Sterically controlled reactivity of palladium(II) tetranuclear cyclometallated complexes. Crystal and molecular structure of the novel tetranuclear compound $[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}\text{-}(\mu\text{-}Cl)(Cl)(PPh_3)]_2$†

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Received (in London, UK) 21st December 2001, Accepted 3rd March 2002
First published as an Advance Article on the web 5th June 2002

The reaction of the Schiff base ligands $1,3\text{-}[C{=}N(H)CH_2C_4H_7O]_2C_6H_4$ (**1**) and $1,4\text{-}[C{=}N(H)CH_2C_4H_7O]_2C_6H_4$ (**14**) with palladium(II) acetate in toluene gave the acetato-bridged cyclometallated compounds $[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}AcO)_2]_2$ (**2**) and $[(\mu\text{-}AcO)Pd\{1,4\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}Pd(\mu\text{-}AcO)]_n$ (**15**). Reaction of **2** and **15** with aqueous sodium chloride gave the chloro-bridged cyclometallated compounds $[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Cl)_2]_2$ (**3**) and $[(\mu\text{-}Cl)Pd\{1,4\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}Pd(\mu\text{-}Cl)]_n$ (**16**), respectively, after a metathesis reaction. Reaction of **3** with triphenylphosphine in a 1:2 molar ratio gave the tetranuclear complex $[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Cl)(Cl)(PPh_3)]_2$ (**4**), where only one of the bridging $PdCl_2Pd$ moieties was cleaved, and which was characterized by X-ray crystal structure analysis. However, reaction of **16** with PPh_3 gave the dinuclear complex $[(PPh_3)(Cl)Pd\{1,4\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}Pd(PPh_3)(Cl)]$ (**17**) after a full bridge-splitting reaction. Similarly, treatment of **3** with PMe_2Ph, pyridine and thallium acetylacetonate produced the dinuclear complexes **5**, **6** and **7**, respectively. Treatment of **4** with pyridine in a 1:2 molar ratio, and with 4,4′-dipyridyl in an 1:1 molar ratio, gave the di- and tetranuclear complexes **12** and **13**, respectively. Reaction of **3** with the tertiary diphosphine *cis*-$Ph_2PCH{=}CHPPh_2$ in a 1:2 molar ratio yielded the tetranuclear complex $[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Cl)(Ph_2PCH{=}CHPPh_2\text{-}P,P)][Cl]_2$ (**8**) after selective splitting of one of the $PdCl_2Pd$ bridging moieties. However, reaction of **3** with *cis*-$Ph_2PCH{=}CHPPh_2$ and $Ph_2P(CH_2)_2PPh_2$ in 1:4 molar ratios gave the dinuclear complexes **9** and **10**, respectively. Reaction of **3** with the diphosphine $Ph_2PC_5H_4FeC_5H_4PPh_2$ in a 1:2 molar ratio yielded the trinuclear complex $[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Ph_2PC_5H_4FeC_5H_4PPh_2)]$ (**11**), with the diphosphine bridging the two palladium atoms of the dicyclometallated moiety.

Introduction

The study of cyclometallated compounds has attracted much attention over the last three decades.[1–5] They present numerous applications in organic and organometallic synthesis,[6] in insertion reactions,[7] in the synthesis of new metal mesogenic compounds[8] and biologically active compounds[9,10] and in catalytic materials.[11]

By far, the most widely studied examples are five-membered palladacycles with nitrogen donors. We are interested in the study of cyclometallated complexes derived from potentially [C,N,X], (X = O, S, N) terdentate ligands. For example, semicarbazones,[12,13] thiosemicarbazones[14,15] or Schiff bases[16–19] react readily with palladium(II), platinum(II) and palladium(0) to give cyclometallated complexes with two fused rings at the metal.

We are also interested in the synthesis of complexes with doubly cyclometallated ligands.[20–22] Among these, complexes containing two metallated phenyl rings are common.[23] However, relatively few are known with two metallated sites on the same phenyl ring,[24–29] and examples where each metal atom coordinates to the ligand through three donor atoms are also less well known.[30] Much less common still are complexes derived from hexadentate ligands in which both metal atoms coordinate to the same phenyl ring.[17,18,31]

As part of these studies, we decided to examine the behaviour of the potentially [O,N,C:C,N,O] hexadentante ligand $1,3\text{-}[C{=}N(H)CH_2C_4H_7O]_2C_6H_4$ (**1**). The reaction of **1** with palladium(II) acetate did not yield the expected complex with the ligand attached in a hexadentate fashion, instead, a tetranuclear dimeric species (**2**), in which the O atoms of the THF moieties were not bonded to the metals, was obtained. However, the tetranuclear chloro-bridged derivative of **2** showed an unusual reactivity towards triphenylphosphine. The bulky nature of this ligand hinders simultaneous coordination of two triphenylphosphines to each palladium atom of the dinuclear cyclometallated moiety; in its place, a tetranuclear complex in which only one phosphine was bonded to the metal was obtained. Reactivity with other neutral and anionic ligands is also reported.

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† Electronic supplementary information (ESI) available: ^1H and ^{31}P NMR data for compounds **1**–**15** and **17**. See http://www.rsc.org/suppdata/nj/b1/b111671a/

DOI: 10.1039/b111671a

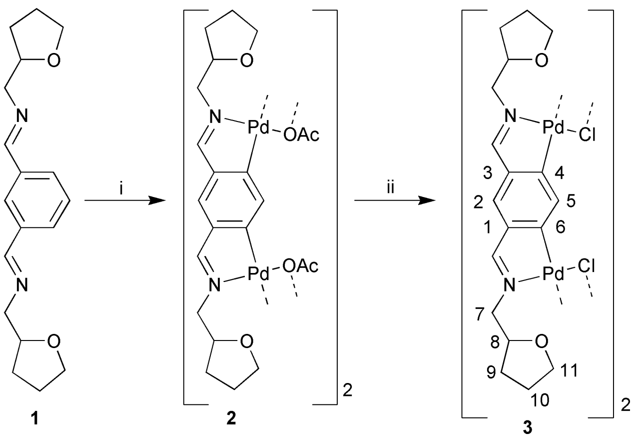
Results and discussion

For the convenience of the reader, the compounds and reactions are shown in Schemes 1–4. The compounds described in this paper were characterized by elemental analysis and IR spectroscopy (data in the Experimental section), by ^{1}H, ^{31}P-{^{1}H} and, in part, ^{13}C-{^{1}H} NMR spectroscopy (see Experimental section), and FAB mass spectrometry.

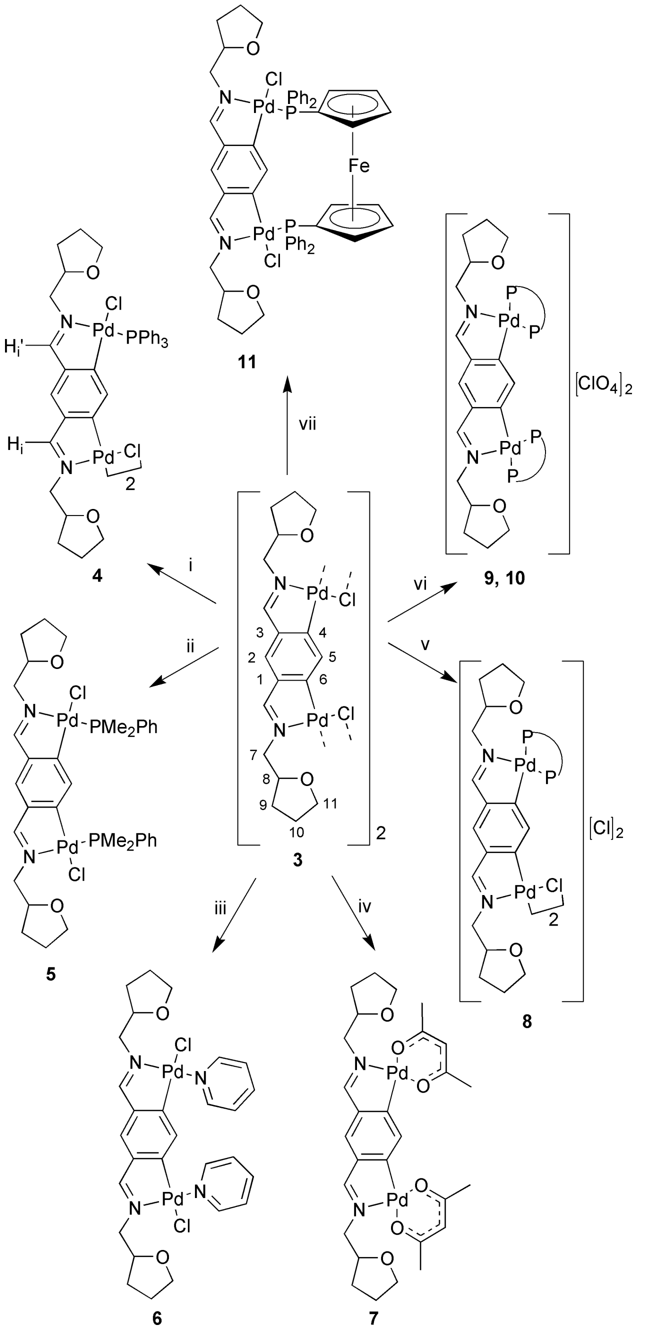
The reaction of the Schiff base ligand 1,3-[C(H)=N-$CH_2C_4H_7O]_2C_6H_4$ (**1**) with palladium(II) acetate in toluene gave the tetranuclear cyclometallated compound **2** as an orange air-stable solid. The HC=N proton resonance in the ^{1}H NMR spectrum of **2** was shifted upfield as compared to the free ligand, showing coordination of the palladium atom *via* the lone pair of the nitrogen atom.[32] Two singlets at δ 2.23 and 2.00 were assigned to the two pairs of non-equivalent bridging acetate groups; the bridging mode of the latter was confirmed by the presence of two strong ν(COO) bands at 1580s and 1430s cm^{-1} in the IR spectrum.[33] The mass FAB spectrum of **2** showed a cluster of peaks centered at 1119 amu due to the $[M - AcO]^+$ fragment. The isotopic pattern was in good agreement with the proposed tetranuclear structure. The metallated phenyl rings mutually shield each others protons, a consequence of the folded structure of the complex, therefore, the H^2 and H^5 proton resonances (*ca.* δ 6.7) were shifted to lower frequency (as compared to the free ligand). The proposed structure is in agreement with those reported previously in related complexes.[25,34] Furthermore, the H^2 and H^5 resonances appeared as a multiplet and three signals were assigned to the HC=N protons. Two factors account for these observations: the open-book structure of complex **2** and the presence of (*S*,*S*), (*R*,*R*) and (*R*,*S*) stereomers for **2**, as a consequence of the (−)-(*R*) and (+)-(*S*) enantiomers of tetrahydrofurfurylamine used in the synthesis of Schiff base **1**.

In order to confirm these observations, we synthesized an enantiopure isomer using the ligand prepared by reaction of (−)-(*R*)-tetrahydrofurfurylamine and isophthalaldehyde as the organic substrate. Two singlets, at δ 7.60 and 7.56, were assigned to the inequivalent HC=N proton resonances, H^a and H^b, respectively, in the ^{1}H NMR spectrum. Two singlets at δ 6.69 and 6.63 were ascribed to the H^2 and H^5 protons, respectively. Furthermore, neither ligand **1** nor the remaining compounds, where the open-book structure is absent, showed the ^{1}H NMR patterns observed for compound **2**.

The reaction of **2** with aqueous sodium chloride yielded the tetranuclear chloro-bridged complex **3**. The ^{1}H NMR spectrum showed only one set of signals for the H^2, H^5 and HC=N proton resonances. The H^2 and H^5 resonances appeared at δ 8.02 and 7.16 shifted downfield as compared to complex **2**.

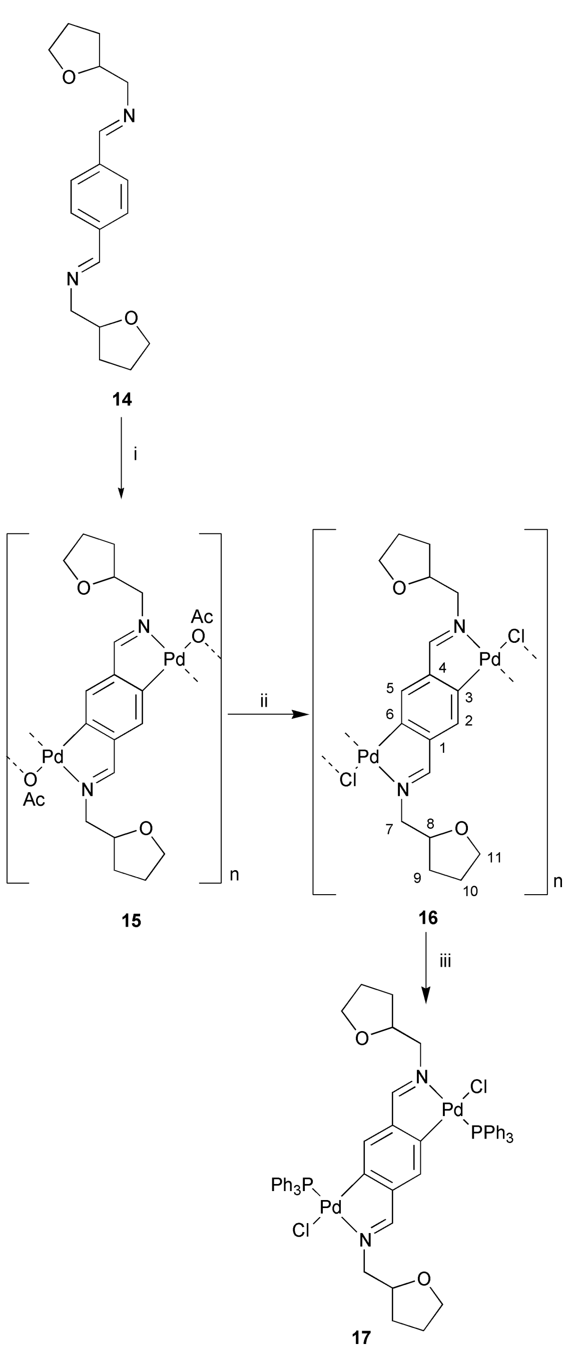


Scheme 1 *Reagents and conditions*: (i) $Pd(AcO)_2$ (toluene); (ii) NaCl (acetone–water).



Scheme 2 *Reagents and conditions*: (i) PPh_3 (acetone,1:2 molar ratio); (ii) PMe_2Ph (chloroform, 1:4 molar ratio); (iii) pyridine (acetone, 1:4 molar ratio); (iv) Tl(acac) (chloroform, 1:4 molar ratio); (v) *cis*-dppe (chloroform, 1:2 molar ratio); (vi) *cis*-dppe or dppe, $NaClO_4$ (acetone, 1:4 molar ratio); (vii) dppf (acetone, 1:2 molar ratio). The phosphine phenyl rings in **8**, **9** and **10** have been omitted for clarity.

Treatment of **3** with triphenylphosphine in a 1:4 molar ratio did not yield the expected dinuclear complex in which each metal atom is coordinated to a chlorine atom and to a phosphine ligand; only an unseparable mixture and black palladium was obtained. However, reaction of **3** with triphenylphosphine in a 1:2 molar ratio gave the tetranuclear complex **4**. It is known that cleavage of dinuclear or tetranuclear cyclometallated palladium(II) compounds by tertiary phosphines usually yields identical metal atom coordination environments in the resulting complexes, however, complex **4** constitutes an unprecedented example of a tetranuclear cyclometallated palladium(II) compound where the two metal centers show quite different coordination geometries; the remaining Pd_2Cl_2 moiety may undergo further bridge-splitting

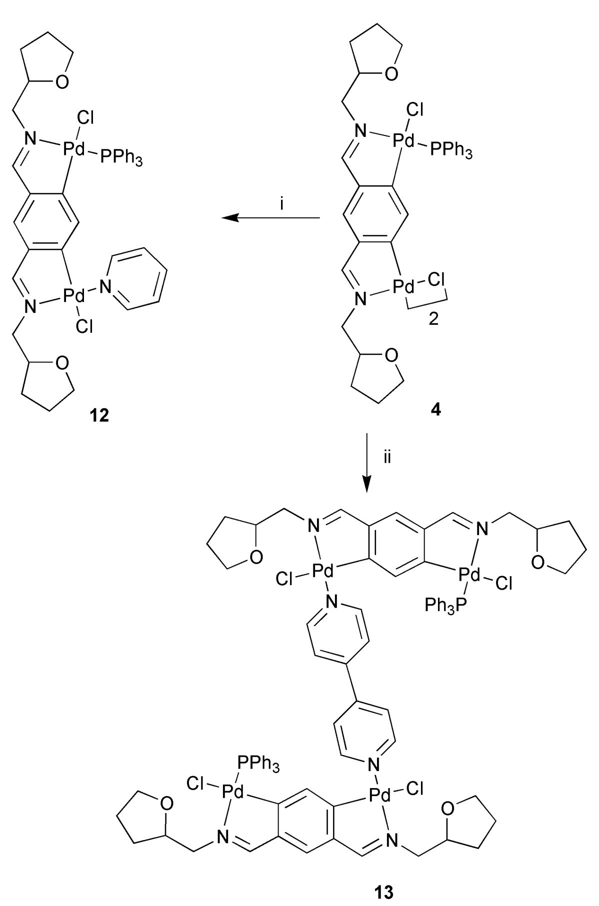


Scheme 3 *Reagents and conditions*: (i) Pd(AcO)$_2$ (toluene); (ii) NaCl (acetone/water); (iii) PPh$_3$ (acetone).

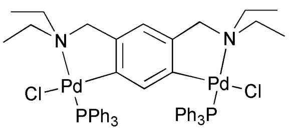
reactions, as is described below. The ^{1}H NMR spectrum of **4** showed the H′C=N proton to be coupled to the ^{31}P nucleus. The other HC=N proton resonance was occluded by the aromatic phosphine protons. The H^5 resonance appeared at δ 6.54 as a doublet showing coupling to only one phosphorus nucleus. This is in accordance with coordination of only one triphenylphosphine for each dinuclear cyclometallated moiety. The chemical shifts as well as the coupling constants are characteristic of cyclometallated complexes with a phosphorus *trans* to nitrogen arrangement.[16,35–38] This was supported by the chemical shift value of the ^{31}P nucleus in the ^{31}P-{^{1}H} NMR spectrum. The above findings were confirmed by the resolution of the molecular structure of complex **4**.

A related compound has been described and its crystal structure reported (see Fig. 1).[26]

The molecular structure of **I** showed large distortions of the square planar geometry around the palladium atoms in order to avoid contact between the bulky triphenylphosphine ligands, which was made possible owing to the flexibility of the CH$_2$N groups. However, the superior rigidity of Schiff base **1** hinders simultaneous coordination of the two bulky phosphine ligands.



Scheme 4 *Reagents and conditions*: (i) pyridine (chloroform, 1:2 molar ratio); (ii) 4,4′-dipyridyl (chloroform, 1:1 molar ratio).



I

Fig. 1 The molecular structure of compound **I**.

In order to confirm this supposition, we decided to synthesize the analogous complex **17**, in which no steric interaction between the phosphine ligands was possible.

Thus, reaction of the Schiff base ligand 1,4-[C(H)=N-CH$_2$C$_4$H$_7$O]$_2$C$_6$H$_4$ (**14**) with palladium(II) acetate in toluene gave cyclometallated compound **15**. The ^{1}H NMR spectrum showed a singlet resonance assigned to the equivalent H^2 and H^5 protons at *ca.* δ 6.50, shifted to lower frequency as compared to the free ligand **14**. Two signals at δ 2.20 and 1.90 were assigned to the acetate methyl groups. Reaction of **15** with sodium chloride afforded complex **16** after substitution of the acetate ligands by bridging chlorine ligands, and subsequent treatment of **16** with triphenylphosphine gave the dinuclear complex **17**, in which a phosphine ligand was coordinated to each palladium atom. The ^{1}H NMR spectrum showed resonances assigned to H^2, H^5 and HC=N as doublets due to coupling to the ^{31}P nucleus.

Whereas coordination of a PPh$_3$ ligand to one of the palladium atoms in **4** hinders access by a second PPh$_3$ at the other palladium, bridge-splitting reactions are nevertheless possible, provided they meet the necessary steric requirements. Thus, reaction of complex **4** with pyridine in a 1:2 molar ratio gave the dinuclear complex **12**. Two resonances in the ^{1}H NMR spectrum {δ 8.11 [d, J(PH) = 8.3], 7.83 (s)} were assigned to the HC=N protons, only one being coupled to the ^{31}P nucleus. The H^5 resonance appeared as a doublet at δ 5.87, shifted to lower frequency compared to complex **4** as a result of the coordination of pyridine. Similarly, when **4** was reacted with 4,4′-dipyridyl in a 1:1 molar ratio, the tetranuclear complex **13** was obtained. The ^{1}H NMR spectrum of the latter showed only one set of signals, indicating the symmetric nature of the complex.

In order to determine whether less bulky tertiary phosphines were able to coordinate to both palladium atoms simultaneously, complex **3** was reacted with $PMePh_2$ and PMe_2Ph in a 1:4 molar ratio. The reaction of **3** with $PMePh_2$ gave an untreatable mixture, which was not further investigated, but when **3** was reacted with PMe_2Ph under similar reaction conditions, complex **5** was obtained in good yield. The ^{1}H NMR spectrum showed a doublet resonance assigned to the two equivalent HC=N protons {δ 8.05 [J(PH) = 8.3 Hz]}. The signal assigned to the H^5 resonance appeared as a triplet at δ 6.40 [J(PH) = 5.4 Hz] coupled to both phosphorus nuclei. Other less sterically demanding ligands, such as pyridine and acetylacetone, yielded similar results. Thus, treatment of **3** with pyridine or thallium acetylacetonate gave compounds **6** and **7**, respectively, as air-stable solids, which were fully characterized. The HC=N proton resonances appeared as singlets at δ 7.86 (**6**) and 7.90 (**7**). The H^5 resonance in **6** appeared at δ 5.10, showing a shift to lower frequency due to the shielding effect of the pyridine rings. The resonances due to the CH and CH_3 protons of the acetylacetonate appeared at δ 5.93, 2.07 and 1.97, respectively.

Reaction of **3** with the diphosphine *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppen) in a 1:2 molar ratio yielded the tetranuclear complex **8**. The ^{31}P-{^{1}H} NMR spectrum of **8** showed two doublets at δ 61.0 and 43.9 [J(PP) = 24.2 Hz], showing the different chemical environment of the phosphorus atoms and the ^{1}H NMR spectrum showed two signals due to the HC=N protons, only one of which showed coupling to the ^{31}P nuclei. The molar conductivity measurements carried out in dry acetonitrile showed the compound to be a 1:2 electrolyte.

Treatment of **3** with the diphosphines *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppen) and $Ph_2P(CH_2)_2PPh_2$ (dppe) in a 1:4 molar ratio gave the dinuclear complexes **9** and **10**, respectively. The ^{31}P-{^{1}H} NMR spectra of complexes **9** and **10** proved the phosphorus atoms to be non-equivalent. Molar conductivity measurements showed the complexes to be 1:2 electrolytes.

Reaction of **3** with the diphosphine $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) in a 1:2 molar ratio yielded the trinuclear complex **11**, which was fully characterized. The two equivalent HC=N proton resonances appeared as a doublet at δ 8.10 [J(PH) = 7.8 Hz]. The signal assigned to the H^5 proton appeared at δ 8.04 [J(PH) = 5.9 Hz] coupled to both phosphorus nuclei. The ^{31}P-{^{1}H} spectrum showed a singlet at δ 32.1. An hexanuclear structure in which two dppf ligands bridge two dinuclear cyclometallated fragments is also possible for complex **11**. Nevertheless, the FAB mass spectrum showed sets of peaks centered at 1136 and 1101 amu assignable to the $[M]^+$ and $[M - Cl]^+$ fragments. Their isotopic patterns agree with a trinuclear formulation. Furthermore, we have recently synthesized a related hexanuclear cyclometallated complex with bridging dppf ligands.[39] The ^{1}H NMR spectrum of the complex showed the resonance due to the proton adjacent to the metallation position shifted to higher field, as compared to the free ligand. However the spectrum of **11** showed the resonance of H^5 shifted to higher frequency.

Crystal structure of 4

Single crystals of complex **4** suitable for X-ray analysis were grown by slowly evaporating an *n*-hexane–chloroform solution at room temperature. The molecular structure is shown in Fig. 2 and 3. Crystal data are given in the Experimental section and selected bond distances and angles with estimated standard deviations are shown in Table 1.

The structure comprises a molecule of **4** (two half molecules per asymmetric unit) and six chloroform solvent molecules. The complex can be regarded as a dimeric supramolecular structure in which two dinuclear cyclometallated moieties are linked by chlorine bridging ligands. Each monomeric dinuclear moiety contains the Schiff base ligand **1** coordinated to two palladium atoms. One palladium atom, Pd(1), is bonded to the ligand through the imine nitrogen and the C(1) carbon atom; the coordination sphere is completed by the phosphorus atom of the triphenylphosphine ligand and one terminal chlorine ligand. The other palladium atom, Pd(2), is bonded to the remaining imine nitrogen and to the C(3) carbon atom of the Schiff base and to two bridging chlorine ligands. The molecule is centrosymmetric, with the inversion centre located in the middle of the Pd–Pd axis. The sum of the angles about the palladiums is approximately 360°, with the only noteworthy deviation being the somewhat reduced CPd–N bond angles of 81.8(2), 81.8(2), 81.1(3) and 81.6(3)° for Pd(1) to (4), respectively. The geometry around the palladium atoms is planar [mean deviation from the least square planes for planes Pd(1), N(1), C(1), P(1), Cl(1); Pd(2), N(2), C(3), Cl(2), Cl(2′)

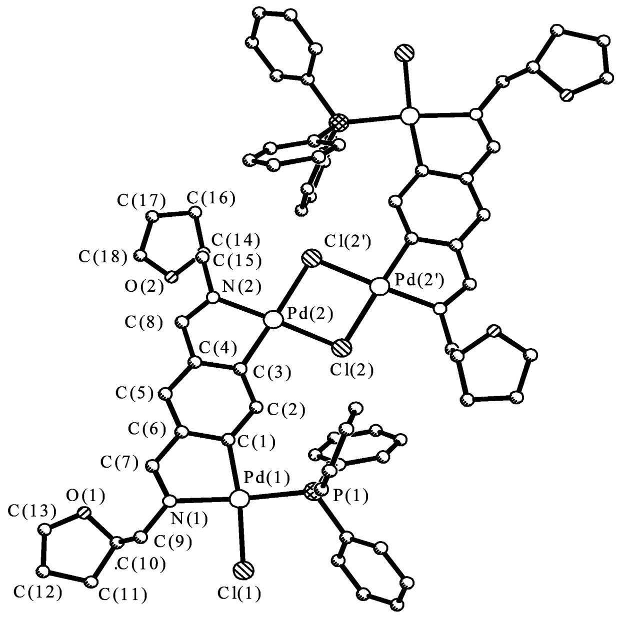


Fig. 2 Molecular structure of complex **4**, with labelling scheme. Hydrogen atoms have been omitted for clarity.

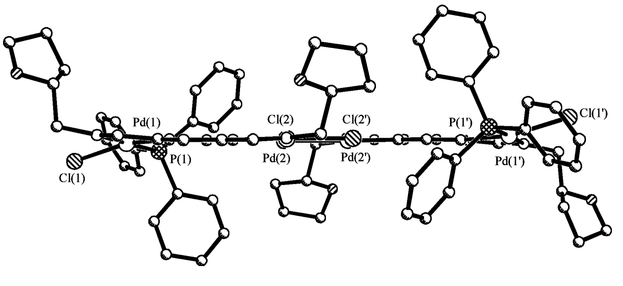


Fig. 3 Another view of the molecular structure of complex **4**, showing the planar disposition of the cyclometallated moieties.

Table 1 Selected bond lengths (Å) and angles (°) for **4**[a]

Pd(1)–C(1)	2.013(6)	Pd(3)–Cl(3)	2.383(2)
Pd(3)–C(41)	2.026(7)	Pd(2)–C(3)	1.984(6)
Pd(1)–N(1)	2.105(6)	Pd(4)–C(43)	1.980(7)
Pd(3)–N(3)	2.086(6)	Pd(2)–N(2)	2.020(6)
Pd(1)–P(1)	2.265(2)	Pd(4)–N(4)	2.021(6)
Pd(3)–P(2)	2.257(2)	Pd(2)–Cl(2)	2.322(2)
Pd(1)–Cl(1)	2.400(2)	Pd(4)–Cl(4)	2.457(2)
Pd(2)–Cl(2′)#1	2.452(2)	Pd(4)–Cl(4′)#2	2.322(2)
C(3)–Pd(2)–N(2)	81.8(2)	C(43)–Pd(4)–N(4)	81.6(3)
C(1)–Pd(1)–N(1)	81.8(2)	C(3)–Pd(2)–Cl(2)	96.0(2)
C(41)–Pd(3)–N(3)	81.1(3)	C(43)–Pd(4)–Cl(4′)#2	95.9(2)
C(1)–Pd(1)–P(1)	94.1(2)	N(2)–Pd(2)–Cl(2)	177.6(2)
C(41)–Pd(3)–P(2)	95.9(2)	N(4)–Pd(4)–Cl(4′)#2	177.2(2)
N(1)–Pd(1)–P(1)	175.6(2)	C(3)–Pd(2)–Cl(2′)#1	177.7(2)
N(3)–Pd(3)–P(2)	177.0(2)	C(43)–Pd(4)–Cl(4)	177.5(2)
C(1)–Pd(1)–Cl(1)	171.2(2)	N(2)–Pd(2)–Cl(2′)#1	96.6(2)
C(41)–Pd(3)–Cl(3)	164.7(2)	N(4)–Pd(4)–Cl(4)	96.1(2)
N(1)–Pd(1)–Cl(1)	91.2(2)	Cl(2)–Pd(2)–Cl(2′)#1	85.68(6)
N(3)–Pd(3)–Cl(3)	91.8(2)	Cl(4′)#2–Pd(4)–Cl(4)	86.39(6)
P(1)–Pd(1)–Cl(1)	92.68(7)	Pd(2)–Cl(2)–Pd(2′)#1	94.32(6)
P(2)–Pd(3)–Cl(3)	91.19(7)	Pd(4′)#2–Cl(4)–Pd(4)	93.61(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x-2,-y+3,-z$; #2 $-x,-y+1,-z+1$.

and P(4), N(4), C(43), Cl(4), Cl(4′) (symmetry equivalent atoms are labelled with ′) of 0.0387, 0.0188 and 0.0069 Å, respectively]. However, coordination about Pd(3) is slightly distorted, with Cl(3) 0.57 Å above the mean plane defined by Pd(3), C(41), N(3′) and P(2) (r.m.s. 0.0026 Å).

The long Pd(1)–N(1) [2.105(6) Å] and Pd(3)–N(3) [2.086(6) Å] bond distances {as compared to Pd(2)–N(2) [2.020(6) Å] and Pd(4)–N(4) [2.021(6) Å]} reflects the stronger *trans* influence of the phosphorus atom.[26,40–42] The Pd–C bond lengths of 2.016(6), 1.984(6), 2.026(7) and 1.987(7) Å for Pd(1) to (4), respectively, are shorter than the values predicted for their covalent radii, consistent with those found in related complexes.[40–42] The asymmetric nature of the $PdCl_2P$ moiety, demonstrated by the Pd–Cl bond distances [Pd(2)–Cl(2), 2.3216(18); Pd(2)–Cl(2′), 2.4520(17) and Pd(4)–Cl(4), 2.4575(18); Pd(4)–Cl(4′), 2.3220(17) Å], results from the differing *trans* influence of the nitrogen and carbon atoms of the Schiff base ligand. These values are consistent with those reported for similar complexes.[41–43] The Pd–P [Pd(1)–P(1), 2.253(17); Pd(3)–P(2), 2.2567(19) Å] bond lengths are within the range reported for related compounds.[43,44] The units in the crystal lattice show a nearly parallel disposition.

Experimental

General remarks

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with care.

Solvents were purified by standard methods.[45] All chemicals were reagent grade. The phosphines PPh_3, PMe_2Ph, $Ph_2P(CH_2)_2PPh_2$ (dppe), *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppen) and $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf), were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Model 1108 elemental analyser. IR spectra were recorded from Nujol mulls or polythene discs on Perkin-Elmer 1330 and Mattson spectrophotometers. NMR spectra were obtained from $CDCl_3$ or DMSO-d^6 solutions and referenced to $SiMe_4$ (^1H, $^{13}C\text{-}\{^1H\}$) or 85% H_3PO_4 ($^{31}P\text{-}\{^1H\}$) and were recorded on a Bruker AC-200F spectrometer. All chemical shifts are reported downfield from standards. The FAB mass spectra were recorded using a VG Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

The syntheses of 1,3-$[C(H){=}NCH_2C_4H_7O]_2C_6H_4$ (**1**) and 1,4-$[C(H){=}NCH_2C_4H_7O]_2C_6H_4$ (**14**) were performed by heating chloroform solutions of the appropriate quantities of tetrahydrofufurylamine and isophthalaldehyde or terephthalaldehyde, respectively, in a Dean–Stark apparatus under reflux. $^{13}C\text{-}\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): (**1**) δ 161.7 (C=N); 136.4 (C^1, C^3); 129.9 (C^4, C^6); 128.6 (C^5); 128.2 (C^2); 65.6, 68.0 (C^7, C^{11}); 78.2 (C^8); 29.1, 25.6 (C^9, C^{10}). IR: (**1**) ν(C=N), 1645s; (**14**) ν(C=N), 1643s cm^{-1}.

Syntheses

$[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}AcO)_2]_2$ (2). A pressure tube containing 1,3-$[C(H){=}NCH_2C_4H_7O]_2C_6H_4$ (**1**) (111 mg, 0.39 mmol), palladium(II) acetate (150 mg, 0.69 mmol) and 25 cm^3 of dry toluene was sealed under argon. The resulting mixture was heated at 60 °C for 1 h. After cooling to room temperature (r.t.) the red precipitate formed was filtered off and dissolved in chloroform. The red solution obtained was filtered through Celite to remove the remeining black palladium. The solvent was removed under vacuum and the yellow solid obtained recrystallized from chloroform–hexane to give the desired product. Yield 54%. Anal. found: C, 41.5; H, 4.4; N, 4.2; $C_{44}H_{56}N_4O_{12}Pd_4$ requires C, 42.0; H, 4.5; N, 4.4%. IR: ν(C=N), 1610s; ν_{as}(COO), 1580s; ν_s(COO), 1430s cm^{-1}. FAB-MS: m/z = 1119 $[M - AcO]^+$.

***(R,R,R,R)*-$[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}AcO)_2]_2$ (2a).** The enantiomerically pure complex **2a** was prepared similarly to **2** and obtained as a yellow solid. Yield 65%. Anal. found: C, 41.2; H, 4.7; N, 3.9; $C_{44}H_{56}N_4O_{12}Pd_4$ requires C, 42.0; H, 4.5; N, 4.4%. IR: ν(C=N), 1610s; ν_{as}(COO), 1580s; ν_s(COO), 1430s cm^{-1}.

$[(\mu\text{-}AcO)Pd\{1,4\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}Pd(\mu\text{-}AcO)]_n$ (15). Compound **15** was obtained following a similar procedure to that used to prepare **2** and isolated as a yellow solid. Yield 60%. Anal. found: C, 40.5; H, 4.0; N, 4.7; $C_{44}H_{56}N_4O_{12}Pd_4$ requires C, 42.0; H, 4.5; N, 4.4%. IR: ν(C=N), 1610s; ν_{as}(COO), 1560s; ν_s(COO), 1420s cm^{-1}. FAB-MS: m/z = 513 $[14 + Pd_2]^+$.

$[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Cl)_2]_2$ (3). An aqueous solution of NaCl (*ca.* 10^{-2} M) was added dropwise to a solution of **2** (100 mg, 0.79 mmol) in 15 cm^3 of acetone. The resulting mixture was stirred for 6 h. The yellow precipitate formed was filtered off, washed with water and dried under vacuum. Yield 97%. Anal. found: C, 37.7; H, 3.1; N, 4.7; $C_{36}H_{44}N_4O_4Cl_4Pd_4$ requires C, 37.1; H, 3.8, N, 4.8%. IR: ν(C=N), 1610s cm^{-1}.

$[(\mu\text{-}Cl)Pd\{1,4\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}Pd(\mu\text{-}Cl)]_n$ (16). Compound **16** was obtained following a similar procedure to that used to prepare **3** and was isolated as a yellow solid. Yield 91%. Anal. found: C, 36.5; H, 3.6; N, 4.6; $(C_{18}H_{22}N_2O_2Cl_2Pd_2)_n$ requires C, 37.1; H, 3.8, N, 4.8%. IR: ν(C=N), 1610s cm^{-1}.

$[Pd_2\{1,3\text{-}[C(H){=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Cl)(Cl)(PPh_3)]_2$ (4). PPh_3 (13.5 mg, 0.052 mmol) was added to a suspension of **3** (30 mg, 0.026 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the precipitate formed filtered off and dried under vacuum to give a yellow solid, which was recrystallized from chloroform–hexane. Yield 30%. Anal. found: C, 45.7; H, 3.9; N, 2.7; $C_{72}H_{74}N_4O_4Cl_4Pd_4P_2\cdot 2CHCl_3$ requires C, 46.1; H, 4.0; N, 2.9%. IR: ν(C=N), 1610s cm^{-1}.

Preparation of [Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}$(Cl)_2$-$(PMe_2Ph)_2$] (5). PMe_2Ph (14.1 mg, 0.102 mmol) was added to a suspension of **3** (30 mg, 0.026 mmol) in chloroform (10 cm^3). The mixture was stirred for 4 h under nitrogen, after which the solid disssolved. The solvent was removed to give a yellow solid which was recrystallized from chloroform–hexane. Yield 97%. Anal. found: C, 47.7; H, 5.1; N, 3.0; $C_{34}H_{44}N_2O_2Cl_2Pd_2P_2$ requires C, 47.6; H, 5.2; N, 3.3%. IR: ν(C=N), 1620s cm^{-1}. ^{13}C-{^1H} NMR (75.48 MHz, $CDCl_3$): δ 175.6 [d, J(CP) = 4.3 Hz, C=N]; 144.3 m (C^1, C^3); 167.5 [d, J(CP) = 2.8 Hz, C^4, C^6]; 127.0 (C^2); 77.2 (C^8); 67.9 (C^{11}); 61.5 [d, J(CP) = 12.8 Hz, C^7]; 28.9, 25.8 (C^9, C^{10}); 134.6 [dd, J(PC) = 10.6, 22.7 Hz, C_o (PPh)]; 126.8 [dd, J(PC) = 8.5, 10.6 Hz, C_m (PPh)]; 130.1 (C_p).

[(PPh_3)(Cl)Pd{1,4-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}Pd(Cl)-(PPh_3)] (17). Compound **17** was synthesized similarly to **5** and obtained as a yellow solid. Yield 77.5%. Anal. found: C, 57.9; H, 5.1; N, 2.9; $C_{54}H_{52}N_2O_2Cl_2Pd_2P_2$ requires C, 58.6; H, 4.7; N, 2.5%. IR: ν(C=N), 1620s cm^{-1}.

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}$(Cl)_2(C_6H_5N)_2$] (6). Pyridine (py) (11.0 mg, 0.137 mmol) was added to a suspension of **3** (40 mg, 0.034 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h, after which the yellow solution obtained was filtered through Celite to remove the small amount of black palladium formed. The solvent was then removed to give a pale yellow solid which was recrystallized from dichloromethane–hexane. Yield 68%. Anal. found: C, 45.7; H, 4.1; N, 7.2; $C_{28}H_{32}N_4O_2Cl_2Pd_2$ requires C, 45.4; H, 4.3; N, 7.6%. IR: ν(C=N), 1607s cm^{-1}.

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}$(acac)_2$] (7). To a suspension of **3** (15 mg, 0.013 mmol) in chloroform (25 cm^3), thallium acetylacetonate (Tlacac) (15.6 mg, 0.052 mmol), was added and the mixture stirred at room temperature for 24 h. The solution was filtered through Celite to eliminate the TlCl precipitate and the solvent removed to give the desired complex as a yellow solid, which was recrystallized from chloroform–hexane. Yield 68%. Anal. found: C, 47.7; H, 5.1; N, 3.8; $C_{28}H_{36}N_2O_6Pd_2$ requires C, 47.4; H, 5.1; N, 3.9%. IR: ν(C=N), occluded; 2,4-pentanedionate ν(C=C), 1513s; ν(C=O), 1567s, 1391s cm^{-1}.

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}(μ-Cl)(Ph_2PCH=CH-PPh_2-*P*,*P*)$]_2[Cl]_2$ (8). To a suspension of **3** (30 mg, 0.027 mmol) in chloroform (10 cm^3), *cis*-Ph_2PCH=$CHPPh_2$ (*cis*-dppe) (21.6 mg, 0.052 mmol) was added. The mixture stirred at room temperature for 24 h and the solvent removed to give the desired complex as a white solid, which was recrystallized from chloroform–hexane. Yield 91%. Anal. found: C, 51.9; H, 4.0; N, 3.0; $C_{88}H_{88}N_4O_4Cl_4P_4Pd_4 \cdot CHCl_3$ requires C, 51.5; H, 4.3; N, 2.7%. IR: ν(C=N), 1615 cm^{-1}. Specific molar conductivity, Λ_m = 180.9 cm^2 Ω^{-1} mol^{-1} (in acetonitrile).

Preparation of [Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}(Ph_2-PCH=$CHPPh_2$-*P*,*P*$)_2][ClO_4]_2$ (9). *cis*-Ph_2PCH=$CHPPh_2$ (*cis*-dppe) (13.7 mg, 0.034 mmol) was added to a suspension of **3** (10 mg, 0.008 mmol) in acetone (20 cm^3). The mixture was stirred for 1 h, after which an excess of sodium perchlorate was added. The complex was then precipitated by addition of water, filtered off and dried *in vacuo*. Recrystallization from chloroform–hexane gave the pure compound as a yellow solid. Yield 91%. Anal. found: C, 55.9; H, 4.2; N, 2.0; $C_{70}H_{66}N_2O_{10}Cl_2P_4Pd_2$ requires C, 55.9; H, 4.1; N, 1.9%. IR: ν(C=N), 1615 cm^{-1}. Specific molar conductivity, Λ_m = 231.4 cm^2 Ω^{-1} mol^{-1} (in acetonitrile).

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}($Ph_2PCH_2CH_2PPh_2$-*P*,*P*$)_2][ClO_4]_2$ (10). Compound **10** was synthesized following a similar procedure to that used for the preparation of **9** and was obtained as a white solid. Yield 93%. Anal. found: C, 52.3; H, 4.6; N, 2.0; $C_{70}H_{70}N_2O_{10}Cl_2P_4Pd_2 .CHCl_3$ requires C, 52.4; H, 4.4; N, 1.7%. IR: ν(C=N), 1620 cm^{-1}. Specific molar conductivity, Λ_m = 311.89 cm^2 Ω^{-1} mol^{-1} (in acetonitrile). FAB-MS: m/z = 1407, $[M - ClO_4]^+$; 1009, $[M - dppe - ClO_4]^+$.

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}(μ-$Ph_2PC_5H_4FeC_5H_4$-PPh_2-*P*,*P*)] (11). $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) (28.6 mg, 0.052 mmol) was added to a suspension of **3** (30 mg, 0.027 mmol) in acetone (20 cm^3). The mixture was stirred for 1 h, after which the solid dissolved. The solvent was removed to give the desired complex as a red solid which was recrystallized from chloroform–hexane. Yield 75%. Anal. found: C, 54.7; H, 4.2; N, 2.4; $C_{52}H_{50}N_2O_2Cl_2P_2Pd_2Fe$ requires C, 54.9; H, 4.4; N, 2.5%. IR: ν(C=N), 1609 cm^{-1}. FAB-MS: m/z = 1136, $[M]^+$; 1101, $[M - Cl]^+$. ^{13}C-{^1H} NMR (75.48 MHz, $CDCl_3$): δ 175.2 [dd, J(CP) = 7.1, 4.3 Hz, C=N]; 142.9 (C^1, C^3); 167.5 [t, J(CP) = 2.5 Hz, C^4, C^6]; 150.0 [t, J(CP) = 12.1 Hz, C^5]; 126.0 (C^2); 68.1 (C^{11}); 61.8 (C^7); 28.7, 26.0 (C^9, C^{10}); 134.6 [dd, J(PC) = 10.6, 22.7 Hz, C_o (PPh_2)]; 126.8 [dd, J(PC) = 8.5, 10.6 Hz, C_m (PPh_2)]; 130.1 [C_p (PPh_2)]; 75.2 [d, J(PC) = 45.4 Hz, C_i (PCp)]; 72.2 [dd, J(PC) = 8.5 Hz, C_m (PCp)].

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}$(Cl)_2(PPh_3)$(Py)] (12). Pyridine (py) (3.1 mg, 0.039 mmol) was added to a suspension of **4** (33 mg, 0.020 mmol) in chloroform (20 cm^3). The mixture was stirred for 12 h, after which the solid went into solution. The solvent was removed to give the desired complex as a white solid which was recrystallized from chloroform–hexane. Yield 71%. Anal. found: C, 53.4; H, 4.5; N, 4.5; $C_{41}H_{42}N_3O_2Cl_2PPd_2$ requires C, 53.3; H, 4.6; N, 4.5%. IR: ν(C=N), 1610s cm^{-1}.

[Pd_2{1,3-[C(H)=$NCH_2C_4H_7O]_2C_6H_2$}$(Cl)_2(PPh_3)]_2$(dipy) (13). 4,4′-Dipyridyl (2.4 mg, 0.015 mmol) was added to a suspension of **4** (26 mg, 0.015 mmol) in chloroform (15 cm^3). The mixture was stirred for 12 h, after which the solution obtained was filtered through Celite to remove the small amount of black palladium formed. The solvent was then removed to give a white solid which was recrystallized from chloroform–hexane. Yield 68%. Anal. found: C, 51.0; H, 4.1; N, 4.3; $C_{82}H_{82}N_6O_4Cl_4P_2Pd_4 \cdot CHCl_3$ requires C, 50.7; H, 4.2; N, 4.3%. IR: ν(C=N), 1610m cm^{-1}.

Single-crystal X-ray diffraction analysis

Crystal data for $C_{72}H_{74}Cl_4N_4O_4P_2Pd_4 \cdot 6CHCl_3$; M = 2404.90; crystallizes from chloroform as yellow blocks; crystal dimensions 0.55 × 0.45 × 0.30 mm, triclinic, a = 13.264(1), b = 16.464(1) c = 23.788(1) Å, α = 84.508(1), β = 80.9080(1), γ = 67.808(1)°, U = 4746.0(2) $Å^3$, Z = 2, D_c = 1.683 g cm^{-3}, space group P$\bar{1}$ (no. 2), Mo-Kα radiation λ = 0.71073 Å, μ(Mo-Kα) = 1.447 mm^{-1}, F(000) = 2392, T = 100 K.

Three-dimensional, room temperature X-ray data were collected in the range $0.8 < 2\theta < 56.5°$ 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 32809 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption using a semi-empirical correction based on symmetry-equivalent and repeated reflections (max, min transmissions 0.67, 0.50), 15144 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 = 0.0722 (wR_2 = 0.2158 for all 22629 unique data, 1093 parameters), with allowance for the thermal anisotropy of all non-hydrogen atoms. The C(10) and C(11) carbon atoms of one THF ring were found to be disordered over two positions [C(10), C(10a) and C(11), C(11a)]. The occupancies of the two pairs of positions were tied to give an overall value of 1.0 and then refined, giving values of approximately 0.5 for each component. Other atoms of the THF rings showed less than ideal thermal parameters. Disorder was also found in the Cl(8), Cl(9), Cl(10), C(5s) and Cl(19) atoms of two chloroform solvent molecules. The refinement was carried out taking into account the minor components of the disorder. Minimum and maximum final electron density −1.323 and 1.511e Å^{-3}. The structure solution and refinement were carried out using the program package SHELX-97.[46]

CCDC reference number 183215. See http://www.rsc.org/suppdata/nj/b1/b111671a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Ministerio de Educación y Cultura (Proyecto PB98-0638-C02-01/02), the Xunta de Galicia (Proyecto PGIDT99PXI20907B) and the Universidad de La Coruña for financial support.

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