometallated complexes $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(L)(X)]$ (**6**: L = PPh_3, X = Cl; **7**: L = PPh_3, X = Br; **8**: L = PPh_3, X = I; **9**: L = $PMePh_2$, X = Cl; **10**: L = PMe_2Ph, X = Cl) and $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2CH_2NMe_2\}(L)(Br)]$ (**22**: L = PPh_3; **23**: L = $PMePh_2$; **24**: L = PMe_2Ph). A fluxional behaviour due to an uncoordinated $CH_2CH_2CH_2NMe_2$ could be determined by variable temperature NMR spectroscopy. Treatment of **2**, **3** and **4** with silver trifluoromethanesulfonate followed by reaction with triphenylphosphine gave the mononuclear complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(PPh_3)][F_3CSO_3]$ (**11**) where the Pd–NMe_2 bond was retained. Reaction of **2**, **3** and **4** with ditertiary diphosphines in a cyclometallated complex–diphosphine 2:1 molar ratio gave the binuclear complexes $[\{Pd[C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2](X)\}_2(\mu\text{-}L\text{–}L)][L\text{–}L = PPh_2(CH_2)_4PPh_2(dppb)$ (**13**, X = Cl; **14**, X = Br; **15**, X = I; L–L = $PPh_2(CH_2)_5PPh_2$(dpppe): **16**, X = Cl; **17**, X = Br; **18**, X = I) with palladium–NMe_2 bond cleavage. Treatment of **2**, **3** and **4** with ditertiary diphosphines, in a cyclometallated complex–diphosphine 2:1, molar ratio and $AgSO_3CF_3$ gave the binuclear cyclometallated complexes $[\{Pd[C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2]\}_2(\mu\text{-}L\text{–}L)][F_3CSO_3]_2$ (**11**: L–L = $PPh_2(CH_2)_4PPh_2$(dppb), X = Cl; **12**: L–L = $PPh_2(CH_2)_5PPh_2$ (dpppe), X = Cl). Reaction of **2** with the ditertiary diphosphine *cis*-dppe in a cyclometallated complex–diphosphine 1:1 molar ratio followed by treatment with sodium perchlorate gave the mononuclear cyclometallated complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(cis\text{-}PPh_2CH{=}CHPPh_2\text{–}P,P)][ClO_4]$ (**19**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium(II); Terdentate ligands; Cyclometallated

1. Introduction

Cyclometallated compounds have been widely studied over the last three decades [1–5]; such compounds having found numerous applications in organic and organometallic synthesis [6], in insertion reactions [7], in the synthesis of new metal mesogenic compounds [8], in 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. Nevertheless, when the use of palladium(II) salts as precursors did not yield the ex-

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pected cyclometallated complexes, the synthesis via oxidative addition of the halogenated ligands has proved to be an alternative method [11,12].

In previous work we have shown that potentially terdentate lignads 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 compounds with two five-membered fused rings at the metal centre (Fig. 1).

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

In the present paper we report the intramolecular oxidative addition of *N*-(2-chlorobenzylidene)-*N*,*N*-dimethyl-1,3-propanediamine and of *N*-{2-bromo-3,4-$(MeO)_2$ - benzylidene} - *N*,*N* - dimethyl - 1,3 - propanediamine with tris(dibenzylideneacetone)dipalladium(0) to give new cyclometallated complexes with two fused rings at palladium, **2** and **21**, respectively. The crystal structures of **2** and of its bromine and iodine derivatives are described. The reactivity of these complexes with mono, and diphosphines in different reaction conditions is also reported. One interesting feature is the spectroscopic evidence of five-coordinated species in solution by intramolecular nucleophilic attack of the NMe_2 nitrogen to the palladium atom.

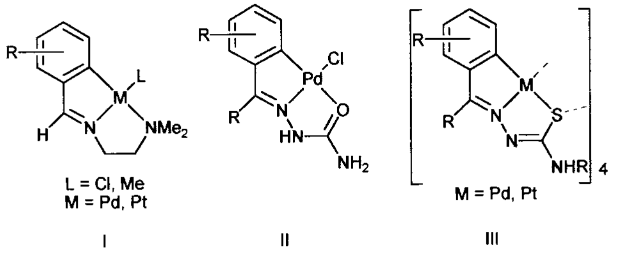
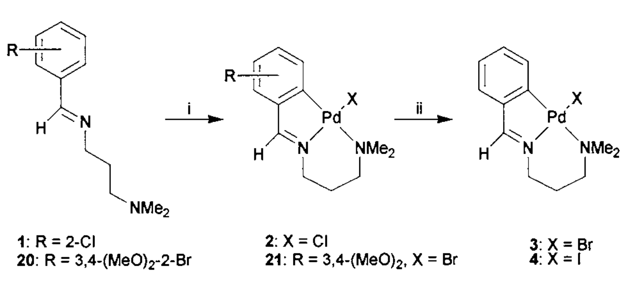


Fig. 1.



Scheme 1. (i) $[Pd_2(dba)_3]$ (toluene); (ii) NaX (acetone–water).

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}P-$\{^1H\}$- (see Table 1) and, in part, ^{13}C-$\{^1H\}$-NMR spectroscopy (Section 3) and FAB mass spectrometry.

The oxidative addition reaction of *N*-(2-chlorobenzylidene)-*N*,*N*-dimethyl-1,3-propanediamine, $2\text{-}ClC_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$ (**1**), with tris(dibenzylideneacetone)dipalladium(0) in toluene gave the cyclometallated complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(Cl)]$ (**2**), which was fully characterised. The ^1H-NMR spectrum showed a singlet resonance at δ 7.93 ppm assigned to the HC=N proton, shifted to lower frequency due to coordination of the imine group to the palladium atom via the lone pair of the nitrogen atom [18]. The resonances at δ 3.64, 2.59 and 1.91 ppm were assigned to the $C{=}NCH_2$, CH_2NMe_2 and $CH_2CH_2NMe_2$ protons, respectively. A singlet at δ 2.67 ppm was assigned to the NMe_2 protons and was shifted to higher frequency consequent upon coordination of the amine nitrogen atom to palladium [11].

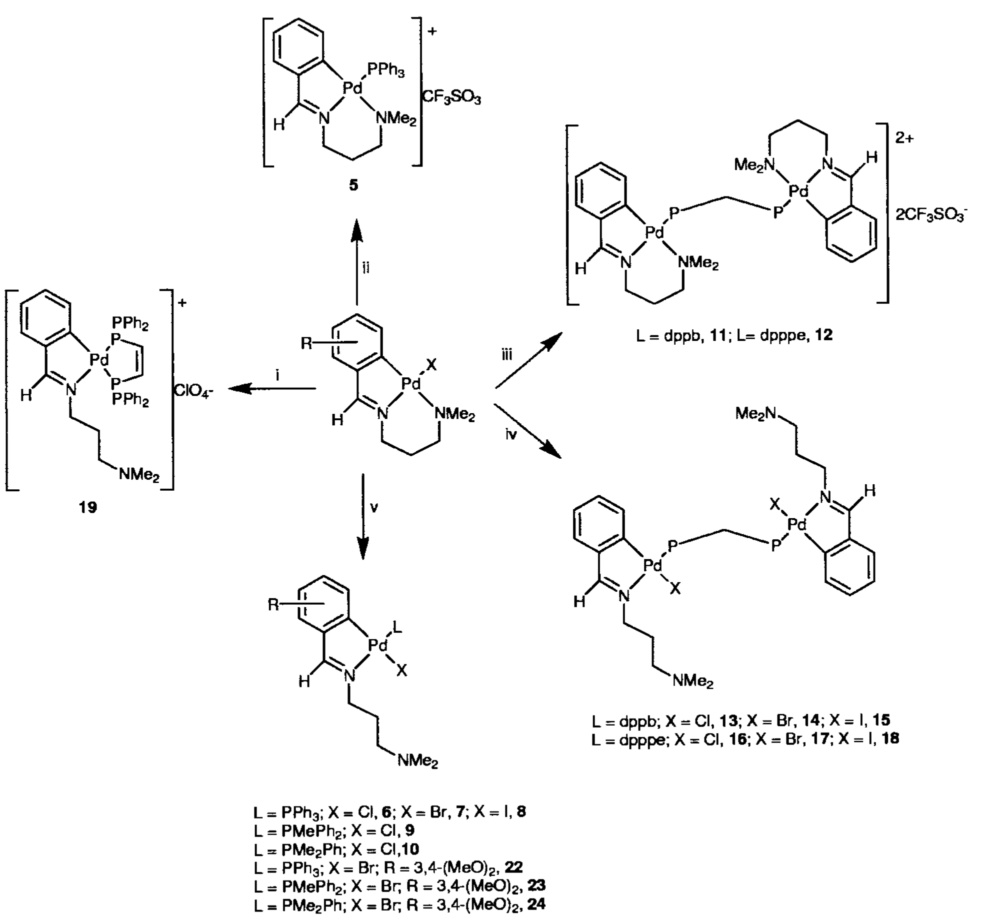
The ^{13}C-$\{^1H\}$ spectrum showed resonances at δ 175.0 (C=N), δ 155.8 (C6) and δ 145.4 (C1) downfield shifted from those for the free ligand in accordance with formation of the cyclometallated ring [11,19]. The signal assigned to the NMe_2 group was also shifted to higher frequency showing coordination of the amino nitrogen atom. Formation of the coordinated ring was confirmed by the separation of the two methylene resonances $C{=}NCH_2 \cdots CH_2NMe_2$ (ca. 5 ppm) as compared to the uncoordinated ligand.

The IR spectrum showed the ν(C=N) band at 1610 cm^{-1} shifted to lower wavenumbers in accordance with coordination of the palladium atom to the C=N moiety [20].

The FAB mass spectrum showed signals assigned to $[M]^+$ and $[M-Cl]^+$, as well as signals due to recombination peaks $[2M+Cl]^+$ and $[2M-Cl]^+$; all had reasonable isotopic patterns.

Thus, the palladium atom is bonded to a phenyl carbon atom, the imine and amine nitrogen atoms and a chlorine atom, giving a compound with two fused rings at the metal center, a five-membered ring (the metallacycle) and a six-memebered ring (the coordination cycle).

Reaction of $3,4\text{-}(MeO)_2\text{-}2\text{-}Br\text{-}C_6H_2(H){=}NCH_2CH_2CH_2NMe_2$ (**20**) with tris(dibenzylideneacetone)dipalladium(0) yielded the cyclometallated complex $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2CH_2NMe_2\}(Br)]$ (**21**), via an oxidative addition reaction, which was fully



Scheme 2. (i) *cis*-dppe, $NaClO_4$ (acetone, 1:1 molar ratio); (ii) $AgCF_3SO_3$, PPh_3 (acetone); (iii) $AgCF_3SO_3$, dppb or dpppe (acetone, 2:1 molar ratio); (iv) dppb or dpppe (acetone, 2:1 molar ratio); (v) PR_3 (acetone).

characterised (see Table 1 and Section 3). The NMR and IR data are similar to those for compound **2** confirming metallation of the organic ligand and coordination of both amino and imino nitrogen atoms to palladium.

When **2** was treated with aqueous sodium bromide or sodium iodide solutions the complexes $[Pd\{C_6H_4C(H)=NCH_2CH_2CH_2NMe_2\}(Br)]$ (**3**) and $[Pd\{C_6H_4C(H)=NCH_2CH_2CH_2NMe_2\}(I)]$ (**4**) were obtained as pure air-stable solids which were fully characterised (see Table 1 and Section 3). NMR spectra for the complexes were similar to those for **2** with the most noticeable difference in the low-field shift of the H5 resonance (δ 7.97 ppm, δ 8.28 ppm and δ 8.77 ppm for **2**, **3** and **4**, respectively) suggesting some interaction between the halogen and the hydrogen atoms. All these observations were confirmed by the X-ray determination of the molecular structures for **2**, **3** and **4**.

Treatment of the cyclometallated complexes **2**, **3** or **4** with silver trifluormethanesulfonate followed by reaction with triphenylphosphine in acetone yielded the cyclometallated complex $[Pd\{C_6H_4C(H)=NCH_2CH_2CH_2NMe_2\}(PPh_3)][CF_3SO_3]$ (see Scheme 2) (**5**) after halide extraction as silver halide. The complex was fully characterised (see Section 3 and Table 1). The ^1H-NMR spectrum showed a doublet of doublets at δ 6.25 ppm assigned to H5. The resonance at δ 8.40 ppm was assigned to the imine proton. Both signals showed coupling to the ^{31}P nucleus of the phosphine ligand (JHP = 5.8, 7.8 Hz for H5 and Hi, respectively), indicating the relative *cis* disposition of the phosphine and the metallated phenyl carbon atom [11,21–24]. The NMe_2 resonance appeared at δ 2.17 ppm shifted to lower frequency when compared with compound **2**, suggesting shielding of the methyl protons by the phosphine phenyl rings [12]. Coordination of the amine nitrogen atom to palladium was confirmed by the low-field shift of the NMe_2 resonance in their ^{13}C-NMR spectrum, assigned at δ 48.6 ppm (δ 49.4 for **2**) and by the separation of the two methylene resonances $C=NCH_2\cdots CH_2NMe_2$ (6.5 ppm) in the ^{13}C-$\{^1H\}$-NMR. The ^{31}P-$\{^1H\}$-NMR spectrum showed a singlet resonance at δ 40.5 ppm in accordance with a phosphorus-to-nitrogen *trans* geometry [12,23]. Thus, the palladium atom is coordinated to both the imine and amine nitrogen atoms and the phosphine ligand occupies the

Table 1
^{31}P ^{a}- and ^{1}H ^{b}-NMR data ^{c,d}

Compound	^{31}P	Aromatic	Others
1		7.91[d, 1H, H^2, 7.3 ^{f}] 7.20[m, 3H, H^3, H^4, H^5]	8.61[s, 1H, HC=N] 3.58[m, 2H, CH_2 ^{i}] 2.26[m, 2H, CH_2 ^{k}] 1.77[m, 2H, CH_2 ^{j}] 2.14[s, 3H, Me]
2		7.97[dd, 1H, H^5, 7.3 ^{f}, 1.5 ^{h}] 7.04[m, 2H, H^3, H^4] 7.19[dd, 1H, H^2, 7.3 ^{f}, 1.9 ^{h}]	7.93[s, 1H, HC=N] 3.64[m, 2H, CH_2 ^{i}] 2.59[m, 2H, CH_2 ^{k}] 1.91[m, 2H, CH_2 ^{j}] 2.67[s, 3H, Me]
3		8.28[dd, 1H, H^5, 7.1 ^{f}, 1.9 ^{h}] 7.12[m, 3H, H^2, H^3, H^4]	8.04[s, 1H, HC=N] 3.68[m, 2H, CH_2 ^{i}] 2.62[m, 2H, CH_2 ^{k}] 1.95[m, 2H, CH_2 ^{j}] 2.73[s, 3H, Me]
4		8.77[dd, 1H, H^5, 7.0 ^{f}, 1.9 ^{h}] 6.97[m, 2H, H^3, H^4] 7.23[dd, 1H, H^2, 7.0 ^{f}, 1.9 ^{h}]	8.11[s, 1H, HC=N] 3.66[m, 2H, CH_2 ^{i}] 2.55[m, 2H, CH_2 ^{k}] 1.97[m, 2H, CH_2 ^{j}] 2.80[s, 3H, Me]
5	40.5s	7.34[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.87[t, 1H, H^3, 7.3 ^{f},] 6.40[dt, 1H, H^4, 7.3 ^{f}] 6.25[dd, 1H, H^5, 5.8 ^{g}]	8.40[d, 1H, HC=N, 7.8 ^{g}] 3.92[br, 2H, CH_2 ^{i}] 2.75[br, 2H, CH_2 ^{k}] 2.16[m, 5H, Me, CH_2 ^{j}] 2.17[s, 3H, Me]
6	41.7s	7.26[dd, 1H, H^2, 7.6 ^{f}, 1.5 ^{h}] 6.89[t, 1H, H^3, 7.6 ^{f}, 1.0 ^{h}] 6.51[dt, 1H, H^4, 7.6 ^{f}] 6.39[d, 1H, H^5]	8.14[s, 1H, HC=N] 3.96[m, 2H, CH_2 ^{i}] 2.34[m, 2H, CH_2 ^{k}] 2.04[m, 2H, CH_2 ^{j}] 2.21[s, 3H, Me]
7	42.6s	6.91[t, 1H, H^3, 7.3 ^{f}] 6.53[dt, 1H, H^4, 7.3 ^{f}, 1.5 ^{h}] 6.38[d, 1H, H^5]	8.17[s, 1H, HC=N] 4.11[m, 2H, CH_2 ^{i}] 2.37[m, 2H, CH_2 ^{k}] 2.07[m, 2H, CH_2 ^{j}] 2.23[s, 3H, Me]
8	40.6s	7.25[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.90[t, 1H, H^3, 7.6 ^{f}] 6.53[br, 1H, H^4] 6.39[br, 1H, H^5]	8.20[s, 1H, HC=N] 4.32[br, 2H, CH_2 ^{i}] 2.37[br, 2H, CH_2 ^{k}] 2.23[s, 3H, Me]
9 ^{1}	24.2s	^{m} 6.90[dt, 1H, H^3, 7.3 ^{f}, 1.0 ^{h}] 6.59[dt, 1H, H^4, 7.3 ^{f}, 1.5 ^{h}] 6.40[d, 1H, H^5, 6.3 ^{n}]	8.10[s, 1H, HC=N, 7.8 ^{g}] 3.97[m, 2H, CH_2 ^{i}] 2.37[m, 2H, CH_2 ^{k}] 2.07[m, 2H, CH_2 ^{j}] 2.23[s, 3H, Me]
10 ^{1}	11.2s	^{m} 6.95[dt, 1H, H^3, 7.3 ^{f}, 1.0 ^{h}] 6.76[dt, 1H, H^4, 7.3 ^{f}, 1.5 ^{h}] 6.51[dd, 1H, H^5, 6.3 ^{g}]	8.07[d, 1H, HC=N, 7.8 ^{g}] 3.94[m, 2H, CH_2 ^{i}] 2.35[m, 2H, CH_2 ^{k}] 2.08[m, 2H, CH_2 ^{j}] 2.23[s, 3H, Me]
11	32.0s	7.32[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.90[t, 1H, H^3, 7.3 ^{f},] 6.63[dt, 1H, H^4, 7.3 ^{f}] 6.39[dd, 1H, H^5, 5.7 ^{g}]	8.30[d, 1H, HC=N, 7.8 ^{g}] 3.87[br, 2H, CH_2 ^{i}] 2.04[br, 2H, CH_2 ^{j}] 2.16[s, 3H, Me]
12	32.1s	^{m} 6.93[t, 1H, H^3, 7.3 ^{f}] 6.65[dt, 1H, H^4, 7.3 ^{f}, 1.5 ^{h}] 6.43[dd, 1H, H^5, 5.8 ^{g}]	8.30[d, 1H, HC=N, 7.3 ^{g}] 3.86[br, 2H, CH_2 ^{i}] 2.65[br, 2H, CH_2 ^{k}] 2.03[br, 2H, CH_2 ^{j}] 2.16[s, 3H, Me]
13	34.3s	7.22[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.89[dt, 1H, H^3, 7.3 ^{f}, 1.0 ^{h}] 6.57[dt, 1H, H^4, 7.3 ^{f}] 6.40[d, 1H, H^5, 5.9 ^{n}]	8.08[s, 1H, HC=N, 7.8 ^{n}] 3.96[m, 2H, CH_2 ^{i}] 2.36[m, 2H, CH_2 ^{k}] 2.05[m, 2H, CH_2 ^{j}] 2.23[s, 3H, Me]
14	33.2s	^{m} 6.90[t, 1H, H^3, 7.3 ^{f}] 6.57[t, 1H, H^4, 7.3 ^{f}] 6.37[d, 1H, H^5]	8.12[s, 1H, HC=N] 4.08[m, 2H, CH_2 ^{i}] 2.43[m, 2H, CH_2 ^{k}] 2.09[m, 2H, CH_2 ^{j}] 2.28[s, 3H, Me]
15	35.6s	7.22[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.89[t, 1H, H^3, 7.3 ^{f}, 1.0 ^{h}] 6.58[dt, 1H, H^4, 7.3 ^{f}] 6.31[d, 1H, H^5]	8.15[s, 1H, HC=N] 4.26[m, 2H, CH_2 ^{i}] 2.38[m, 2H, CH_2 ^{k}] 2.05[m, 2H, CH_2 ^{j}] 2.24[s, 3H, Me]
16	34.4s	7.22[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.87[dt, 1H, H^3, 7.3 ^{f}, 1.0 ^{h}] 6.55[dt, 1H, H^4, 7.3 ^{f}] 6.40[d, 1H, H^5]	8.08[s, 1H, HC=N] 3.94[m, 2H, CH_2 ^{i}] 2.37[m, 2H, CH_2 ^{k}] 2.04[m, 2H, CH_2 ^{j}] 2.23[s, 3H, Me]
17	30.4s	7.22[dd, 1H, H^2, 7.3 ^{f}, 1.5 ^{h}] 6.88[t, 1H, H^3, 7.3 ^{f}] 6.56[dt, 1H, H^4, 7.3 ^{f}] 6.37[d, 1H, H^5]	8.10[s, 1H, HC=N] 4.06[m, 2H, CH_2 ^{i}] 2.36[m, 2H, CH_2 ^{k}] 2.04[m, 2H, CH_2 ^{j}] 2.22[s, 3H, Me]
18	35.1s	7.21[dd, 1H, H^2, 7.3 ^{f}, 1.9 ^{h}] 6.89[t, 1H, H^3, 7.3 ^{f}] 6.57[dt, 1H, H^4, 7.3 ^{f}] 6.31[d, 1H, H^5]	8.15[s, 1H, HC=N] 4.25[m, 2H, CH_2 ^{i}] 2.37[m, 2H, CH_2 ^{k}] 2.04[m, 2H, CH_2 ^{j}] 2.23[s, 3H, Me]
19	62.6d 51.2d J(PP) 10.5	^{m} 7.21[dt, 1H, H^3, 7.8 ^{f}, 1.4 ^{h}] 6.93[m, 2H, H^4, H^5]	8.36[d, 1H, HC=N, 8.3 ^{g}] 3.61[br, 2H, CH_2 ^{i}] 1.95[m, 2H, CH_2 ^{k}] 1.25[m, 2H, CH_2 ^{j}] 2.05[s, 3H, Me]
20		7.50[s, 1H, H^2] 6.97[s, 1H, H^5]	8.50[s, 1H, HC=N] 3.90[s, 3H, OMe] 3.87[s, 3H, OMe] 3.63[m, 2H, CH_2 ^{i}] 2.46[m, 2H, CH_2 ^{k}] 1.90[m, 2H, CH_2 ^{j}] 2.31[s, 3H, Me]
21		7.90[s, 1H, H^5] 6.79[s, 1H, H^2]	7.92[s, 1H, HC=N] 3.95[s, 3H, OMe] 3.80[s, 3H, OMe] 3.63[m, 2H, CH_2 ^{i}] 2.57[m, 2H, CH_2 ^{k}] 1.95[m, 2H, CH_2 ^{j}] 2.72[s, 3H, Me]

Table 1 (*Continued*)

Compound	^{31}P	Aromatic	Others
22	42.0s	6.84[s, 1H, H^2] 5.93[s, 1H, H^5]	8.06[s, 1H, HC=N] 3.77[s, 3H, OMe] 2.83[s, 3H, OMe [o]] 4.03[m, 2H, CH$_2$ [i]] 2.35[m, 2H, CH$_2$ [k]] 2.04[m, 2H, CH$_2$ [j]] 2.22[s, 3H, Me]
23 [l]	24.8s	6.88[s, 1H, H^2] 6.04[s, 1H, H^5]	8.13[s, 1H, HC=N] 3.77[s, 3H, OMe] 3.01[s, 3H, OMe [o]] 3.89[m, 2H, CH$_2$ [i]] 2.37[m, 2H, CH$_2$ [k]] 2.00[m, 2H, CH$_2$ [j]] 2.24[s, 3H, Me]
24 [l]	12.1s	6.77[s, 1H, H^2] 5.85[d, 1H, H^5, 6.84 [g]]	7.93[d, 1H, HC=N, 7.8 [g]] 3.77[s, 3H, OMe] 3.02[s, 3H, OMe [o]] 3.97[br, 2H, CH$_2$ [i]] 2.35[m, 2H, CH$_2$ [k]] 2.00[br, 2H, CH$_2$ [j]] 2.23[s, 3H, Me]

[a] In CDCl$_3$ unless otherwise stated. Measured at 80.9 MHz (ca. ± 20°C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H$_3$PO$_4$.

[b] In CDCl$_3$ unless otherwise stated. Measured at 200 MHz (ca. ± 20°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 doublet of triplets; m, multiplet; br, broad.

[f] ^3J(HH).

[g] ^4J(PH).

[h] ^4J(HH).

[i] HC=NCH_2.

[j] HC=NCH$_2$CH_2.

[k] CH_2NMe$_2$.

[l] δ(phosphine methyl protons), 2.20d (**9**),1.88d (**10**), 2.21d (**23**), 1.86d (**24**); $^2J(CH_3P) = 10.2$(**9**), 10.7 (**10**), 11.7(**23**), 10.2 (**24**).

[m] Occluded by methylene or aromatic (phosphine) resonances.

[n] ^4J(PH), taken from a low temperature ^{1}H-NMR spectrum (243 K).

[o] C(4)–MeO.

fourth co-ordination site which was left vacant after removal of the chlorine atom.

Reaction of the cyclometallated complexes **2**, **3** and **4** with silver trifluoromethanesulfonate followed by treatment with the ditertiary diphosphines dppb and dpppe in a complex–diphosphine 2:1 molar ratio gave the dinuclear cyclometallated complexes $[\{Pd[C_6H_4C(H)=NCH_2CH_2CH_2NMe_2]\}_2(\mu\text{-}PPh_2(CH_2)_nPPh_2)][F_3CSO_3]_2$ (**11**, $n = 4$; 12, $n = 5$). The IR, ^{1}H- and ^{13}C-{^{1}H}-NMR data are in agreement with tri-coordination of the organic ligand. The ^{31}P-{^{1}H}-NMR spectra showed a singlet resonance at ca. δ 32 ppm, in each case, suggesting that the compounds are centrosymmetric as we have shown before in related species [14,16].

Treatment of **2**, **3**, **4** and **21** with tertiary phosphines gave the mononuclear cyclometallated complexes $[Pd\{C_6H_4C(H)=NCH_2CH_2CH_2NMe_2\}(L)(X)]$ (**6**: L = PPh$_3$, X = Cl; **7**: L = PPh$_3$, X = Br; **8**: L = PPh$_3$, X = I; **9**: L = PMePh$_2$, X = Cl; **10**: L = PMe$_2$Ph, X = Cl) and $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2CH_2CH_2NMe_2\}(L)(Br)]$: (**22**: L = PPh$_3$; **23**: L = PMePh$_2$; **24**: L = PMe$_2$Ph) which were fully characterised (see Section 3 and Table 1). The NMe$_2$ resonance in the ^{1}H-NMR spectra appeared at ca. δ 2.2 ppm (δ 2.14 and 2.31 for **1** and **20**, respectively) suggesting that the NMe$_2$ group was not coordinated. In the ^{13}C-{^{1}H}-NMR spectra of complex **6** the resonance corresponding to the NMe$_2$ carbon appeared at δ 45.3 ppm (δ 45.4 ppm for the non-coordinated ligand) and the separation of the two methylene resonances C=NCH$_2$···CH$_2$NMe$_2$ (0.6 ppm) confirmed Pd–NMe$_2$ bond cleavage. The IR spectra showed ν(C=N) bands in the range 1620–1630 cm^{-1}, shifted to lower wavenumbers as compared with the non-coordinated ligands, consistent with palladium coordination to the imine nitrogen atom. Reaction of these mononuclear complexes with silver trifluoromethanesulfonate gave a silver halide precipitate showing the presence of a halide ligand coordinated to the palladium. This has been confirmed by the microanalytical data.

When the cyclometallated complexes **2**, **3** and **4** were treated with the diphosphines dppb and dpppe in a complex/phosphine 2:1 molar ratio the binuclear cyclometallated complexes $[\{Pd[C_6H_4C(H)=NCH_2CH_2CH_2NMe_2](X)\}_2(\mu\text{-}PPh_2(CH_2)_nPPh_2)]$ (**13**: $n = 4$, X = Cl; **14**: $n = 4$, X = Br; **15**: $n = 4$, X = I; **16**: $n = 5$, X = Cl; **17**: $n = 5$, X = Br; **18**: $n = 5$, X = I) were obtained (see Section 3 and Table 1). The ^{1}H- and ^{13}C-{^{1}H}-NMR of the complexes again showed the resonance corresponding to the NMe$_2$ groups close to their position in the free ligand, as well as a small separation between the methylene signals in the ^{13}C-{^{1}H}-NMR spectra indicating the cleavage of the palladium–N$_{amine}$ bond. The IR spectra showed the shift towards lower wavenumbers of the ν(C=N) band as a consequence of imine nitrogen coordination to the palladium atom. The ^{31}P-{^{1}H}-NMR spectra showed a singlet resonance as a consequence of the centrosymmetric nature of the binuclear complexes.

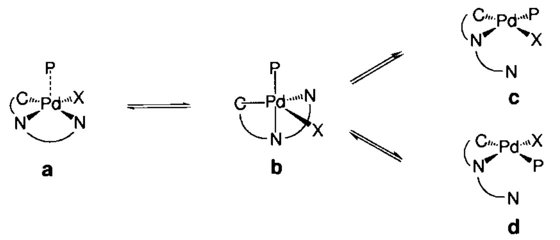
In the ^{1}H-NMR spectra of the mononuclear complexes **22**, **23** and **24** the C(4)–OMe resonance was shifted towards lower frequency by ca. 0.8 ppm as compared to the parent cyclometallated complex, due to the shielding effects of the phosphine phenyl rings, in accordance with a N–Pd–P *trans* geometry [13,14,25]. In related cyclometallated palladium(II) Schiff base complexes with a tertiary phosphine ligand *trans* to the C=N nitrogen atom the HC=N and H5 resonances show coupling to the ^{31}P nucleus, except in the cases when the Pd–N was cleaved. This seems to be the case for complexes **10** and **24** (with PMe$_2$Ph). However, the

^{1}H-NMR spectra of complexes **6**–**9** and **22**, **23** showed no coupling of the HC=N and H5 resonances to the ^{31}P nucleus. This coupling is also absent in the spectra of compounds **13**–**18**; this would lead us to believe the phosphine is *trans* to the metallated carbon atom. A similar behaviour has been observed by us in related cyclometallated complexes where in the starting material there are two fused rings at the metal centre and the coordination site of the phosphine ligand is dependent on the nature of its substituents [11]; the less basic phosphines (PPh_3, $PMePh_2$, $-CH_2PPh_2$) seem to prefer a C–Pd–P *trans* geometry, whereas the more basic phosphines (PMe_2Ph) favor a N–Pd–P *trans* arrangement. This reactivity is different to that observed in dinuclear halide-bridged palladium(II) cyclometallated complexes where it is known that bridge-splitting reactions with tertiary phosphines invariably give mononuclear species with the incoming phosphine adopting a N–Pd–P *trans* geometry [24]. Nevertheless, the shift of the C(4)–OMe resonance mentioned above controverts this and an improved argument is needed. Therefore, in an attempt to throw some light on this subject we carried out further experiments, and thus in an NMR tube excess PMe_2Ph was added to a chloroform solution of compound **21** (**21**–PMe_2Ph 1:1.5 molar ratio). At 298 K the ^{1}H-NMR spectrum showed two singlets assigned to the HC=N and H5 resonances; the ^{31}P-{^{1}H}-NMR spectrum showed a slightly broad singlet. At 253 K the HC=N and H5 resonances appeared as sharp doublets and the ^{31}P-{^{1}H}-NMR spectrum showed two singlets at δ 12.7 and δ −8.7 ppm, which were assigned to the coordinated phosphine and to the free phosphine, respectively. The P*Me*$_2$Ph resonance appeared as a broad singlet in the ^{1}H-NMR spectrum at 298 K, which collapsed to a doublet at 253 K. Furthermore, the ^{1}H-NMR spectrum of compound **9** at 298 K showed doublet and singlet signals for the H5 and HC=N protons, respectively, whereas at 273 K a triplet and a doublet were observed, respectively; the same was found in the ^{1}H-NMR spectrum of compound **13**. No further changes were observed at lower temperatures. The ^{31}P-{^{1}H}-NMR spectra showed only one singlet in each case for the phosphorus resonance. In view that nucleophilic substitutions reactions in square-planar palladium(II) usually proceeds through a five-coordinated intermediate [26], we believe that a possible equilibrium at room temperature between four- and five-coordinated species could be responsible for the behaviour of these complexes, as is depicted in Scheme 3.

Once interaction between the palladium atom and the phosphine ligand has been established, the complex goes through a five-coordinate intermediate that evolves either to a square-planar geometry with the phosphine ligand *trans* to nitrogen (c), favoured by the more basic phosphines, or *trans* to carbon (d), preferred by the less basic ones. The (c)↔(d) equilibrium, through (b), holds at room temperature; the key step being interaction of the amine nitrogen with the palla-

Table 2
Crystal and structure refinement data

	2	**3**	**4**
Formula	$C_{12}H_{17}N_2ClPd$	$C_{12}H_{17}N_2BrPd$	$C_{12}H_{17}N_2IPd$
M_r	331.13	375.58	422.58
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	*Pccn*	$P2_1/c$
Unit cell dimensions			
a (Å)	10.093(1)	16.104(3)	8.994(1)
b (Å)	10.376(1)	18.718(1)	16.669(1)
c (Å)	12.666(1)	8.800(1)	9.583(1)
β (°)			100.359(1)
V (Å^3)	1326.4(1)	2652.5(8)	1413.3(1)
Z	4	8	4
μ (mm^{-1})	1.576	4.388	3.475
Crystal size (mm)	0.60 × 0.50 × 0.40	0.50 × 0.40 × 0.35	0.35 × 0.20 × 0.15
$2\theta_{max}$ (°)	66.3	56.6	59.9
Reflections collected	12564	13805	7657
Reflections unique	4950 ($R_{int} = 0.03$)	3295 ($R_{int} = 0.05$)	3442 ($R_{int} = 0.02$)
Transmissions	0.57, 0.45	0.31, 0.22	0.62, 0.38
No. of parameters	150	150	150
R [F, $I>2\sigma(I)$]	0.0295	0.0397	0.0288
wR [F^2, all data]	0.0787	0.0942	0.0830
Max ρ (e Å^{-3})	0.555	1.248	0.984
Extinction coefficient	0.0273(12)	0.0068(3)	0.0068(4)
Absolute structure parameter	−0.02(4)		



Scheme 3.

dium atom, which is not possible in complexes with monodentate Schiff base ligands. In complexes **9** and **13** cooling the sample yields form (c), as confirmed by the NMR spectra, whereas in complex **24** excess phosphine at room temperature gives the complex with two mutually *trans* phosphine ligands which seems to be in equilibrium with form (c); in this case the more basic phosphine, PMe_2Ph, occupies the fifth coordination position, displacing the NMe_2 group in the reaction intermediate.

Reaction of **2** with the ditertiary diphosphine *cis*-dppe in a cyclometallated complex–diphosphine 1:1 molar ratio followed by treatment with sodium perchlorate gave the mononuclear cyclometallated complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}$(*cis* - $PPh_2CH{=}CHPPh_2$–P,P)]$[ClO_4]$ (**19**) which was fully characterised (see Section 3 and Table 1). The ^{31}P-$\{^1H\}$-NMR spectrum 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 [27]. The *H*C=N resonance was only coupled to the ^{31}P nucleus *trans* to nitrogen. This was confirmed by selective decoupling experiments on the ^{31}P atoms. In the ^1H-NMR the δ (Me_2) resonance was shifted to lower frequency as a consequence of the Pd–NMe_2 bond cleavage.

2.1. Crystal structures of $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(X)]$; X=Cl (**2**), Br (**3**), I (**4**)

Suitable crystals of the title compounds were grown by slowly evaporating a chloroform solution. The molecular structures which are illustrated in the Figs. 2–4 consist of discrete molecules separated by van der Waals distances.

In all cases the palladium is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the phenyl ring, the iminic N(1) and amine N(2) nitrogen atoms and to the corresponding halogen atom. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90° with the most noticeable distortions corresponding to the C(1)–Pd(1)–N(1) angles of 81.08(12)° and 80.92(16)° for **2** and **3**, respectively, and the N(2)–Pd(1)–I(1) angle of 99.88(10)° for **4** (Table 3). The sum of the angles about palladium is approximately 360° in all cases.

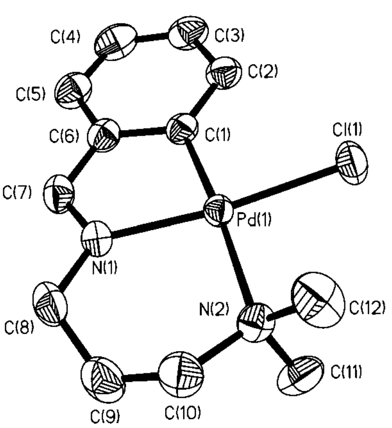


Fig. 2. Molecular structure of complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(Cl)]$ (**2**). Hydrogen atoms have been omitted for clarity.

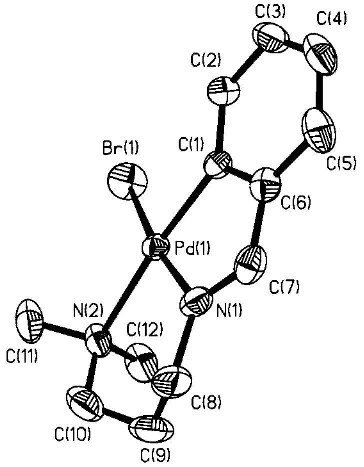


Fig. 3. Molecular structure of complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(Br)]$ (**3**). Hydrogen atoms have been omitted for clarity.

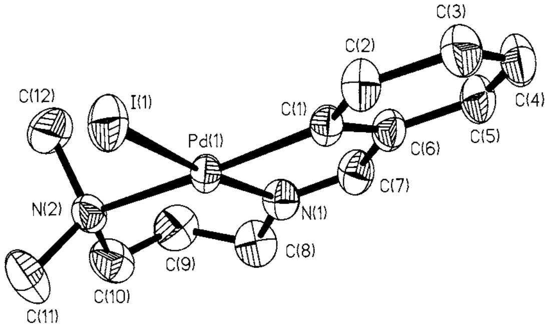


Fig. 4. Molecular structure of complex $[Pd\{C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2\}(I)]$ (**4**). Hydrogen atoms have been omitted for clarity.

The Pd–N(1) (2.029(3), 2.028(4) and 2.071(3) Å for **2**, **3** and **4**, respectively) and Pd–N(2) (2.203(3),

Table 3
Selected bond distances (Å) and angles (°) for complexes **2**, **3** and **4**

2		**3**		**4**	
Pd(1)–C(1)	1.991(3)	Pd(1)–C(1)	1.985(4)	Pd(1)–C(1)	1.990(3)
Pd(1)–N(1)	2.029(3)	Pd(1)–N(1)	2.028(4)	Pd(1)–N(1)	2.071(3)
Pd(1)–N(2)	2.203(3)	Pd(1)–N(2)	2.208(4)	Pd(1)–N(2)	2.243(3)
Pd(1)–Cl(1)	2.3071(8)	Pd(1)–Br(1)	2.4219(7)	Pd(1)–I(1)	2.6556(4)
C(1)–C(6)	1.398(4)	C(1)–C(6)	1.400(6)	C(1)–C(6)	1.387(5)
C(6)–C(7)	1.449(5)	C(6)–C(7)	1.441(6)	C(6)–C(7)	1.532(6)
N(1)–C(7)	1.290(4)	N(1)–C(7)	1.263(6)	N(1)–C(7)	1.228(5)
Cl(1)–H(2)	2.82(4)	Br(1)–H(2)	2.72(5)	I(1)–H(2)	2.86(4)
C(1)–Pd(1)–N(1)	81.08(12)	C(1)–Pd(1)–N(1)	80.92(16)	C(1)–Pd(1)–N(1)	87.71(13)
C(1)–Pd(1)–N(2)	173.39(10)	C(1)–Pd(1)–N(2)	174.67(16)	C(1)–Pd(1)–N(2)	172.12(13)
N(1)–Pd(1)–N(2)	94.94(11)	N(1)–Pd(1)–N(2)	94.79(17)	N(1)–Pd(1)–N(2)	86.29(13)
C(1)–Pd(1)–Cl(1)	92.29(9)	C(1)–Pd(1)–Br(1)	92.38(12)	C(1)–Pd(1)–I(1)	86.02(10)
N(2)–Pd(1)–Cl(1)	91.86(8)	N(2)–Pd(1)–Br(1)	91.69(13)	N(2)–Pd(1)–I(1)	99.88(10)
C(6)–C(1)–Pd(1)	113.1(2)	C(6)–C(1)–Pd(1)	112.4(3)	C(6)–C(1)–Pd(1)	105.2(3)
C(1)–C(6)–C(7)	114.0(3)	C(1)–C(6)–C(7)	113.9(4)	C(1)–C(6)–C(7)	118.9(3)
N(1)–C(7)–C(6)	117.3(3)	N(1)–C(7)–C(6)	117.9(4)	N(1)–C(7)–C(6)	119.7(3)
C(7)–N(1)–Pd(1)	114.3(2)	C(7)–N(1)–Pd(1)	114.1(3)	C(7)–N(1)–Pd(1)	108.1(3)
C(8)–N(1)–Pd(1)	125.7(2)	C(8)–N(1)–Pd(1)	126.1(4)	C(8)–N(1)–Pd(1)	131.0(3)

2.208(4) and 2.243(3) Å for **2**, **3** and **4**, respectively) bond distances are similar to others reported for related compounds [14,16,28]. The Pd–N(2) bond length, longer than Pd–N(1) distance, shows the stronger *trans* influence of the donor ligand.

The Pd–C(1) bond distances of 1.991(3), 1.985(4) and 1.990(3) Å (for **2**, **3** and **4**, respectively) are somewhat shorter than the values predicted from their covalent radii [29] but similar to values found earlier [14,16]. The Pd–Cl(1) and Pd–Br(1) bond distances (2.3071(8), 2.4219(7) Å for **2** and **3**, respectively) are in accordance with the values found earlier in similar cyclometallated compounds [30–34]. Nevertheless the Pd–I(1) bond length of 2.6556 (4) Å is somewhat longer than the values found in related complexes with I *trans* to N [28]. We think this is due to the important steric repulsion between the large iodine atom and the $-NMe_2$ methyl groups. This is confirmed by the enlarged I(1)–Pd–N(2) bond angle of 99.88(10)° (as compared to the Cl(1)–Pd–N(2) and Br(1)–Pd–N(2) angles of 91.86(8) and 91.69(13)° for **2** and **3**, respectively.

The geometry around the palladium atom [Pd, C(1), N(1), C(2), X(1)] is planar (r.m.s. = 0.0567, 0.0208 and 0.0380 Å for **2**, **3** and **4**, respectively; plane 1). The metallated ring [Pd, C(1), C(6), C(7), N(1)] is also planar (r.m.s. = 0.0167, 0.0429 and 0.0320 Å for **2**, **3** and **4**, respectively; plane 2). Angles between planes are as follows: plane 1/plane 2 = 4.3°, 6.2° and 5.6° for **2**, **3** and **4**. As expected, the coordination ring (Pd, N(1), C(8), C(9), C(10), N(2)) shows large deviations from planarity with C(8) and C(10) lying above the least-square plane and C(9) below.

The distance between the aromatic hydrogen H2 and the halogen atom (Cl(1)–H(2), 2.82(4) Å; Br(1)–H(2), 2.72(5) Å; I(1)–H(2), 2.86(4) Å) shows some interaction between these atoms. This observation is in agreement with the low-field shift observed for the resonance corresponding to this proton in the ^1H-NMR spectra of the complexes.

3. Experimental

Safety note: CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

3.1. General procedures

Solvents were purified by standard methods [35]. Chemicals were reagent grade. The phosphines PPh_3, $PMePh_2$, PMe_2Ph, *cis*-$Ph_2P(H)C{=}C(H)PPh_2$, (*cis*-dppe) $Ph_2P(CH_2)_4PPh_2$ (dppb) and $Ph_2P(CH_2)_5PPh_2$ (dpppe) were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Elemental Analyser, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin–Elmer 1330 spectrometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C-{^1H}) or 85% H_3PO_4 (^{31}P-{^1H}) and were recorded on a Bruker AC-2005 spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

The synthesis of $2\text{-}ClC_6H_4(H){=}NCH_2CH_2CH_2NMe_2$ (**1**) and $3,4\text{-}(MeO)_2\text{-}6\text{-}BrC_6H_2(H){=}NCH_2CH_2CH_2NMe_2$ (**20**) were performed by heating a chloroform solution of the appropriate quantities of *N*,*N*-dimethyl-1,3-propanediamine and 2-chlorobenzaldehyde or 6-bromoveratraldehyde, respectively, in a Dean–Stark apparatus under reflux. IR (ν_{max} (cm^{-1})), (C=N) 1640s (**1**), 1650 s (**20**). ^{13}C-{^{1}H}-NMR for ligand **1** (50.28 MHz, $CDCl_3$): δ 157.9 (C=N); δ 134.9 (C1); δ 133.2 (C6); δ 131.1, 129.7, 128.8, 126.9 (C2, C3, C4, C5); δ 59.6, 57.3 ($C{=}N\mathit{C}H_2CH_2\mathit{C}H_2NMe_2$): δ 28.7 ($C{=}NCH_2\mathit{C}H_2CH_2NMe_2$); δ 45.4 ($NMe_2$). FAB (*m*/*z*) (**1**): [M]$^+$ 225.

3.2. Syntheses

3.2.1. [Pd{$C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$}(Cl)] (2)

A pressure tube containing 2-$ClC_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$ (**1**) (0.172 g, 0.770 mmol), tris-(dibenzylideneacetone)dipalladium(0) (0.400 g, 0.350 mmol) and 20 cm^3 of dry toluene was sealed under argon. The dark-red solution was heated at 80°C for 1 h. After this time the dark solution turned to bright yellow and a black palladium precipitate appeared. After cooling to room temperature (r.t.) the solution was filtered through Celite. The solvent was removed under vacuum to give a yellow oil which was treated with ca. 10 cm^3 of diethylether and stirred for 5 min; the resulting yellow solid filtered off, washed with ether and dried in vacuo. Yield: 67%. Elemental analysis (EA): Found: C,43.5; H, 5.1; N, 8.5. $C_{12}H_{17}N_2ClPd$ requires C, 43.5; H, 5.2; N, 8.5%. IR (ν_{max} (cm^{-1})), (C=N) 1610s. ^{13}C-{^{1}H}-NMR (50.28 MHz, $CDCl_3$): δ 175.0 (C=N); δ 155.8 (C6); δ145.4 (C1); δ136.7 (C5); δ 130.1, 127.0, 124.2 (C2, C3, C4); δ 63.2, 58.0 ($C{=}N\mathit{C}H_2CH_2\mathit{C}H_2NMe_2$); δ 26.4 ($C{=}NCH_2\mathit{C}H_2CH_2NMe_2$); δ 49.4 ($NMe_2$). FAB (*m*/*z*): [M]$^+$ 330; [M–Cl]$^+$ 295; [M–Cl, M]$^+$ 627; [2M + Cl]$^+$ 699.

Compound **21** was obtained similarly as an orange solid.

3.2.2. [Pd{3,4-$(MeO)_2C_6H_2C(H){=}NCH_2CH_2CH_2NMe_2$}(Br)] (21)

Yield: 64%. EA: Found: C,38.4; H, 4.8; N, 6.3. $C_{14}H_{21}N_2BrO_2Pd$ requires C, 38.6; H, 4.9; N, 6.4%. IR (ν_{max} (cm^{-1})) (C=N) 1620s.

3.2.3. [Pd{$C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$}(Br)] (3)

An aqueous solution of NaBr (ca. 10^{-2} M) was added dropwise to a solution of **2** (0.030 g, 0.091 mmol) in 15 cm^3 of acetone. The product separated immediately as a yellow solid. After stirring for 1 h, the solid was filtered off and recrystallized from dichloromethane–hexane. Yield: 77%. EA: Found: C, 38.2; H, 4.6; N, 7.3. $C_{12}H_{17}N_2BrPd$ requires C, 38.4; H, 4.6; N, 7.4%. IR (ν_{max} (cm^{-1})), (C=N) 1610 s. ^{13}C-{^{1}H}-NMR (50.28 MHz, $CDCl_3$): δ 175.2 (C=N); δ 154.5 (C6); δ 145.7 (C1); δ 139.7 (C5); δ 130.5, 127.3, 124.2 (C2, C3, C4); δ 63.6, 57.8 ($C{=}N\mathit{C}H_2CH_2\mathit{C}H_2NMe_2$); δ 26.3 ($C{=}NCH_2\mathit{C}H_2CH_2NMe_2$); δ 50.4 ($NMe_2$). FAB (*m*/*z*): [MH]$^+$ 377; [M–Br]$^+$ 295; [M–Br, M]$^+$ 670.

Compound **4** was obtained following a similar procedure but treating **2** with NaI, as a yellow solid.

3.2.4. [Pd{$C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$}(I)] (4)

Yield: 73%. Found: C, 34.0; H, 4.2; N, 6.3. $C_{12}H_{17}N_2IPd$ requires C, 34.1; H, 4.1; N, 6.6%. IR (ν_{max} (cm^{-1})), (C=N) 1620 w. ^{13}C-{^{1}H}-NMR (50.28 MHz, $CDCl_3$): δ 175.5 (C=N); δ 153.0 (C6); δ146.2 (C1); δ153.0 (C5); δ 131.0, 127.7, 123.9 (C2, C3, C4); δ 64.1, 57.7 ($C{=}N\mathit{C}H_2CH_2\mathit{C}H_2NMe_2$); δ 26.3 ($C{=}NCH_2\mathit{C}H_2CH_2NMe_2$); δ 52.3 ($NMe_2$). FAB (*m*/*z*): [M]$^+$ 423.

3.2.5. [Pd{$C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$}($PPh_3$)]-[$CF_3SO_3$] (5)

A suspension of **2** (0.030 g, 0.091mmol) in acetone (15 cm^3) was treated with silver trifluoromethanesulfonate (0.026 g, 0.100 mmol) and stirred for 2 h. The resulting solution was filtered through Celite to eliminate the AgCl precipitate. PPh_3 (0.024, 0.091 mmol) was added to the filtrate, the solution stirred for another 4 h and the solvent removed to give a yellow solid which was recrystallized from dichloromethane–hexane. Yield: 80%. E.A.: Found: C, 52.6; H, 4.4; N, 3.9. $C_{31}H_{32}F_3N_2O_3PSPd$ requires C, 52.7; H, 4.6; N, 4.0%. IR (ν_{max} (cm^{-1})), (C=N) 1639 m. ^{13}C-{^{1}H}-NMR (50.28 MHz, $CDCl_3$): δ 178.0 (C=N); δ 153.4 (C6); δ 146.8 (C1); δ 138.8d *J*(PC) 12.0 (C5); δ 129.9, 129.3, 125.2 (C2, C3, C4); δ 62.0, 55.5 ($C{=}N\mathit{C}H_2CH_2\mathit{C}H_2NMe_2$); δ 25.3 ($C{=}NCH_2\mathit{C}H_2CH_2NMe_2$); δ 48.6 ($NMe_2$). P-Phenyl: δ 130.7d, *J*(PC) 39.7 (Ci); δ 135.4d, *J*(PC) 12.1 (Co); δ 129.1d, *J*(PC) 10.7 (Cm); δ 132.0 (Cp).

Compound **5** was also obtained following a similar procedure but using compounds **3** or **4** as starting materials.

3.2.6. [Pd{$C_6H_4C(H){=}NCH_2CH_2CH_2NMe_2$}($PPh_3$)(Cl)] (6)

PPh_3 (0.024 g, 0.091 mmol) was added to a suspension of **2** (0.030 g, 0.091 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the solvent removed and the resulting yellow oil recrystallized from dichloromehane–hexane to give a pale yellow solid. Yield: 60%. EA: Found: C, 60.7; H, 5.2; N, 4.4. $C_{30}H_{32}N_2ClPdP$ requires C, 60.7; H, 5.4; N, 4.7%. IR (ν_{max} (cm^{-1})), (C=N) 1626 s. ^{13}C-{^{1}H}-NMR (50.28 MHz, $CDCl_3$): δ 175.6 (C=N); δ 157.9 (C6); δ 148.1 (C1); δ 138.1 (C5); δ 129.6, 128.6, 123.9 (C2, C3, C4); δ 56.9, 56.4 ($C{=}N\mathit{C}H_2CH_2\mathit{C}H_2NMe_2$); δ 28.3 ($C{=}NCH_2\mathit{C}H_2CH_2NMe_2$); δ 45.3 ($NMe_2$). P-Phenyl: δ 131.6d, *J*(PC) 42.6 (Ci); δ 135.1d, *J*(PC) 12.8 (Co); δ 128.0d, *J*(PC) 10.7 (Cm); δ 130.4d (Cp) *J*(PC) 1.4.

Compounds **7** and **8** were synthesized following a similar procedure as yellow solids.

3.2.7. *[Pd{$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$}(PPh_3)(Br)]* ***(7)***

Yield: 73%. EA: Found: C, 55.3; H, 5.3; N, 4.0. $C_{30}H_{32}N_2BrPdP$ requires C, 56.5; H, 5.1; N, 4.4%. IR (ν_{max} (cm^{-1})), (C=N) 1620 s.

3.2.8. *[Pd{$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$}(PPh_3)(I)]* ***(8)***

Yield: 60%. EA: Found: C, 52.3; H, 4.6; N, 4.5. $C_{30}H_{32}N_2IPdP$ requires C, 52.6; H, 4.7; N, 4.1%. IR (ν_{max} (cm^{-1})), (C=N) 1625 s.

3.2.9. *[Pd{$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$}-($PMePh_2$)(Cl)]* ***(9)***

$PMePh_2$ (0.018 g, 0.090 mmol) was added to a suspension of **2** (0.030 g, 0.091 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h and the solvent removed to give a yellow oil which could not be recrystallized. Yield: 90%. EA: Found: C, 55.0; H, 5.3; N, 5.0. $C_{25}H_{30}N_2ClPdP$ requires C, 56.5; H, 5.7; N, 5.3%. IR (ν_{max} (cm^{-1})), (C=N) 1630 m.

Compound **10** was obtained following a similar procedure as a yellow oil.

3.2.10. *[Pd{$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$}-(PMe_2Ph)(Cl)]* ***(10)***

Yield: 90%. EA: Found: C, 49.0; H, 5.8; N, 6.5. $C_{20}H_{28}N_2ClPdP$ requires C, 51.2; H, 6.0; N, 6.0%. IR (ν_{max} (cm^{-1})), (C=N) 1625 s.

Compounds **22** and **24** were obtained following a similar procedure to that for **6** as yellow solids.

3.2.11. *[Pd{3,4-$(MeO)_2C_6H_2C(H)$=$NCH_2CH_2CH_2$-NMe_2}(PPh_3)(Br)]* ***(22)***

Yield: 90%. EA: Found: C, 55.0; H, 5.0; N, 4.4. $C_{32}H_{36}N_2BrO_2PdP$ requires C, 55.1; H, 5.2; N, 4.1%. IR (ν_{max} (cm^{-1})), (C=N) 1625 m.

3.2.12. *[Pd{3,4-$(MeO)_2C_6H_2C(H)$=NCH_2CH_2-CH_2NMe_2}(PMe_2Ph)(Br)]* ***(24)***

Yield: 63%. EA: Found: C, 45.3; H, 5.5; N, 4.8. $C_{22}H_{32}N_2BrO_2PdP$ requires C, 46.0; H, 5.6; N, 4.9%. IR (ν_{max} (cm^{-1})), (C=N) 1630 m.

Compound **23** was obtained following a similar procedure to that for **9** as a yellow oil.

3.2.13. *[Pd{3,4-$(MeO)_2C_6H_2C(H)$=NCH_2CH_2-CH_2NMe_2}($PMePh_2$)(Br)]* ***(23)***

Yield: 90%. EA: Found: C, 47.0; H, 5.0; N, 4.1. $C_{27}H_{34}N_2BrO_2PdP$ requires C, 51.0; H, 5.4; N, 4.4%. IR (ν_{max} (cm^{-1})), (C=N) 1620 w.

3.2.14. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$]}$_2$-(μ-$PPh_2(CH_2)_4PPh_2$)][CF_3SO_3]$_2$* ***(11)***

A suspension of **2** (0.030 g, 0.091 mmol) in acetone (15 cm^3) was treated with silver trifluoromethanesulfonate (0.026 g, 0.100 mmol) and stirred for 2 h. The solution was filtered through Celite to eliminate the AgCl precipitate. $PPh_2(CH_2)_4PPh_2$ (0.019, 0.045 mmol) was added to the filtrate, the solution stirred for 4 h and the solvent removed to give a yellow oil which was recrystallized from chloroform–hexane to give a yellow solid. Yield: 60%. EA: Found: C, 49.5; H, 4.6; N, 4.4. $C_{54}H_{62}F_6N_4O_6P_2S_2Pd_2$ requires C, 49.3; H, 4.7; N, 4.2%. IR (ν_{max} (cm^{-1})), (C=N) 1638 s. ^{13}C-{^1H}-NMR (50.28 MHz, $CDCl_3$): δ 176.8 (C=N); δ 153.1 (C6); δ 147.2 (C1); δ 136.8d *J*(PC) 10.7 (C5); δ 130.5, 129.9, 125.4 (C2, C3, C4); δ 69.6, 54.6 (C=N*C*H_2CH_2-*C*H_2NMe_2); δ 26.0 (C=NCH_2*C*$H_2CH_2NMe_2$); δ 48.2 (NMe_2). P-Phenyl: δ 131.3d, *J*(PC) 49.7 (Ci); δ 133.8d, *J*(PC) 11.4 (Co); δ 129.3d, *J*(PC) 10.8 (Cm); δ 131.8 (Cp). CH_2-Phosphine: 28.5, 27.5.

Compound **11** was also obtained following a similar procedure but using **3** or **4** as starting materials.

Compound **12** was obtained following a similar procedure as a yellow solid.

3.2.15. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$]}$_2$-(μ-$PPh_2(CH_2)_5PPh_2$)][CF_3SO_3]$_2$* ***(12)***

Yield: 60%. EA: Found: C, 49.5; H, 4.8; N, 4.6. $C_{55}H_{64}F_6N_4O_6P_2S_2Pd_2$ requires C, 49.6; H, 4.8; N, 4.2%. IR (ν_{max} (cm^{-1})), (C=N) 1636 s. ^{13}C-{^1H}-NMR (50.28 MHz, $CDCl_3$): δ 176.8 (C=N); δ 155.7 (C6); δ 147.3 (C1); δ 137.0 (C5); δ 130.7, 130.0, 125.3 (C2, C3, C4); δ 69.2, 54.6 (C=N*C*H_2CH_2*C*H_2NMe_2); δ 28.2 (C=NCH_2*C*$H_2CH_2NMe_2$); δ 49.4 (NMe_2). P-Phenyl: δ 133.8d, *J*(PC) 11.4 (Co); δ 129.2d, *J*(PC) 9.9 (Cm); δ 131.8 (Cp). CH_2-Phosphine: 29.2, 27.8, 21.6.

3.2.16. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$](Cl)}$_2$(μ-$PPh_2(CH_2)_4PPh_2$)]* ***(13)***

$PPh_2(CH_2)_4PPh_2$ (0.019 g, 0.045 mmol) was added to a suspension of **2** (0.030 g, 0.091 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the resulting yellow precipitate was filtered off and dried in air. Yield: 57%. EA: Found: C, 57.7; H, 5.8; N, 5.2. $C_{52}H_{62}Cl_2N_4P_2Pd_2$ requires C, 57.4; H, 5.7; N, 5.1%. IR (ν_{max} (cm^{-1})), (C=N) 1625s. ^{13}C-{^1H}-NMR (50.28 MHz, $CDCl_3$): δ 175.0 (C=N); δ 157.8 (C6); δ 148.0 (C1); δ 137.5 (C5); δ 129.9, 128.6, 123.9 (C2, C3, C4); δ 56.4 (C=N*C*H_2CH_2*C*H_2NMe_2); δ 28.2 (C=NCH_2-*C*$H_2CH_2NMe_2$); δ 45.3 (NMe_2). P-Phenyl: δ 128.1d, *J*(PC) 41.2 (Ci); δ 134.0d, *J*(PC) 11.4 (Co); δ 128.4d, *J*(PC) 9.9 (Cm); δ 130.7 (Cp). CH_2-Phosphine: 29.6, 26.4 *J*(PC) 33.4, 9.9.

Compounds **14, 15, 16, 17** and **18** were synthesized following a similar procedure as yellow solids.

3.2.17. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$](Br)}$_2$-(μ-$PPh_2(CH_2)_4PPh_2$)] (**14**)*

Yield: 55%. EA: Found: C, 53.2; H, 5.2; N, 4.6 $C_{52}H_{62}Br_2N_4P_2Pd_2$ requires C, 53.0; H, 5.3; N, 4.7%. IR (ν_{max} (cm^{-1})), (C=N) 1630s.

3.2.18. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$](I)}$_2$-(μ-$PPh_2(CH_2)_4PPh_2$)] (**15**)*

Yield: 51%. EA: Found: C, 49.3; H, 4.9; N, 4.5. $C_{52}H_{62}I_2N_4P_2Pd_2$ requires C, 49.1; H, 4.9; N, 4.4%. IR (ν_{max} (cm^{-1})), (C=N) 1620w.

3.2.19. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$](Cl)}$_2$-(μ-$PPh_2(CH_2)_5PPh_2$)] (**16**)*

Yield: 60%. EA: Found: C, 57.4; H, 5.6; N, 4.6. $C_{53}H_{64}Cl_2N_4P_2Pd_2$ requires C, 57.7; H, 5.8; N, 5.1%. IR (ν_{max} (cm^{-1})), (C=N) 1625s. ^{13}C-{^{1}H}-NMR (50.28 MHz, $CDCl_3$): δ 175.0 (C=N); δ 157.8 (C6); δ 148.0 (C1); δ 137.6 (C5); δ 129.9, 128.7, 124.0 (C2, C3, C4); δ 56.5, 56.4 (C=N*C*H_2CH_2*C*H_2NMe_2); δ 29.5 (C=NCH_2*C*$H_2CH_2NMe_2$); δ 45.3 (NMe_2). P-Phenyl: δ 128.1d, *J*(PC) 51.8 (Ci); δ 134.0d, *J*(PC) 11.7 (Co); δ 128.4d, *J*(PC) 9.9 (Cm); δ 130.7 (Cp). CH_2-Phosphine: 31.9, 28.9, 24.0.

3.2.20. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$](Br)}$_2$-(μ-$PPh_2(CH_2)_5PPh_2$)] (**17**)*

Yield: 75%. EA: Found: C, 53.2; H, 5.3; N, 4.4. $C_{53}H_{64}Br_2N_4P_2Pd_2$ requires C, 53.4; H, 5.4; N, 4.7%. IR (ν_{max} (cm^{-1})), (C=N) 1620s.

3.2.21. *[{Pd[$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$](I)}$_2$-(μ-$PPh_2(CH_2)_5PPh_2$)] (**18**)*

Yield: 45%. EA: Found: C, 49.3; H, 5.0; N, 4.3. $C_{53}H_{64}I_2N_4P_2Pd_2$ requires C, 49.5; H, 5.0; N, 4.4%. IR (ν_{max} (cm^{-1})), (C=N) 1630s.

3.2.22. *[Pd{$C_6H_4C(H)$=$NCH_2CH_2CH_2NMe_2$}-(cis-PPh_2CH=$CHPPh_2$-P,P)][ClO_4] (**19**)*

$PPh_2(CH)_2PPh_2$ (0.036 g, 0.091 mmol) was added to a suspension of **2** (0.030 g, 0.091 mmol) in acetone (20 cm^3). The resulting solution was stirred for 1 h after which, $NaClO_4$ was added and the mixture stirred for a further 6 h. The complex was then precipitated out by addition of water, filtered of and dried in vacuo. Recrystallization from dichloromethane–hexane gave the compound as a yellow solid. Yield: 90%. EA: Found: C, 57.5; H, 4.3; N, 3.7. $C_{38}H_{39}N_2PdClO_4P_2$ requires C, 57.7; H, 5.0; N, 3.5%. IR (ν_{max} (cm^{-1})), (C=N) 1618 m.

3.3. *Single-crystal X-ray diffraction analysis. Crystal structure determination of complexes **2**, **3** and **4***

Three-dimensional, r.t. X-ray data were collected on a Siemens Smart CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. Of the reflections measured, all of which were corrected from Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 4419 for **2**, 2394 for **3** and 2917 for **4** independent reflections exceeded the significance level $|F|/\sigma|F| > 4.0$ (Table 2). 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. Hydrogen atoms were included in calculated positions and refined in riding mode (except H2 which was located in a difference Fourier map and refined isotropically). The structure solution and refinement were carried out using the program package SHELX-97 [36].

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144952, for compound **2**, CCDC no. 144951 for compound **3**, and CCDC no. 144950 for compound **4**. 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 http://www.ccdc.cam.ac.uk).

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