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

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The reaction of the Schiff base ligands 1,3-[C=N(H)CH₂C₄H₇O]₂C₆H₄ (1) and 1,4-[C=N(H)CH₂C₄H₇O]₂C₆H₄ (14) with palladium(II) acetate in toluene gave the acetato-bridged cyclometallated compounds [Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ -AcO)₂]₂ (2) and [(μ -AcO)Pd{1,4-[C(H)=NCH₂C₄H₇O]₂C₆H₂}Pd(μ -AcO)]_n (15). Reaction of 2 and 15 with aqueous sodium chloride gave the chloro-bridged cyclometallated compounds [Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}Pd(μ -Cl)]₂ (3) and [(μ -Cl)Pd{1,4-[C(H)=NCH₂C₄H₇O]₂C₆H₂}Pd(μ -Cl)]_n (16), respectively, after a metathesis reaction. Reaction of 3 with triphenylphosphine in a 1:2 molar ratio gave the tetranuclear complex [Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ -Cl)(Cl)(PPh₃)]₂ (4), where only one of the bridging PdCl₂Pd moieties was cleaved, and which was characterized by X-ray crystal structure analysis. However, reaction of 16 with PPh₃ gave the dinuclear complex [(PPh₃)(Cl)Pd{1,4-

 $[C(H)=NCH_2C_4H_7O]_2C_6H_2$ Pd(PPh₃)(Cl)] (17) after a full bridge-splitting reaction. Similarly, treatment of **3** with PMe₂Ph, 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*-Ph₂PCH=CHPPh₂ in a 1:2 molar ratio yielded the tetranuclear complex [Pd₂{1,3-

 $[C(H)=NCH_2C_4H_7O]_2C_6H_2\}(\mu-Cl)(Ph_2PCH=CHPPh_2-P,P)][Cl]_2$ (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-

 $[C(H)=NCH_2C_4H_7O]_2C_6H_2\}(\mu-Ph_2PC_5H_4FeC_5H_4PPh_2)]$ (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 compounds⁸ 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- $[C=N(H)CH_2C_4H_7O]_2C_6H_4$ (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.

[†] Electronic supplementary information (ESI) available: ¹H and ³¹P NMR data for compounds 1–15 and 17. See http://www.rsc.org/ suppdata/nj/b1/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 ¹H, ³¹P-{¹H} and, in part, ¹³C-{¹H} 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 ¹H 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 v(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 H² and H⁵ 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 H² and H⁵ 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 ¹H NMR spectrum. Two singlets at δ 6.69 and 6.63 were ascribed to the H² and H⁵ protons, respectively. Furthermore, neither ligand 1 nor the remaining compounds, where the open-book structure is absent, showed the ¹H NMR patterns observed for compound 2.

The reaction of **2** with aqueous sodium chloride yielded the tetranuclear chloro-bridged complex **3**. The ¹H NMR spectrum showed only one set of signals for the H², H⁵ and HC=N proton resonances. The H² and H⁵ resonances appeared at δ 8.02 and 7.16 shifted downfield as compared to complex **2**.

Pḋ∼ÓAc

P,ḋ∼ċ

6

10

3

2

3

2

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

2



Scheme 2 *Reagents and conditions*: (i) PPh₃ (acetone,1:2 molar ratio); (ii) PMe₂Ph (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, NaClO₄ (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) PPh3 (acetone).

reactions, as is described below. The ¹H 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 H⁵ 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



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



Fig. 1 The molecular structure of compound I.

ligands, which was made possible owing to the flexibility of the CH₂N groups. However, the superior rigidity of Schiff base 1 hinders simultaneous coordination of the two bulky phosphine ligands.

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- $CH_2C_4H_7O]_2C_6H_4$ (14) with palladium(II) acetate in toluene gave cyclometallated compound 15. The ¹H NMR spectrum showed a singlet resonance assigned to the equivalent H² and H⁵ 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 ¹H NMR spectrum showed resonances assigned to H², H⁵ and HC=N as doublets due to coupling to the ³¹P nucleus.

Whereas coordination of a PPh₃ ligand to one of the palladium atoms in 4 hinders access by a second PPh₃ 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 ¹H 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 ³¹P nucleus. The H⁵ 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 ¹H 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 PMePh₂ and PMe₂Ph in a 1:4 molar ratio. The reaction of 3 with PMePh₂ gave an untreatable mixture, which was not further investigated, but when 3 was reacted with PMe₂Ph under similar reaction conditions, complex 5 was obtained in good yield. The ¹H 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 H⁵ 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 H⁵ 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 CH₃ protons of the acetylacetonate appeared at δ 5.93, 2.07 and 1.97, respectively.

Reaction of **3** with the diphosphine cis-Ph₂PCH=CHPPh₂ (cis-dppen) in a 1:2 molar ratio yielded the tetranuclear complex **8**. The ³¹P-{¹H} 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 ¹H NMR spectrum showed two signals due to the HC=N protons, only one of which showed coupling to the ³¹P 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-Ph₂PCH=CHPPh₂ (cis-dppen) and Ph₂P(CH₂)₂PPh₂ (dppe) in a 1:4 molar ratio gave the dinuclear complexes **9** and **10**, respectively. The ³¹P-{¹H} 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 Ph₂PC₅H₄FeC₅H₄PPh₂ (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 H⁵ proton appeared at δ 8.04 [*J*(PH) = 5.9 Hz] coupled to both phosphorus nuclei. The ³¹P-{¹H} 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 ¹H 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 H⁵ 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 transfo	rmations use	ed 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 PdCl₂P 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 PPh₃, PMe₂Ph, Ph₂P(CH₂)₂PPh₂ (dppe), *cis*-Ph₂PCH=CHPPh₂ (*cis*-dppen) and Ph₂PC₅H₄FeC₅H₄PPh₂ (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 CDCl₃ or DMSO-d⁶ solutions and referenced to SiMe₄ (¹H, ¹³C-{¹H}) or 85% H₃PO₄ (³¹P-{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)=NCH₂C₄H₇O]₂C₆H₄ (1) and 1,4-[C(H)=NCH₂C₄H₇O]₂C₆H₄ (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. ¹³C-{¹H} NMR (75.48 MHz, CDCl₃): (1) δ 161.7 (C=N); 136.4 (C¹, C³); 129.9 (C⁴, C⁶); 128.6 (C⁵); 128.2 (C²); 65.6, 68.0 (C⁷, C¹¹); 78.2 (C⁸); 29.1, 25.6 (C⁹, C¹⁰). IR: (1) ν (C=N), 1645s; (14) ν (C=N), 1643s cm⁻¹.

Syntheses

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ-AcO)₂]₂ (2). A pressure tube containing 1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₄ (1) (111 mg, 0.39 mmol), palladium(II) acetate (150 mg, 0.69 mmol) and 25 cm³ 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; C₄₄H₅₆N₄O₁₂Pd₄ requires C, 42.0; H, 4.5; N, 44%. 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*)-[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ -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; C₄₄H₅₆N₄O₁₂Pd₄ 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.

$[(\mu-AcO)Pd{1,4-[C(H)=NCH_2C_4H_7O]_2C_6H_2}Pd(\mu-AcO)]_n$

(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; C₄₄H₅₆N₄O₁₂Pd₄ requires C, 42.0; H, 4.5; N, 4.4%. IR: v(C=N), 1610s; $v_{as}(COO)$, 1560s; $v_{s}(COO)$, 1420s cm⁻¹. FAB-MS: $m/z = 513 [14 + Pd_2]^+$.

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ-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 cm³ 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; C₃₆H₄₄N₄O₄Cl₄Pd₄ requires C, 37.1; H, 3.8, N, 4.8%. IR: ν (C=N), 1610s cm⁻¹.

 $[(\mu-Cl)Pd\{1,4-[C(H)=NCH_2C_4H_7O]_2C_6H_2\}Pd(\mu-Cl)]_n$ (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.

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ -Cl)(Cl)(PPh₃)]₂ (4). PPh₃ (13.5 mg, 0.052 mmol) was added to a suspension of **3** (30 mg, 0.026 mmol) in acetone (15 cm³). 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; C₇₂H₇₄N₄O₄Cl₄Pd₄P₂·2CHCl₃ requires C, 46.1; H, 4.0; N, 2.9%. IR: ν (C=N), 1610s cm⁻¹. **Preparation of [Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(Cl)₂-(PMe₂Ph)₂] (5). PMe₂Ph (14.1 mg, 0.102 mmol) was added to a suspension of 3** (30 mg, 0.026 mmol) in chloroform (10 cm³). The mixture was stirred for 4 h under nitrogen, after which the solid dissolved. 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; C₃₄H₄₄N₂O₂Cl₂Pd₂P₂ requires C, 47.6; H, 5.2; N, 3.3%. IR: ν (C=N), 1620s cm⁻¹. ¹³C-{¹H} NMR (75.48 MHz, CDCl₃): δ 175.6 [d, *J*(CP) = 4.3 Hz, C=N]; 144.3 m (C¹, C³); 167.5 [d, *J*(CP) = 2.8 Hz, C⁴, C⁶]; 127.0 (C²); 77.2 (C⁸); 67.9 (C¹¹); 61.5 [d, *J*(CP) = 12.8 Hz, C⁷]; 28.9, 25.8 (C⁹, C¹⁰); 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).

[(PPh₃)(Cl)Pd{1,4-[C(H)=NCH₂C₄H₇O]₂C₆H₂}Pd(Cl)-

(**PPh₃**)] (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 cm³). 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; C₂₈H₃₂N₄O₂Cl₂Pd₂ requires C, 45.4; H, 4.3; N, 7.6%. IR: ν (C=N), 1607s cm⁻¹.

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(acac)₂] (7). To a suspension of 3 (15 mg, 0.013 mmol) in chloroform (25 cm³), 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; C₂₈H₃₆N₂O₆Pd₂ requires C, 47.4; H, 5.1; N, 3.9%. IR: v(C=N), occluded; 2,4-pentanedionate v(C=C), 1513s; v(C=O), 1567s, 1391s cm⁻¹.

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ-Cl)(Ph₂PCH=CH-PPh₂-*P*,*P*)]₂[Cl]₂ (8). To a suspension of 3 (30 mg, 0.027 mmol) in chloroform (10 cm³), *cis*-Ph₂PCH=CHPPh₂ (*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; C₈₈H₈₈N₄O₄Cl₄P₄Pd₄·CHCl₃ requires C, 51.5; H, 4.3; N, 2.7%. IR: v(C=N), 1615 cm⁻¹. Specific molar conductivity, $A_{\rm m} = 180.9$ cm² Ω⁻¹ mol⁻¹ (in acetonitrile).

Preparation of [Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(Ph₂-PCH=CHPPh₂-*P*,*P*)₂][ClO₄]₂ (9). *cis*-Ph₂PCH=CHPPh₂ (*cis*-dppe) (13.7 mg, 0.034 mmol) was added to a suspension of **3** (10 mg, 0.008 mmol) in acetone (20 cm³). 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; C₇₀H₆₆N₂O₁₀Cl₂P₄Pd₂ requires C, 55.9; H, 4.1; N, 1.9%. IR: ν (C=N), 1615 cm⁻¹. Specific molar conductivity, $A_m = 231.4$ cm² Ω⁻¹ mol⁻¹ (in acetonitrile).

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(Ph₂PCH₂CH₂PPh₂-P,P)₂][ClO₄]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, $\Lambda_m = 311.89$ cm² Ω^{-1} mol⁻¹ (in acetonitrile). FAB-MS: m/z = 1407, $[M - ClO_4]^+$; 1009, $[M - dppe - ClO_4]^+$.

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(μ-Ph₂PC₅H₄FeC₅H₄-PPh₂-*P*,*P*)] (11). Ph₂PC₅H₄FeC₅H₄PPh₂ (dppf) (28.6 mg, 0.052 mmol) was added to a suspension of **3** (30 mg, 0.027 mmol) in acetone (20 cm³). 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; C₅₂H₅₀N₂O₂Cl₂P₂Pd₂Fe 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]⁺. ¹³C-{¹H} NMR (75.48 MHz, CDCl₃): δ 175.2 [dd, *J*(CP) = 7.1, 4.3 Hz, C=N]; 142.9 (C¹, C³); 167.5 [t, *J*(CP) = 2.5 Hz, C⁴, C⁶]; 150.0 [t, *J*(CP) = 12.1 Hz, C⁵]; 126.0 (C²); 68.1 (C¹¹); 61.8 (C⁷); 28.7, 26.0 (C⁹, C¹⁰); 134.6 [dd, *J*(PC) = 10.6, 22.7 Hz, C_o (PPh₂)]; 126.8 [dd, *J*(PC) = 8.5, 10.6 Hz, C_m (PPh₂)]; 130.1 [C_p (PPh₂)]; 75.2 [d, *J*(PC) = 45.4 Hz, C_i (PCp)]; 72.2 [dd, *J*(PC) = 8.5 Hz, C_m (PCp)].

[Pd₂{1,3-[C(H)=NCH₂C₄H₇O]₂C₆H₂}(Cl)₂(PPh₃)(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 cm³). 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; C₄₁H₄₂N₃O₂Cl₂PPd₂ requires C, 53.3; H, 4.6; N, 4.5%. IR: ν (C=N), 1610s cm⁻¹.

$[Pd_{2}\{1,3-[C(H)=NCH_{2}C_{4}H_{7}O]_{2}C_{6}H_{2}\}(Cl)_{2}(PPh_{3})]_{2}(dipy)$

(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 cm³). 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; $C_{82}H_{82}N_6O_4Cl_4P_2Pd_4$ ·CHCl₃ 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 C₇₂H₇₄Cl₄N₄O₄P₂Pd₄·6CHCl₃; 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, $\alpha = 84.508(1)$, $\beta = 80.9080(1)$, $\gamma = 67.808(1)^{\circ}$, U = 4746.0(2) Å³, Z = 2, $D_c = 1.683$ g cm⁻³, space group PI (no. 2), Mo-K α radiation $\lambda = 0.71073$ Å, μ (Mo-K α) = 1.447 mm⁻¹, F(000) = 2392, T = 100 K.

Three-dimensional, room temperature X-ray data were collected in the range $0.8 < 2\theta < 56.5^{\circ}$ 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 $1.511e \text{ Å}^{-3}$. 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.

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