



# The chemistry of *N*-benzylidene-1,4-phenylenediamine palladacycles: The crystal and molecular structure of the first tetranuclear palladacycle with bridging $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligands

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## ABSTRACT

The reaction of the tetranuclear halide-bridged complexes **1–2(a–d)** with  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) or  $\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$  (vdpp) in 1:2 molar ratio and  $\text{NH}_4\text{PF}_6$  afforded the novel tetranuclear palladacycles **3–6 (a, c, d)** as 1:2 electrolytes with bridging diphosphine and halogen ligands. The structure of **4a** has been determined by X-ray diffraction analysis, and represents the first example of a tetranuclear palladacycle with bridging dppm and halogen ligands. Reaction of **1–2(a–d)** with  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$  (triphos) in 1:2 molar ratio gave **7(a–d)** bearing two pentacoordinated palladium atoms. The structure of **7a**, as determined by X-ray diffraction analysis, shows the distorted square pyramidal geometry around the metal centers. Treatment of **1–2(a–d)** with dppm, vdpp or  $\text{Ph}_2\text{PN}(\text{Me})\text{PPh}_2$  (dppma) in 1:4 molar ratio gave the dinuclear palladacycles **8–10(a–d)** with a chelating diphosphine ligand at each metal center; further treatment of **9(a–c)** with the nucleophiles pyrrolidine, piperidine, morpholine or 4-methylpiperidine gave the Michael addition derivatives **11–12(a–c)**, **13b**, **13c** and **14c**, promoted by the withdrawing effect of the palladacycle which activates the  $\text{C}=\text{CH}_2$  double bond.

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## 1. Introduction

The cyclometallation reaction has been profusely investigated in view of the rich chemistry it renders and is well documented for a great variety of metal centers and ligands [1]. The ensuing compounds are successfully used in organic synthesis [2], catalysis [3], photochemistry [4] and optical resolution process [5], and are rather promising as potential biologically active materials [6] and liquid crystals [7].

Multidentate ligands are particularly interesting due to their ability to induce new structural features or properties in the ensuing compounds; these ligands may be classified according to the number and type of atoms that are bonded to the metal, e.g., [C–E, C–E], [E–C–E], and [C–E–E], where E denotes a donor atom and C the metallated carbon atom. In the past we and others have dealt with cyclometallated compounds derived from multidentate ligands of the tridentate [C, N, X] (X = N [8], O [9], S [10]) and tetradentate [C–N, C–N] [11] types; phenolate Schiff base (X = O) and thiosemicarbazone (X = S) palladacycles display tetranuclear structures, with an eight-membered  $\text{Pd}_4\text{X}_4$  core, with two pairs of parallel metallated units set mutually at ca. 90°. In the latter case, reaction with small

bite angle diphosphines yields the new cyclometallated bidentate *P,S* metaloligands [10f,12]. We have shown that tetradentate bis(*N*-benzylidene)-1,4-phenylenediamines give tetranuclear halide-bridged compounds [11a] as opposed to related complexes of polymeric nature [13]. Reaction of the latter with tertiary diphosphines gave either tetranuclear complexes, with 26 or 28-membered rings, or dinuclear species, with bridging [11c] and chelating phosphines [11d], respectively. However, analogous compounds with bridging short-bite diphosphines, such as  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) or  $\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$  (vdpp), bearing a six-membered homodimetallic ring bridging the two organic ligands, were still outstanding, owing in part to the strong tendency towards chelation of the diphosphines, and these are the first reported examples. Furthermore, we also relate several aspects concerning the reactivity of the aforementioned tetranuclear complexes, e.g., to give species that may undergo Michael addition, as well as reactions with the tridentate phosphine ligand  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$ , triphos.

## 2. Experimental

### 2.1. General comments

Solvents were purified by standard methods [14]. Chemicals were used as supplied from commercial sources. Elemental analy-

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ses were carried out by the Unidade de Análise Elemental da Universidade de Santiago de Compostela using a Carlo-Erba elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on Perkin–Elmer 1330, Mattson Model Cygnus-100 and Bruker Model IFS-66V spectrophotometers. NMR spectra were obtained as CDCl<sub>3</sub> or (CD<sub>3</sub>)<sub>2</sub>O solutions and referenced to SiMe<sub>4</sub>, and were recorded on a Bruker AMX 300 spectrometer. All chemical shifts are reported downfield from standards. The FAB mass spectra were recorded with a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix. Conductivity measurements were made on a WTW model LF3 conductivimeter using 10<sup>-4</sup> M solutions in dry acetonitrile at room temperature (298 K).

## 2.2. Preparation of the tetranuclear complexes

The synthesis of the tetranuclear complexes, **1a–d**, **2a–d**, has been reported previously in papers from this laboratory [11a,c,d]. Their spectroscopic data are given for comparative purposes with the new compounds reported herein.

### 2.2.1. Compound 1a

IR (cm<sup>-1</sup>): ν(C=N): 1605m, ν(Pd–Cl): 320m, 280m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 3.79 (s, 3H, MeO); 3.95 (s, 3H, MeO); 3.96 (s, 3H, MeO); 6.70 (s, 1H, H5); 7.21 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.03 (s, 1H, HC=N).

### 2.2.2. Compound 2a

IR (cm<sup>-1</sup>): ν(C=N): 1601m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 3.79 (s, 3H, MeO); 3.95 (s, 3H, MeO); 3.96 (s, 3H, MeO); 6.86 (s, 1H, H5); 7.20 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.06 (s, 1H, HC=N).

### 2.2.3. Compound 1b

IR (cm<sup>-1</sup>): ν(C=N): 1611m, ν(Pd–Cl): 340m, 285m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 6.09 (s, 2H, OCH<sub>2</sub>O); 6.94 (d, 1H, H3, <sup>3</sup>J(H2H3) = 8.0); 7.42 (d, 1H, H2); 7.25 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 7.34 (s, 1H, HC=N).

### 2.2.4. Compound 2b

IR (cm<sup>-1</sup>): ν(C=N): 1610m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 6.08 (s, 2H, OCH<sub>2</sub>O); 6.94 (s, 1H, H3, <sup>3</sup>J(H2H3) = 7.9); 7.42 (s, 1H, H2); 7.25 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 7.35 (s, 1H, HC=N).

### 2.2.5. Compound 1c

IR (cm<sup>-1</sup>): ν(C=N): 1596m, ν(Pd–Cl): 333m, 274m. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, δ ppm, J Hz): 3.78 (s, 3H, MeO); 3.80 (s, 3H, MeO); 6.29 (d, 1H, H3, <sup>3</sup>J(H3H5) = 2.0); 7.17 (d, 1H, H5, <sup>3</sup>J(H3H5) = 2.0); 7.30 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.22 (s, 1H, HC=N).

### 2.2.6. Compound 2c

IR (cm<sup>-1</sup>): ν(C=N): 1597m. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, δ ppm, J Hz): 3.78 (s, 3H, MeO); 3.80 (s, 3H, MeO); 6.27 (d, 1H, H3, <sup>3</sup>J(H3H5) = 2.0); 6.96 (d, 1H, H5, <sup>3</sup>J(H3H5) = 2.0); 7.29 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.20 (s, 1H, HC=N).

### 2.2.7. Compound 1d

IR (cm<sup>-1</sup>): ν(C=N): 1599m, ν(Pd–Cl): 331m, 255m. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, δ ppm, J Hz): 2.06 (s, 3H, Me); 3.78 (s, 3H, MeO); 7.33 (b, 4H, H2, H5, C<sub>6</sub>H<sub>4</sub>); 8.26 (s, 1H, HC=N).

### 2.2.8. Compound 2d

IR (cm<sup>-1</sup>): ν(C=N): 1600m. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, δ ppm, J Hz): 2.07 (s, 3H, Me); 3.80 (s, 3H, MeO); 7.32 (b, 4H, H2, H5, C<sub>6</sub>H<sub>4</sub>); 8.24 (s, 1H, HC=N).

## 2.3. Preparation of 3a

To a suspension of **1a** (50.0 mg, 0.034 mmol) in acetone (ca. 15 cm<sup>3</sup>), Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (25.8 mg, 0.067 mmol) was added. The mixture was stirred for 6 h at room temperature and then NH<sub>4</sub>PF<sub>6</sub> (10.9 mg, 0.067 mmol) was added. The mixture was stirred for a further 6 h at room temperature, after which the solvent was removed under reduced pressure and the solid residue was chromatographed on a column packed with silica gel. Elution with a mixture of CH<sub>2</sub>Cl<sub>2</sub>:EtOH (97:3, v/v) afforded the final product, which after concentration, was recrystallized from chloroform/*n*-hexane to give a yellow solid.

Yield 56.5 mg 67%. Anal. Calc. for C<sub>102</sub>H<sub>96</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>O<sub>12</sub>P<sub>6</sub>Pd<sub>4</sub> (2480.28): C, 49.4, H, 3.9, N, 2.3. Found: C, 49.1, H, 3.8, N, 2.2%. IR (cm<sup>-1</sup>): ν(C=N): 1601m, ν(Pd–Cl): 244m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 2.82 (s, 3H, MeO); 3.69 (s, 3H, MeO); 3.98 (s, 3H, MeO); 4.1 (d, 2H, PCH<sub>2</sub>P); 5.51 (d, 1H, H5, <sup>4</sup>J(H5P) = 7.7); 7.47 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.45 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.8). <sup>31</sup>P–{<sup>1</sup>H} NMR: δ = 30.59s. Specific molar conductivity  $\Lambda_M = 226 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2190 [M–2PF<sub>6</sub>]<sup>+</sup>.

Compounds **3–6(a–d)** were prepared similarly from **1–2(a–d)** and dppm or vdpp, as appropriate.

### 2.3.1. Compound 4a

Yield 54.1 mg 71%. Anal. Calc. for C<sub>102</sub>H<sub>96</sub>N<sub>4</sub>Br<sub>2</sub>F<sub>12</sub>O<sub>12</sub>P<sub>6</sub>Pd<sub>4</sub> (2569.18): C, 47.7, H, 3.8, N, 2.2. Found: C, 47.7, H, 3.6, N, 2.0%. IR (cm<sup>-1</sup>): ν(C=N): 1603m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 2.82 (s, 3H, MeO); 3.70 (s, 3H, MeO); 3.98 (s, 3H, MeO); 4.2 (d, 2H, PCH<sub>2</sub>P); 5.51 (d, 1H, H5, <sup>4</sup>J(H5P) = 7.5); 7.47 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.46 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.9). <sup>31</sup>P–{<sup>1</sup>H} NMR: δ = 30.67s. Specific molar conductivity  $\Lambda_M = 242 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2279 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.2. Compound 5a

Yield 46.0 mg 54%. Anal. Calc. for C<sub>104</sub>H<sub>96</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>O<sub>12</sub>P<sub>6</sub>Pd<sub>4</sub> (2504.30): C, 49.9, H, 3.9, N, 2.2. Found: C, 49.4, H, 3.6, N, 2.1%. IR (cm<sup>-1</sup>): ν(C=N): 1602m, ν(Pd–Cl): 262m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 2.77 (s, 3H, MeO); 3.69 (s, 3H, MeO); 4.00 (s, 3H, MeO); 6.03 (m, 2H, PC(=CH<sub>2</sub>)P); 5.41 (d, 1H, H5, <sup>4</sup>J(H5P) = 7.7); 7.55 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.55 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.7). <sup>31</sup>P–{<sup>1</sup>H} NMR: δ = 44.93s. Specific molar conductivity  $\Lambda_M = 217 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2214 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.3. Compound 6a

Yield 61.5 mg 79%. Anal. Calc. for C<sub>104</sub>H<sub>96</sub>N<sub>4</sub>Br<sub>2</sub>F<sub>12</sub>O<sub>12</sub>P<sub>6</sub>Pd<sub>4</sub> (2593.21): C, 48.2, H, 3.7, N, 2.2. Found: C, 48.3, H, 3.6, N, 2.2%. IR (cm<sup>-1</sup>): ν(C=N): 1604m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, J Hz): 2.78 (s, 3H, MeO); 3.70 (s, 3H, MeO); 4.00 (s, 3H, MeO); 5.97 (m, 2H, PC(=CH<sub>2</sub>)P); 5.40 (d, 1H, H5, <sup>4</sup>J(H5P) = 7.1); 7.56 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.56 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.3). <sup>31</sup>P–{<sup>1</sup>H} NMR: δ = 41.80s. Specific molar conductivity  $\Lambda_M = 234 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2303 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.4. Compound 3c

Yield 58.5 mg 67%. Anal. Calc. for C<sub>98</sub>H<sub>88</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>O<sub>8</sub>P<sub>6</sub>Pd<sub>4</sub> (2360.18): C, 49.9, H, 3.8, N, 2.4. Found: C, 49.5, H, 3.9, N, 2.0%. IR (cm<sup>-1</sup>): ν(C=N): 1601m, ν(Pd–Cl): 242m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, J Hz): 3.08 (s, 3H, MeO); 3.82 (s, 3H, MeO); 4.1 (d, 2H, PCH<sub>2</sub>P); 5.48 (dd, 1H, H5, <sup>4</sup>J(H5P) = 9.7, <sup>4</sup>J(H3H5) = 1.9); 6.17 (d, 1H, H3, <sup>4</sup>J(H3H5) = 1.9); 7.65 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.51 (d, 1H, HC=N, <sup>4</sup>J(HP) = 7.1). <sup>31</sup>P–{<sup>1</sup>H} NMR: δ = 30.72 s. Specific molar conductivity  $\Lambda_M = 209 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2360 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.5. Compound 4c

Yield 65.1 mg 83%. Anal. Calc. for C<sub>98</sub>H<sub>88</sub>N<sub>4</sub>Br<sub>2</sub>F<sub>12</sub>O<sub>8</sub>P<sub>6</sub>Pd<sub>4</sub> (2449.08): C, 48.1, H, 3.6, N, 2.3. Found: C, 48.6, H, 3.6, N, 2.4%. IR (cm<sup>-1</sup>): ν(C=N): 1600m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, J Hz): 3.08

(s, 3H, MeO); 3.82 (s, 3H, MeO); 3.99 (d, 2H, PCH<sub>2</sub>P); 5.47 (dd, 1H, H5, <sup>4</sup>J(H5P) = 9.6, <sup>4</sup>J(H3H5) = 1.8); 6.17 (d, 1H, H3, <sup>4</sup>J(H3H5) = 1.8); 7.66 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.50 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.9). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 30.55s. Specific molar conductivity  $\Lambda_M = 229 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2159 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.6. Compound 5c

Yield 52.1 mg 59%. Anal. Calc. for C<sub>100</sub>H<sub>88</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>O<sub>8</sub>P<sub>6</sub>Pd<sub>4</sub> (2384.20): C, 50.4, H, 3.7, N, 2.4. Found: C, 50.8, H, 3.6, N, 2.0%. IR (cm<sup>-1</sup>): ν(C=N): 1600m, ν(Pd–Cl): 240m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, *J* Hz): 2.91 (s, 3H, MeO); 3.78 (s, 3H, MeO); 5.27 (dd, 1H, H5, <sup>4</sup>J(H5P) = 10.0, <sup>4</sup>J(H3H5) = 1.7); 5.99 (m, 2H, PC(=CH<sub>2</sub>)P); 6.00 (d, 1H, H3, <sup>4</sup>J(H3H5) = 1.7); 8.60 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.9). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 44.96s. Specific molar conductivity  $\Lambda_M = 210 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2094 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.7. Compound 6c

Yield 49.1 mg 62%. Anal. Calc. for C<sub>100</sub>H<sub>88</sub>N<sub>4</sub>Br<sub>2</sub>F<sub>12</sub>O<sub>8</sub>P<sub>6</sub>Pd<sub>4</sub> (2473.10): C, 48.6, H, 3.6, N, 2.3. Found: C, 48.3, H, 3.6, N, 2.2%. IR (cm<sup>-1</sup>): ν(C=N): 1600m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, *J* Hz): 2.90 (s, 3H, MeO); 3.80 (s, 3H, MeO); 5.26 (dd, 1H, H5, <sup>4</sup>J(H5P) = 9.9, <sup>4</sup>J(H3H5) = 1.7); 6.00 (d, 1H, H3, <sup>4</sup>J(H3H5) = 1.7); 6.04 (m, 2H, PC(=CH<sub>2</sub>)P); 8.43 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.7). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 44.95s. Specific molar conductivity  $\Lambda_M = 223 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2183 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.8. Compound 3d

Yield 68.8 mg 79%. Anal. Calc. for C<sub>98</sub>H<sub>88</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>O<sub>4</sub>P<sub>6</sub>Pd<sub>4</sub> (2292.06): C, 51.2, H, 3.9, N, 2.4. Found: C, 51.3, H, 3.7, N, 2.6%. IR (cm<sup>-1</sup>): ν(C=N): 1601m, ν(Pd–Cl): 268m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 1.95 (s, 3H, Me); 2.86 (s, 3H, MeO); 4.12 (d, 2H, PCH<sub>2</sub>P); 5.84 (d, 1H, H5, <sup>4</sup>J(H5P) = 7.4); 7.32 (s, 1H, H2); 7.71 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.47 (d, 1H, HC=N, <sup>4</sup>J(HP) = 7.0). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 31.61s. Specific molar conductivity  $\Lambda_M = 224 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2002 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.9. Compound 4d

Yield 68.9 mg 85%. Anal. Calc. for C<sub>98</sub>H<sub>88</sub>N<sub>4</sub>Br<sub>2</sub>F<sub>12</sub>O<sub>4</sub>P<sub>6</sub>Pd<sub>4</sub> (2385.08): C, 49.4, H, 3.7, N, 2.4. Found: C, 49.3, H, 3.6, N, 2.1%. IR (cm<sup>-1</sup>): ν(C=N): 1599m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 1.96 (s, 3H, Me); 2.86 (s, 3H, MeO); 4.38 (d, 2H, PCH<sub>2</sub>P); 5.83 (d, 1H, H5, <sup>4</sup>J(H5P) = 7.4); 7.34 (s, 1H, H2); 7.68 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.48 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.6). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 31.39s. Specific molar conductivity  $\Lambda_M = 236 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2095 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.10. Compound 5d

Yield 45.0 mg 51%. Anal. Calc. for C<sub>100</sub>H<sub>88</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>O<sub>4</sub>P<sub>6</sub>Pd<sub>4</sub> (2320.20): C, 51.8, H, 3.8, N, 2.4. Found: C, 51.4, H, 3.9, N, 2.4%. IR (cm<sup>-1</sup>): ν(C=N): 1602m, ν(Pd–Cl): 249m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, *J* Hz): 1.98 (s, 3H, Me); 2.75 (s, 3H, MeO); 5.59 (d, 1H, H5, <sup>4</sup>J(H5P) = 6.7); 5.87 (m, 2H, PC(=CH<sub>2</sub>)P); 7.33 (s, 1H, H2); 7.52 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.28 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.0). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 45.67s. Specific molar conductivity  $\Lambda_M = 220 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2030 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.3.11. Compound 6d

Yield 62.9 mg 77%. Anal. Calc. for C<sub>100</sub>H<sub>88</sub>N<sub>4</sub>Br<sub>2</sub>F<sub>12</sub>O<sub>4</sub>P<sub>6</sub>Pd<sub>4</sub> (2403.10): C, 49.9, H, 3.7, N, 2.1. Found: C, 50.0, H, 3.5, N, 2.1%. IR (cm<sup>-1</sup>): ν(C=N): 1603m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, *J* Hz): 1.96 (s, 3H, Me); 2.74 (s, 3H, MeO); 5.57 (d, 1H, H5, <sup>4</sup>J(H5P) = 6.6); 5.92 (m, 2H, PC(=CH<sub>2</sub>)P); 7.34 (s, 1H, H2); 7.55 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.31 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.7). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ = 46.00s. Specific molar conductivity  $\Lambda_M = 218 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 2113 [M–2PF<sub>6</sub>]<sup>+</sup>.

## 2.4. Preparation of 7a

To a suspension of **1a** (50.1 mg, 0.030 mmol) in acetone (ca. 15 cm<sup>3</sup>), NH<sub>4</sub>PF<sub>6</sub> (19.6 mg, 0.120 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (64.2 mg, 0.120 mmol) was added. The mixture was stirred for 12 h at room temperature, after which the solvent was removed under reduced pressure and the solid residue was chromatographed on a column packed with silica gel. Elution with a mixture of DCM:EtOH (97:3) afforded the final product as a yellow solid after concentration.

Yield 108.5 mg 89%. Anal. Calc. for C<sub>94</sub>H<sub>92</sub>N<sub>2</sub>F<sub>12</sub>O<sub>6</sub>P<sub>8</sub>Pd<sub>2</sub> (2032.27): C, 55.5, H, 4.6, N, 1.4. Found: C, 55.5, H, 4.7, N, 1.4%. IR (cm<sup>-1</sup>): ν(C=N): 1593m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 3.23 (m, 2H, PCH<sub>2</sub>); 3.39 (m, 2H, CH<sub>2</sub>P); 3.69 (s, 3H, MeO); 3.86 (s, 3H, MeO); 4.03 (s, 3H, MeO); 5.48 (d, 1H, H5, <sup>4</sup>J(H5P) = 8.6); 5.94 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 6.89 (ddd, 2H, o-H in PPh, <sup>3</sup>J(HP) = 9.4, <sup>3</sup>J(HH) = 8.1, <sup>4</sup>J(HH) = 1.9); 8.35 (s, 1H, HC=N). <sup>31</sup>P-{<sup>1</sup>H} NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 92.71 (t, 1P); 43.30 (d, 2P, *J*(PP) = 52.4). Specific molar conductivity  $\Lambda_M = 290 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 1742 [M–2PF<sub>6</sub>]<sup>+</sup>.

Compounds **7(b–d)** were prepared analogously.

### 2.4.1. Compound 7b

Yield 97.4 mg 76%. Anal. Calc. for C<sub>90</sub>H<sub>80</sub>N<sub>2</sub>F<sub>12</sub>O<sub>4</sub>P<sub>8</sub>Pd<sub>2</sub> (1942.22): C, 55.7, H, 4.2, N, 1.4. Found: C, 55.9, H, 4.0, N, 1.2%. IR (cm<sup>-1</sup>): ν(C=N): 1606m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 3.22 (m, 2H, PCH<sub>2</sub>); 3.34 (m, 2H, CH<sub>2</sub>P); 4.85 (s, 2H, OCH<sub>2</sub>O); 6.54 (d, 1H, H3, <sup>4</sup>J(H2H3) = 6.1); 6.35 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 6.98 (ddd, 2H, o-H in PPh, <sup>3</sup>J(HP) = 9.7, <sup>3</sup>J(HH) = 8.0, <sup>4</sup>J(HH) = 2.0); 8.26 (s, 1H, HC=N). <sup>31</sup>P-{<sup>1</sup>H} NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 89.11 (t, 1P); 42.00 (d, 2P, *J*(PP) = 47.1). Specific molar conductivity  $\Lambda_M = 299 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 1652 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.4.2. Compound 7c

Yield 115.0 mg 91%. Anal. Calc. for C<sub>92</sub>H<sub>88</sub>N<sub>2</sub>F<sub>12</sub>O<sub>4</sub>P<sub>8</sub>Pd<sub>2</sub> (1974.31): C, 56.0, H, 4.5, N, 1.4. Found: C, 55.9, H, 4.5, N, 1.6%. IR (cm<sup>-1</sup>): ν(C=N): 1574s. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 2.89 (s, 3H, MeO); 3.21 (m, 2H, PCH<sub>2</sub>); 3.37 (m, 2H, CH<sub>2</sub>P); 3.93 (s, 3H, MeO); 5.29 (dd, 1H, H5, <sup>4</sup>J(H5P) = 8.6, <sup>4</sup>J(H3H5) = 1.9); 5.86 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 6.07 (d, 2H, H3, <sup>4</sup>J(H3H5) = 1.9); 6.88 (ddd, 2H, Ha, <sup>3</sup>J(HP) = 9.6, <sup>3</sup>J(HH) = 8.1, <sup>4</sup>J(HH) = 1.9); 8.40 (s, 1H, HC=N). <sup>31</sup>P-{<sup>1</sup>H} NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 92.42 (t, 1P); 42.4 (d, 2P, *J*(PP) = 30.0).  $\Lambda_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 1684 [M–2PF<sub>6</sub>]<sup>+</sup>.

### 2.4.3. Compound 7d

Yield 96.3 mg 80%. Anal. Calc. for C<sub>92</sub>H<sub>88</sub>N<sub>2</sub>F<sub>12</sub>O<sub>2</sub>P<sub>8</sub>Pd<sub>2</sub> (1942.31): C, 56.9, H, 4.6, N, 1.4. Found: C, 57.0, H, 4.6, N, 1.4%. IR (cm<sup>-1</sup>): ν(C=N): 1591m. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 2.05 (s, 3H, Me); 2.84 (s, 3H, MeO); 3.22 (m, 2H, PCH<sub>2</sub>); 3.37 (m, 2H, CH<sub>2</sub>P); 6.00 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 6.64 (d, 1H, H5, <sup>4</sup>J(H5P) = 10.4); 6.90 (ddd, 2H, Ha, <sup>3</sup>J(HP) = 9.4, <sup>3</sup>J(HH) = 8.1, <sup>4</sup>J(HH) = 2.4); 8.10 (s, 1H, HC=N). <sup>31</sup>P-{<sup>1</sup>H} NMR (d<sub>6</sub>-acetone, δ ppm, *J* Hz): 89.10 (t, 1P); 42.56 (d, 2P, *J*(PP) = 45.2). Specific molar conductivity  $\Lambda_M = 333 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS: *m/z* 1652 [M–2PF<sub>6</sub>]<sup>+</sup>.

Compounds **8–10(a–d)** were prepared similarly to **7a** from **1a–d**, **2a–d**, and dppm, vdpp, or dppma, as appropriate.

### 2.4.4. Compound 8a

Yield 78.7 mg 84%. Anal. Calc. for C<sub>76</sub>H<sub>70</sub>N<sub>2</sub>F<sub>12</sub>O<sub>6</sub>P<sub>6</sub>Pd<sub>2</sub> (1734.04): C, 52.6, H, 4.1, N, 1.6. Found: C, 52.0, H, 4.3, N, 1.7%. IR (cm<sup>-1</sup>): ν(C=N): 1606m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, *J* Hz): 3.17 (s, 3H, MeO); 3.71 (s, 3H, MeO); 4.05 (s, 3H, MeO); 4.63 (dd, 2H, PCH<sub>2</sub>P, <sup>2</sup>J(HP) = 11.8, <sup>2</sup>J(HP) = 8.4); 6.00 (dd, 1H, H5, <sup>4</sup>J(H5P) = 10.6, <sup>4</sup>J(H5P) = 7.8); 6.63 (s, 2H, C<sub>6</sub>H<sub>4</sub>); 8.27 (d, 1H, HC=N, <sup>4</sup>J(HP) = 6.8). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ ppm, *J* Hz): –27.62 (d,

$J(\text{PP}) = 67.4$ );  $-4.51$  (d,  $J(\text{PP}) = 67.4$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 179 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1444  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.5. Compound 8b

Yield 76.3 mg 75%. Anal. Calc. for  $\text{C}_{72}\text{H}_{58}\text{N}_2\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1641.91): C, 52.7, H, 3.6, N, 1.7. Found: C, 52.5, H, 3.7, N, 1.6%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1606m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 4.51 (dd, 2H,  $\text{PCH}_2\text{P}$ ,  $^2J(\text{HP}) = 11.4$ ,  $^2J(\text{HP}) = 8.7$ ); 5.22 (s, 1H,  $\text{OCHO}$ ); 5.28 (s, 1H,  $\text{OCHO}$ ); 6.72 (d, 1H, H3,  $^3J(\text{H}_2\text{H}_3) = 7.0$ ); 6.95 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.27 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.0$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz):  $-37.51$  (d,  $J(\text{PP}) = 72.8$ );  $-13.63$  (d,  $J(\text{PP}) = 72.8$ ). Specific molar conductivity  $\Lambda_M = 259 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1352  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.6. Compound 8c

Yield 60.5 mg 67%. Anal. Calc. for  $\text{C}_{74}\text{H}_{66}\text{N}_2\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1672.13): C, 53.1, H, 4.0, N, 1.7. Found: C, 53.0, H, 3.9, N, 1.5%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1605w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 3.37 (s, 3H, MeO); 3.94 (s, 3H, MeO); 4.59 (dd, 2H,  $\text{PCH}_2\text{P}$ ,  $^2J(\text{HP}) = 11.7$ ,  $^2J(\text{HP}) = 8.4$ ); 5.87 (ddd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 9.8$ ,  $^4J(\text{H}_5\text{P}) = 7.6$ ,  $^4J(\text{H}_3\text{H}_5) = 1.5$ ); 6.32 (d, 1H, H3,  $^4J(\text{H}_3\text{H}_5) = 1.5$ ); 6.90 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.38 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 6.9$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz):  $-27.87$  (d,  $J(\text{PP}) = 64.2$ );  $-4.49$  (d,  $J(\text{PP}) = 64.2$ ).  $A_M = 182 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1382  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.7. Compound 8d

Yield 76.1 mg 80%. Anal. Calc. for  $\text{C}_{74}\text{H}_{66}\text{N}_2\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1640.14): C, 54.1, H, 4.1, N, 1.7. Found: C, 54.0, H, 4.0, N, 1.9%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1600m.  $^1\text{H}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 2.02 (s, 3H, Me); 3.20 (s, 3H, MeO); 4.62 (dd, 2H,  $\text{PCH}_2\text{P}$ ,  $^2J(\text{HP}) = 11.7$ ,  $^2J(\text{HP}) = 8.4$ ); 6.34 (dd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 11.3$ ,  $^4J(\text{H}_5\text{P}) = 7.1$ ); 6.94 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.26 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 6.4$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-28.77$  (d,  $J(\text{PP}) = 56.4$ );  $-10.41$  (d,  $J(\text{PP}) = 56.4$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 181 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1350  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.8. Compound 9a

Yield 53.2 mg 56%. Anal. Calc. for  $\text{C}_{78}\text{H}_{70}\text{N}_2\text{F}_{12}\text{O}_6\text{P}_6\text{Pd}_2$  (1758.06): C, 53.3, H, 4.0, N, 1.6. Found: C, 53.0, H, 3.9, N, 1.8%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1601m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 3.09 (s, 3H, MeO); 3.74 (s, 3H, MeO); 3.97 (s, 3H, MeO); 5.81 (dd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 10.1$ ,  $^4J(\text{H}_5\text{P}) = 8.1$ ); 6.60 (m, 2H,  $\text{PC}(\text{=CH}_2)\text{P}$ ); 6.86 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.32 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.7$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz):  $-12.66$  (d,  $J(\text{PP}) = 17.5$ );  $8.47$  (d,  $J(\text{PP}) = 17.5$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 198 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1468  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.9. Compound 9b

Yield 69.2 mg 67%. Anal. Calc. for  $\text{C}_{74}\text{H}_{58}\text{N}_2\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1665.93): C, 53.4, H, 3.5, N, 1.7. Found: C, 53.4, H, 3.3, N, 1.6%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1607m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 5.26 (s, 1H,  $\text{OCHO}$ ); 5.28 (s, 1H,  $\text{OCHO}$ ); 5.73 (d, 1H, H3,  $^3J(\text{H}_3\text{H}_5) = 7.0$ ); 6.85 (m, 2H,  $\text{PC}(\text{=CH}_2)\text{P}$ ); 6.81 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.22 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.1$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz):  $-17.33$  (t,  $J(\text{PP}) = 65.7$ );  $2.78$  (d,  $J(\text{PP}) = 16.7$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 235 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1376  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.10. Compound 9c

Yield 75.2 mg 82%. Anal. Calc. for  $\text{C}_{76}\text{H}_{66}\text{N}_2\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1698.01): C, 53.8, H, 3.9, N, 1.7. Found: C, 54.0, H, 3.5, N, 1.4%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1598w.  $^1\text{H}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 3.41 (s, 3H, MeO); 3.95 (s, 3H, MeO); 5.87 (ddd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 9.5$ ,  $^4J(\text{H}_5\text{P}) = 7.5$ ,  $^4J(\text{H}_3\text{H}_5) = 2.0$ ); 6.34 (d, 1H, H3,  $^4J(\text{H}_3\text{H}_5) = 2.0$ );

6.49 (m, 2H,  $\text{PC}(\text{=CH}_2)\text{P}$ ); 6.88 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.23 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.1$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-5.06$  (d,  $J(\text{PP}) = 14.0$ );  $11.03$  (d,  $J(\text{PP}) = 14.0$ ). Specific molar conductivity  $\Lambda_M = 204 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1408  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.11. Compound 9d

Yield 81.2 mg 84%. Anal. Calc. for  $\text{C}_{76}\text{H}_{66}\text{N}_2\text{F}_{12}\text{O}_2\text{P}_6\text{Pd}_2$  (1666.01): C, 54.8, H, 4.0, N, 1.7. Found: C, 55.2, H, 4.1, N, 1.7%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1606w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 2.04 (s, 3H, Me); 3.19 (s, 3H, MeO); 6.32 (dd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 9.9$ ,  $^4J(\text{H}_5\text{P}) = 7.4$ ); 6.56 (m, 2H,  $\text{PC}(\text{=CH}_2)\text{P}$ ); 6.88 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.24 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 6.9$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz):  $-3.03$  (d,  $J(\text{PP}) = 15.1$ );  $13.81$  (d,  $J(\text{PP}) = 15.1$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 199 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1376  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.12. Compound 10a

Yield 94.2 mg 89%. Anal. Calc. for  $\text{C}_{76}\text{H}_{72}\text{N}_4\text{F}_{12}\text{O}_6\text{P}_6\text{Pd}_2$  (1764.07): C, 51.7, H, 4.1, N, 3.2. Found: C, 51.5, H, 4.0, N, 3.3%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1586m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 2.67 (dd, 3H,  $\text{PN}(\text{Me})\text{P}$ ,  $^3J(\text{HP}) = 10.3$ ,  $^3J(\text{HP}) = 9.1$ ); 3.49 (s, 3H, MeO); 3.71 (s, 3H, MeO); 4.00 (s, 3H, MeO); 6.28 (dd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 10.9$ ,  $^4J(\text{H}_5\text{P}) = 7.0$ ); 7.06 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.31 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.1$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 48.8 (d,  $J(\text{PP}) = 58.7$ ); 58.1 (d,  $J(\text{PP}) = 58.7$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 287 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1474  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.13. Compound 10b

Yield 82.3 mg 82%. Anal. Calc. for  $\text{C}_{72}\text{H}_{60}\text{N}_4\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1671.93): C, 51.7, H, 3.6, N, 3.4. Found: C, 51.9, H, 3.6, N, 3.5%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1605m.  $^1\text{H}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 2.77 (dd, 3H,  $\text{PN}(\text{Me})\text{P}$ ,  $^3J(\text{HP}) = 9.6$ ,  $^3J(\text{HP}) = 6.2$ ); 5.56 (s, 2H,  $\text{OCH}_2\text{O}$ ); 6.71 (d, 1H, H3,  $^4J(\text{H}_2\text{H}_3) = 7.8$ ); 7.05 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.32 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.2$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 44.8 (d,  $J(\text{PP}) = 54.0$ ); 54.6 (d,  $J(\text{PP}) = 54.0$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 262 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1382  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.14. Compound 10c

Yield 89.9 mg 91%. Anal. Calc. for  $\text{C}_{74}\text{H}_{68}\text{N}_4\text{F}_{12}\text{O}_4\text{P}_6\text{Pd}_2$  (1704.02): C, 52.2, H, 4.0, N, 3.3. Found: C, 51.9, H, 4.2, N, 3.4%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1599w.  $^1\text{H}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 2.64 (dd, 3H,  $\text{PN}(\text{Me})\text{P}$ ,  $^3J(\text{HP}) = 10.2$ ,  $^3J(\text{HP}) = 8.1$ ); 3.60 (s, 3H, MeO); 3.92 (s, 3H, MeO); 6.28 (ddd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 10.6$ ,  $^4J(\text{H}_5\text{P}) = 8.2$ ,  $^4J(\text{H}_3\text{H}_5) = 2.0$ ); 6.33 (d, 1H, H3,  $^4J(\text{H}_3\text{H}_5) = 2.0$ ); 7.01 (s, 2H,  $\text{C}_6\text{H}_4$ ); 8.30 (dd, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.1$ ,  $^4J(\text{HP}) = 1.2$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 49.0 (d,  $J(\text{PP}) = 58.7$ ); 58.2 (d,  $J(\text{PP}) = 58.7$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 247 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1414  $[\text{M}-2\text{PF}_6]^+$ .

#### 2.4.15. Compound 10d

Yield 90.0 mg 88%. Anal. Calc. for  $\text{C}_{74}\text{H}_{68}\text{N}_4\text{F}_{12}\text{O}_2\text{P}_6\text{Pd}_2$  (1672.02): C, 53.2, H, 4.1, N, 3.2. Found: C, 52.9, H, 4.1, N, 3.2%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ : 1587m.  $^1\text{H}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 2.03 (s, 3H, Me); 2.68 (dd, 3H,  $\text{PN}(\text{Me})\text{P}$ ,  $^3J(\text{HP}) = 10.1$ ,  $^3J(\text{HP}) = 9.1$ ); 3.46 (s, 3H, MeO); 6.47 (dd, 1H, H5,  $^4J(\text{H}_5\text{P}) = 10.8$ ,  $^4J(\text{H}_5\text{P}) = 8.2$ ); 8.30 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J(\text{HP}) = 7.1$ ).  $^{31}\text{P}-\{^1\text{H}\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 49.5 (d,  $J(\text{PP}) = 58.9$ ); 59.1 (d,  $J(\text{PP}) = 58.9$ ).  $A_M = 278 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Specific molar conductivity  $\Lambda_M = 283 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . FAB-MS:  $m/z$  1382  $[\text{M}-2\text{PF}_6]^+$ .

### 2.5. Preparation of 11a

To a suspension of **9a** (40.0 mg, 0.023 mmol) in oxygen-free benzene (ca. 15  $\text{cm}^3$ ), pyrrolidine (3.88 mg, 0.054 mmol) was added. The mixture was stirred for 24 h under argon at room tem-

perature, after which the solvent was removed under reduced pressure and the solid residue was chromatographed on a column packed with silica gel. Elution with a mixture of DCM:EtOH (98:2) afforded the final product as a yellow solid after concentration.

Yield 26.7 mg 61%. Anal. Calc. for  $C_{86}H_{88}N_4F_{12}O_6P_6Pd_2$  (1900.31): C, 54.4, H, 4.7, N, 3.0. Found: C, 54.2, H, 4.5, N, 2.8%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1599m.  $^1H$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 3.10 (s, 3H, MeO); 3.67 (s, 3H, MeO); 3.95 (s, 3H, MeO); 4.84 (m, 1H, PCHP); 5.91 (dd, 1H, H5,  $^4J(H5P) = 10.4$ ,  $^4J(H5P) = 8.1$ ); 6.30 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 8.4$ ); 6.92 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 8.4$ ); 8.36 (dd, 1H,  $HC=N$ ,  $^4J(HP) = 7.4$ ,  $^4J(HP) = 1.0$ ).  $^{31}P\{-^1H\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-7.37$  (d,  $J(PP) = 57.3$ );  $7.45$  (d,  $J(PP) = 57.3$ ). Specific molar conductivity  $\Lambda_M = 235 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1610  $[M-2PF_6]^+$ .

Compounds **11b**, **11c**, **12a–c**, **13b**, **13c**, and **14c** were prepared similarly from **8–10(a–d)**, and pyrrolidine, piperidine, morpholine or 4-Me-piperidine, as appropriate.

### 2.5.1. Compound 11b

Yield 17.5 mg 51%. Anal. Calc. for  $C_{82}H_{76}N_4F_{12}O_4P_6Pd_2$  (1928.33): C, 54.5, H, 4.2, N, 3.1. Found: C, 54.7, H, 4.0, N, 3.0%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1607m.  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  ppm,  $J$  Hz): 4.81 (m, 1H, PCHP); 4.86 (s, 1H, OCHO); 5.13 (s, 1H, OCHO); 6.60 (d, 1H, H3,  $^4J(H2H3) = 7.4$ ); 6.21 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 7.8$ ); 6.76 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 7.8$ ); 8.03 (d, 1H,  $HC=N$ ,  $^4J(HP) = 6.8$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ,  $\delta$  ppm,  $J$  Hz):  $-14.6$  (d,  $J(PP) = 58.2$ ); 6.21 (d,  $J(PP) = 58.2$ ). Specific molar conductivity  $\Lambda_M = 251 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1638  $[M-2PF_6]^+$ .

### 2.5.2. Compound 11c

Yield 16.7 mg 77%. Anal. Calc. for  $C_{84}H_{84}N_4F_{12}O_4P_6Pd_2$  (1840.28): C, 54.8, H, 4.6, N, 3.0. Found: C, 54.7, H, 4.8, N, 3.1%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1604m,sh.  $^1H$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 3.35 (s, 3H, MeO); 3.94 (s, 3H, MeO); 5.03 (m, 1H, PCHP); 5.80 (ddd, 1H, H5,  $^4J(H5P) = 10.7$ ,  $^4J(H5P) = 7.4$ ,  $^4J(H3H5) = 1.7$ ); 6.28 (d, 1H, H3,  $^4J(H3H5) = 1.7$ ); 6.35 (s, 1H,  $C_6H_4$ ); 6.78 (s, 1H,  $C_6H_4$ ); 8.24 (d, 1H,  $HC=N$ ,  $^4J(HP) = 7.7$ ).  $^{31}P\{-^1H\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-13.4$  (d,  $J(PP) = 55.4$ ); 7.19 (d,  $J(PP) = 55.4$ ). Specific molar conductivity  $\Lambda_M = 247 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1550  $[M-2PF_6]^+$ .

### 2.5.3. Compound 12a

Yield 17.4 mg 67%. Anal. Calc. for  $C_{88}H_{92}N_4F_{12}O_6P_6Pd_2$  (1928.33): C, 54.8, H, 4.8, N, 2.9. Found: C, 54.5, H, 4.6, N, 3.0%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1601m.  $^1H$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 3.11 (s, 3H, MeO); 3.68 (s, 3H, MeO); 3.95 (s, 3H, MeO); 4.89 (m, 1H, PCHP); 5.91 (dd, 1H, H5,  $^4J(H5P) = 12.1$ ,  $^4J(H5P) = 8.9$ ); 6.30 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 9.5$ ); 6.92 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 9.5$ ); 8.36 (dd, 1H,  $HC=N$ ,  $^4J(HP) = 7.7$ ,  $^4J(HP) = 0.4$ ).  $^{31}P\{-^1H\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 2.01 (d,  $J(PP) = 46.9$ ); 17.64 (d,  $J(PP) = 46.9$ ). Specific molar conductivity  $\Lambda_M = 259 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1638  $[M-2PF_6]^+$ .

### 2.5.4. Compound 12b

Yield 19.5 mg 56%. Anal. Calc. for  $C_{84}H_{80}N_4F_{12}O_4P_6Pd_2$  (1836.22): C, 54.9, H, 4.4, N, 3.1. Found: C, 55.1, H, 4.1, N, 2.8%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1603m.  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  ppm,  $J$  Hz): 4.69 (m, 1H, PCHP); 4.87 (s, 1H, OCHO); 5.13 (s, 1H, OCHO); 6.58 (d, 1H, H3,  $^4J(H2H3) = 8.4$ ); 6.22 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 8.7$ ); 6.76 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 8.7$ ); 8.03 (d, 1H,  $HC=N$ ,  $^4J(HP) = 6.7$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ,  $\delta$  ppm,  $J$  Hz):  $-16.8$  (d,  $J(PP) = 67.5$ ); 3.22 (d,  $J(PP) = 67.5$ ). Specific molar conductivity  $\Lambda_M = 223 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1546  $[M-2PF_6]^+$ .

### 2.5.5. Compound 12c

Yield 22.7 mg 81%. Anal. Calc. for  $C_{86}H_{88}N_4F_{12}O_4P_6Pd_2$  (1868.31): C, 55.3, H, 4.8, N, 3.0. Found: C, 55.0, H, 4.6, N, 2.8%. IR

( $cm^{-1}$ ):  $\nu(C=N)$ : 1607m.  $^1H$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 3.35 (s, 3H, MeO); 3.96 (s, 3H, MeO); 5.04 (m, 1H, PCHP); 5.79 (ddd, 1H, H5,  $^4J(H5P) = 8.7$ ,  $^4J(H5P) = 7.7$ ,  $^4J(H3H5) = 2.0$ ); 6.30 (d, 1H, H3,  $^4J(H3H5) = 2.0$ ); 6.77 (s, 1H,  $C_6H_4$ ); 6.78 (s, 1H,  $C_6H_4$ ); 8.24 (dd, 1H,  $HC=N$ ,  $^4J(HP) = 7.0$ ,  $^4J(HP) = 1.0$ ).  $^{31}P\{-^1H\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-19.83$  (d,  $J(PP) = 60.5$ ); 6.00 (d,  $J(PP) = 60.5$ ). Specific molar conductivity  $\Lambda_M = 261 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1578  $[M-2PF_6]^+$ .

### 2.5.6. Compound 13b

Yield 21.3 mg 61%. Anal. Calc. for  $C_{82}H_{76}N_4F_{12}O_6P_6Pd_2$  (1840.17): C, 53.5, H, 4.2, N, 3.1. Found: C, 53.3, H, 4.2, N, 3.3%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1600m.  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  ppm,  $J$  Hz): 4.65 (m, 1H, PCHP); 4.86 (s, 1H, OCHO); 5.15 (s, 1H, OCHO); 6.59 (d, 1H, H3,  $^4J(H2H3) = 6.4$ ); 6.23 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 8.4$ ); 6.77 (d, 1H,  $C_6H_4$ ,  $^3J(HH) = 8.4$ ); 8.03 (d, 1H,  $HC=N$ ,  $^4J(HP) = 6.4$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ,  $\delta$  ppm,  $J$  Hz):  $-6.4$  (d,  $J(PP) = 62.2$ ); 13.26 (d,  $J(PP) = 62.2$ ). Specific molar conductivity  $\Lambda_M = 248 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1550  $[M-2PF_6]^+$ .

### 2.5.7. Compound 13c

Yield 26.1 mg 58%. Anal. Calc. for  $C_{84}H_{84}N_4F_{12}O_6P_6Pd_2$  (1872.25): C, 53.9, H, 4.5, N, 3.0. Found: C, 53.5, H, 4.3, N, 2.9%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1599m.  $^1H$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 3.34 (s, 3H, MeO); 3.95 (s, 3H, MeO); 4.97 (m, 1H, PCHP); 5.79 (ddd, 1H, H5,  $^4J(H5P) = 10.7$ ,  $^4J(H5P) = 7.4$ ,  $^4J(H3H5) = 2.0$ ); 6.29 (d, 1H, H3,  $^4J(H3H5) = 2.0$ ); 6.77 (s, 1H,  $C_6H_4$ ); 6.78 (s, 1H,  $C_6H_4$ ); 8.24 (dd, 1H,  $HC=N$ ,  $^4J(HP) = 6.9$ ,  $^4J(HP) = 1.2$ ).  $^{31}P\{-^1H\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-15.8$  (d,  $J(PP) = 56.4$ ); 8.33 (d,  $J(PP) = 56.4$ ). Specific molar conductivity  $\Lambda_M = 245 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1582  $[M-2PF_6]^+$ .

### 2.5.8. Compound 14c

Yield 35.0 mg 88%. Anal. Calc. for  $C_{88}H_{91}N_4F_{12}O_4P_6Pd_2$  (1896.34): C, 55.7, H, 4.9, N, 3.0. Found: C, 55.4, H, 4.7, N, 2.7%. IR ( $cm^{-1}$ ):  $\nu(C=N)$ : 1606m.  $^1H$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz): 2.54 (s, 3H, NMe); 3.34 (s, 3H, MeO); 3.94 (s, 3H, MeO); 4.95 (m, 1H, PCHP); 5.79 (ddd, 1H, H5,  $^4J(H5P) = 9.8$ ,  $^4J(H5P) = 8.1$ ,  $^4J(H3H5) = 1.3$ ); 6.29 (d, 1H, H3,  $^4J(H3H5) = 1.3$ ); 6.79 (s, 1H,  $C_6H_4$ ); 6.80 (s, 1H,  $C_6H_4$ ); 8.13 (dd, 1H,  $HC=N$ ,  $^4J(HP) = 6.7$ ,  $^4J(HP) = 1.1$ ).  $^{31}P\{-^1H\}$  NMR ( $d_6$ -acetone,  $\delta$  ppm,  $J$  Hz):  $-13.68$  (d,  $J(PP) = 47.7$ ); 7.03 (d,  $J(PP) = 47.7$ ). Specific molar conductivity  $\Lambda_M = 221 \Omega^{-1} cm^2 mol^{-1}$ . FAB-MS:  $m/z$  1606  $[M-2PF_6]^+$ .

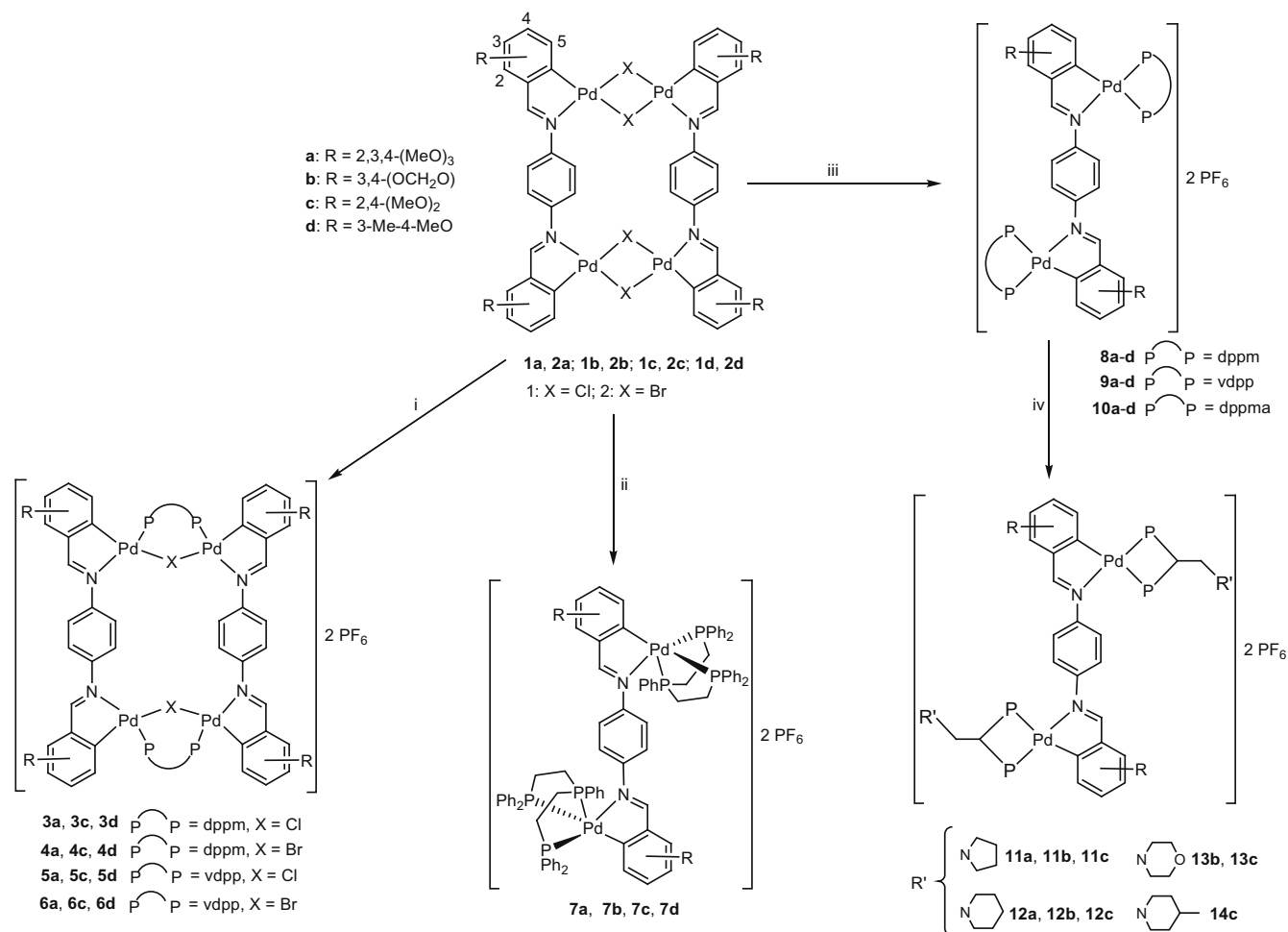
## 2.6. Crystal structure

For **4a** and **7a** room temperature X-ray data were collected on a BRUKER SMART-CCD-1000 diffractometer using monochromated Mo  $K\alpha$  radiation by the omega method. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods (SADABS) based on symmetry-equivalent and repeated reflections. The structures were 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  $R = 0.0545$  and  $wR_2 = 0.1281$  (**4a**),  $R = 0.0662$  and  $wR_2 = 0.1772$  (**7a**) (all unique data,  $F^2$ ), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solutions and refinements were carried out with the SHELX-97 program package [15].

## 3. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. Preparative details, characterising micro-analytical data, mass spectra, conductivity measurements, IR and





**Scheme 1.** (i) Ph<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> or Ph<sub>2</sub>C(=CH<sub>2</sub>)PPh<sub>2</sub> (1:2)/NH<sub>4</sub>PF<sub>6</sub> in acetone. (ii) (Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>PPh (1:2)/NH<sub>4</sub>PF<sub>6</sub> in acetone. (iii) Ph<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, Ph<sub>2</sub>C(=CH<sub>2</sub>)PPh<sub>2</sub> or Ph<sub>2</sub>N(Me)PPh<sub>2</sub> (1:4)/NH<sub>4</sub>PF<sub>6</sub> in acetone. (iv) Pyrrolidine, piperidine, morpholine or 4-Me-piperidine (1:2) in benzene.

NMR data are in the Section 2. The ligands **a–d** and the starting materials, **1–2(a–d)**, have been described by us earlier [11a,c,d].

The reaction of **1–2(a–d)** with Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm) or Ph<sub>2</sub>PC(=CH<sub>2</sub>)PPh<sub>2</sub> (vdpp) in 1:2 molar ratio followed by treatment with ammonium hexafluorophosphate gave **3–6 (a, c, d)** as pure air-stable solids, which were fully characterised (Section 2). We were not able to obtain pure the **b** derivatives. The complexes show two non-symmetrical bridges between two palladium atoms: a tertiary short-bite diphosphine and a halogen atom, thus generating a hexanuclear CXP<sub>2</sub>Pd<sub>2</sub> ring that binds together the two tetradentate Schiff base moieties, and rendering the hitherto unknown tetranuclear palladacycles. The compounds were 1:2 electrolytes as shown by molar conductivity measurements in dry acetonitrile [16]. The mass spectrum (FAB) showed the *m/z* peaks whose isotopic composition was consistent with the proposed tetranuclear complexes. Only one set of signals in the <sup>1</sup>H NMR spectra and one singlet in the <sup>31</sup>P NMR spectra was observed; these findings put forward the equivalence of the four metallated moieties, of the two phenylene rings and of the four phosphorus atoms, in highly symmetrical structures. The <sup>31</sup>P chemical shifts are consistent with a phosphorus *trans* to nitrogen arrangement, with the diphosphine on the “outer” side of the CXP<sub>2</sub>Pd<sub>2</sub> ring [11c]. This was confirmed by the strong upfield shift of the 4-MeO group promoted by shielding of the phosphine phenyl rings. An apparent doublet *ca.* 4 ppm in the <sup>1</sup>H NMR spectra was assigned to the PCH<sub>2</sub>P protons of the AA'XX' spin system, whereas a multiplet *ca.* 6 ppm was assigned to the vinylidene protons of the vdpp phos-

**Table 1**  
Crystal data and structure refinement data for **4a**.

Empirical formula	C <sub>104</sub> H <sub>100</sub> Br <sub>2</sub> Cl <sub>4</sub> F <sub>12</sub> N <sub>4</sub> O <sub>12</sub> P <sub>6</sub> Pd <sub>4</sub>
Formula weight	2738.92
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	C2cb
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	15.0980(10)
<i>b</i> (Å)	28.6010(10)
<i>c</i> (Å)	29.4890(10)
Volume (Å <sup>3</sup> )	12733.9(10)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.429
Absorption coefficient (mm <sup>-1</sup> )	1.412
<i>F</i> (000)	5472
Crystal size (mm <sup>3</sup> )	0.35 × 0.35 × 0.25
$\theta$ Range for data collection (°)	2.51–26.28
Index ranges	–18 ≤ <i>h</i> ≤ 0, –35 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 36
Reflections collected	6952
Independent reflections	6700 [ <i>R</i> <sub>int</sub> = 0.0516]
Completeness to $\theta = 26.28^\circ$ (%)	99.9
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.703 and 0.616
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	6700/1/674
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.915
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0545, <i>wR</i> <sub>2</sub> = 0.1281
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1219, <i>wR</i> <sub>2</sub> = 0.1428
Absolute structure parameter	0.006(19)
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.001 and –1.544

phine. The HC=N and H5 proton resonances were doublets by coupling to the phosphorus atom.

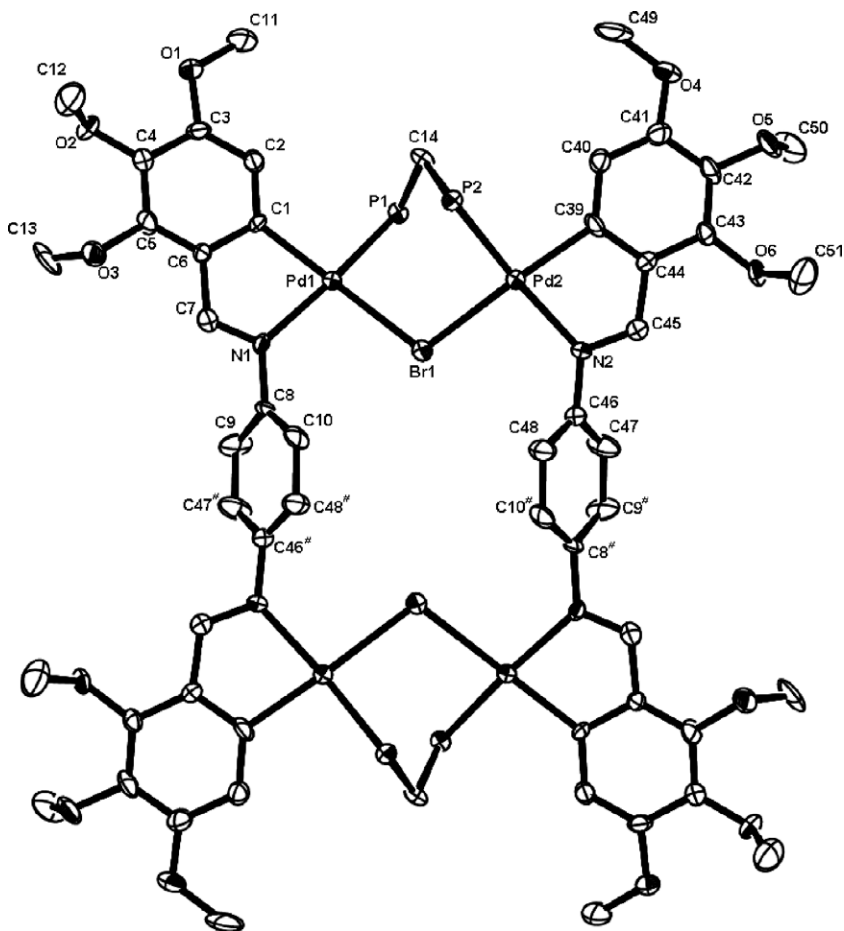
### 3.1. Crystal structure of complex **4a**

Crystals of **4a** were obtained by slow evaporation from a dichloromethane solution, space group *C2cb*, with one centrosymmetric tetrametallic complex dication, two hexafluorophosphate anions and two dichloromethane solvent molecules (half of the dication, one hexafluorophosphate anion and one dichloromethane molecule per asymmetric unit). Crystal data are shown in Table 1 and the ORTEP view of the structure is depicted in Fig. 1. The result from the X-ray crystallographic study on **4a** confirms the NMR-derived structure.

Fig. 1 reveals that in the highly symmetric molecule each four-coordinate palladium atom is bonded to four different atoms: the aromatic carbon and nitrogen atoms from the tetradentate organic ligand, a phosphorus atom from the diphosphine, and a bromine atom which bridges the two metal centers. Each palladium atom belongs to two six- and five-membered rings: the *C,N*-chelate metallacycle and the dimetallic bridging moiety. The angles between adjoining atoms in the coordination sphere of each metal atom are close to the theoretical value of 90°; with the most noteworthy strains in the C–Pd–N values, *ca.* 82°, consequent upon chelation. The sum of angles on each palladium is *ca.* 360°. The Pd–C

[2.045(8)–2.050(9) Å] and Pd–P [2.242(3)–2.248(3) Å] bond distances are somewhat shorter than the theoretical values of 2.081 Å and 2.43 Å [17]; however, the Pd–N [Pd(1)–N(1), 2.120(8); Pd(2)–N(2), 2.096(8)] and Pd–Br [Pd(1)–Br(1), 2.573(1); Pd(2)–Br(1), 2.572(1)] bond lengths are longer than expected, 2.01 Å and 2.45 Å [17], respectively, evidencing the *trans* influence of the phosphine ligand and phenyl carbon [cf. with the Pd–N lengths *ca.* 2.05 Å [11a], in the absence of phosphine]. The palladium coordination planes at Pd(1) and Pd(2) are essentially planar, with rms values of 0.1650 and 0.2075, respectively, from which the palladium atoms deviate by 0.009(2) Å and 0.034(2) Å, also respectively.

As opposed to the nearly planar structure bearing only bridging bromine atoms [11a], herein the need to accommodate both the bromine atom and the greater spanning diphosphine ligand between the two metal centers induces noticeable distortions in the structure, mainly manifested in partial loss of planarity. Thus, the two nearly planar fused phenyl and metallacycle rings [C(1)–C(7), N(1), Pd(1) rms 0.0460; C(39)–C(45), N(2), Pd(2) rms 0.0648] with angle between planes of 16.47°, are at 65.11° and 48.00° with the corresponding phenylene ring, and at 79.74° and 73.27° with the phosphine P(1)–C(14)–P(2) plane; the phenylene rings are not parallel but mutually twisted to 72.43°. Moreover, the molecule shows a Pd(1)···Pd(2) distance of 4.154(2) Å, far greater than those previously reported in related palladacycles



**Fig. 1.** Molecular structure of **4a** with solvent, counterions, hydrogen atoms and phosphine phenyl rings have been omitted for clarity. Thermal ellipsoids are shown at 30% probability. The asymmetric unit is half molecule and the symmetry transformation used to generate equivalent atoms<sup>#</sup> is (x, -y, -z). Selected bond lengths and angles: Pd(1)–C(1), 2.045(8); Pd(1)–N(1), 2.120(8); Pd(1)–P(1) 2.248(3); Pd(1)–Br(1), 2.573(1); N(1)–C(7), 1.257(13); Pd(2)–C(39), 2.050(9); Pd(2)–N(2), 2.096(8); Pd(2)–P(2), 2.242(3); Pd(2)–Br(1), 2.572(1); N(2)–C(45), 1.277(13) Å; Pd(1)···Pd(2), 4.154(2); C(1)–Pd(1)–N(1), 81.4(4); C(1)–Pd(1)–P(1), 94.2(3); N(1)–Pd(1)–Br(1), 94.4(2); P(1)–Pd(1)–Br(1), 91.06(8); C(39)–Pd(2)–N(2), 81.6(4); C(39)–Pd(2)–P(2), 94.7(3); N(2)–Pd(2)–Br(1), 93.7(2); P(2)–Pd(2)–Br(1), 92.05(8)<sup>#</sup>; N(1)–Pd(1)–P(1) 173.0(3); C(1)–Pd(1)–Br(1) 167.0(5); N(2)–Pd(2)–P(2) 170.0(3); C(39)–Pd(2)–Br(1) 165.6(4).

**Table 2**  
Crystal data and structure refinement data for **7a**.

Empirical formula	C <sub>94</sub> H <sub>62</sub> F <sub>12</sub> N <sub>2</sub> O <sub>6</sub> P <sub>8</sub> Pd <sub>2</sub>
Formula weight	2031.74
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	18.042(4)
<i>b</i> (Å)	15.047(3)
<i>c</i> (Å)	19.082(4)
$\beta$ (°)	105.67(3)
Volume (Å <sup>3</sup> )	4987.8(18)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.353
Absorption coefficient (mm <sup>-1</sup> )	0.561
<i>F</i> (000)	2071
Crystal size (mm <sup>3</sup> )	0.45 × 0.34 × 0.23
$\theta$ Range for data collection (°)	3.49–29.13
Index ranges	0 ≤ <i>h</i> ≤ 22, 0 ≤ <i>k</i> ≤ 20, -24 ≤ <i>l</i> ≤ 22
Reflections collected	11902
Independent reflections	8312 [ <i>R</i> <sub>int</sub> = 0.0662]
Completeness to $\theta = 29.13^\circ$	88.7%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.8818 and 0.7864
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	11902/1/563
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.055
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0662, <i>wR</i> <sub>2</sub> = 0.1772
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0968, <i>wR</i> <sub>2</sub> = 0.2021
Extinction coefficient	0.0107(9)
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.878 and -0.650

[11a]. The Cremer and Pople puckering parameters [18] are in accordance with a *twist-boat* conformation [*Q* = 1.468 Å,  $\theta = 91.3^\circ(2)$ ,  $\varphi = 149.6(4)$ ] for the six-membered CBr<sub>2</sub>Pd<sub>2</sub> ring.

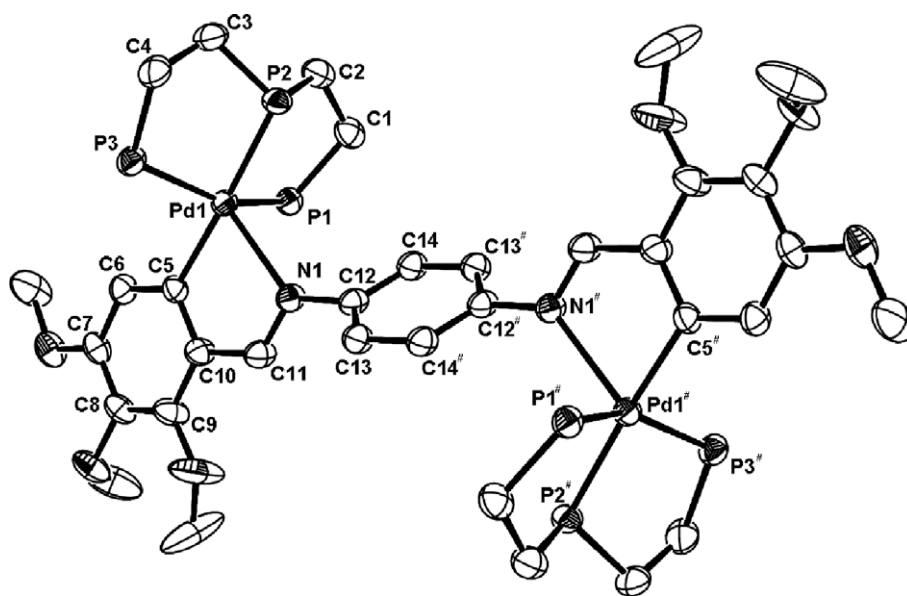
The reaction of **1–2(a–d)** with (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh (triphos) followed by treatment with ammonium hexafluorophosphate gave the novel dinuclear palladacycles as pure air-stable solids, which were fully characterized (see Section 2); conductivity measurements show values in agreement with 1:2 electrolytes [16]. There is

only one previous example of a doubly five-coordinate palladated compound, reported by us [19], with both metal atoms bonded to the same phenyl ring, as opposed to the present case where each palladium atom is linked to a different aromatic ring. The shift of the  $\nu(\text{C}=\text{N})$  stretching vibration to lower wavenumbers [20] as well as the upfield shift of the HC=N proton resonance in the <sup>1</sup>H NMR spectra [21] indicates the existence of palladium–nitrogen interaction in solution, although coupling of the latter to the phosphorus nuclei was not detected; the HC=N resonance appeared as a singlet. The phosphorus resonances in the <sup>31</sup>P–{<sup>1</sup>H} NMR spectra of the complexes were downfield shifted from their values in the free phosphine suggesting coordination of all the phosphorus atoms to the metal center. A triplet *ca.* 90 ppm was assigned to the central <sup>31</sup>P nucleus, *trans* to the phenyl carbon atom, and a doublet signal at *ca.* 42 ppm was assigned to the two equivalent mutually *trans* phosphorus nuclei. The latter signal appeared at lower frequency in accordance with the high *trans* influence of the phosphine ligand [22].

### 3.2. Crystal structure of complex **7a**

Crystals of **7a** were obtained by slow evaporation from a chloroform solution, space group *P*2<sub>1</sub>/*c*, with one centrosymmetric dimetalic complex dication and two hexafluorophosphate anions (half of the dication and one hexafluorophosphate anion per asymmetric unit). Crystal data are shown in Table 2 and the ORTEP view of the structure is depicted in Fig. 2.

The structure reveals that in the symmetric molecule each palladium atom is five-coordinate and bonded to three phosphorus atoms from the tridentate phosphine ligand, and to the aromatic carbon and nitrogen atoms from the tetradentate organic ligand. The geometrical parameter  $\tau$ , *i.e.*,  $\tau = (\beta - \alpha)/60$ , where  $\beta$  and  $\alpha$  are C(5)–Pd(1)–P(2) and P(3)–Pd(1)–P(1) bond angles, respectively, has a value of 0.4. This suggests a square pyramidal geometry with a 40% distortion towards trigonal bipyramid [23]. The axial position may be considered to be occupied by N(1) with C(5), P(1), P(2) and P(3) making up the basal plane (rms 0.2399), and with a palladium atom deviation from this plane of 0.5222(5) Å. As for the Pd–N bond length we have shown [19] that distortion of the



**Fig. 2.** Molecular structure of **7a** with counterions, hydrogen atoms and phosphine phenyl rings omitted for clarity. Thermal ellipsoids are shown at 30% probability. The asymmetric unit is half molecule and the symmetry transformation used to generate equivalent atoms<sup>#</sup> is ( $-x + 1, -y, -z + 1$ ). Selected bond lengths and angles: Pd(1)–C(5), 2.049(4); Pd(1)–P(2), 2.271(1); Pd(1)–P(3), 2.2887(14); Pd(1)–P(1), 2.327(1); Pd(1)–N(1), 2.444(4); P(1)–C(1), 1.855(5); P(2)–C(2), 1.811(6); P(2)–C(3), 1.814(5); P(3)–C(4), 1.855(5); N(1)–C(11), 1.276(6); N(1)–C(12), 1.421(5); C(5)–Pd(1)–P(2), 174.98(13); C(5)–Pd(1)–P(3), 94.70(12); P(2)–Pd(1)–P(3), 85.51(5); C(5)–Pd(1)–P(1), 91.73(13); P(2)–Pd(1)–P(1), 85.68(5); P(3)–Pd(1)–P(1), 150.34(5); C(5)–Pd(1)–N(1), 75.88(15); P(2)–Pd(1)–N(1), 108.55(9); P(3)–Pd(1)–N(1), 115.69(10); P(1)–Pd(1)–N(1), 93.96(10).



palladium geometry towards square-base pyramidal results in lengthening of the bond, i.e., longer bonds correspond to lower  $\tau$  values. Therefore, the Pd(1)–N(1) distance of 2.444(4) Å fits well within the values found by us in related complexes and although longer than single bond value of 2.01 Å [17], is close to the Pd–N bond length of 2.23(2) Å in an authentic pentacoordinated palladium(II) complex [24]. Nevertheless, the distance reported herein is shorter than those found in other Pd(II) five-coordinate complexes where weak Pd···N interactions were found and given in the range 2.576(4)–2.805(5) Å [25]. The Pd(1)–C(5) bond length of 2.049(4) Å, and the Pd–P bond lengths 2.271(1)–2.327(1) Å, are shorter than the expected values of 2.081 Å, and 2.41 Å [17], respectively, suggesting some degree of multiple bond character in the Pd–C<sub>aryl</sub> [26,27] and Pd–P linkages [28].

The two nearly planar fused metallated phenyl ring and metacycle ring moiety [C(5)–C(11), N(1), Pd(1)] rms 0.0460° with the phenylene ring. The stacking parameters [29] are appropriate enough to consider that effective  $\pi$ – $\pi$  stacking interaction is operative. Thus, the centroid–centroid distance between the planes defined by the phosphine phenyl ring [C(30)–C(35)], plane 1, and the phenylene ring, plane 2, is  $d_{c-c} = 3.830(4)$  Å, with  $\alpha = 14.94^\circ$ ; the slipping angles  $\beta$  and  $\gamma$  (defined by the vector  $c_1$ – $c_2$  and the normal to plane 1 or plane 2 from  $c_2$  and  $c_1$ , respectively) are 23.91° and 32.78°, with  $d(\perp c_1$ –plane 2) 3.281 Å and  $d(\perp c_2$ –plane 1) 3.501 Å (see Figs. 3 and 4).

The reaction of **1–2(a–d)** with Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, Ph<sub>2</sub>PC(=CH<sub>2</sub>)PPh<sub>2</sub> or Ph<sub>2</sub>PN(Me)PPh<sub>2</sub> (dppma) in 1:4 molar ratio followed by treatment with ammonium hexafluorophosphate gave the dinuclear palladacycles **8–10(a–d)** as pure air-stable 1:2 electrolytes, which were fully characterized (see Section 2). The <sup>31</sup>P NMR spectra showed two doublets for the two inequivalent phosphorus nuclei. The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom, in agreement with the higher *trans* influence of the latter with respect to the nitrogen atom [22]. A doublet of doublets *ca.* 4.5 and 2.3 ppm, in the <sup>1</sup>H NMR spectra, was assigned to the PCH<sub>2</sub>P (**8a–8d**) and PN(Me)P (**10a–10d**) protons, respectively, whereas the PC(=CH<sub>2</sub>)P resonance was a multiplet in all cases. The H5 resonance showed coupling to both phosphorus nuclei (<sup>4</sup>J<sub>trans–NH5</sub> *ca.* 10 Hz, <sup>4</sup>J<sub>cis–NH5</sub> *ca.* 8 Hz), and the HC=N nucleus was only coupled to the phosphorus *trans* to nitrogen (<sup>4</sup>J<sub>PH</sub> *ca.* 7 Hz).

Treatment of **9a–9c** with pyrrolidine, piperidine, morpholine or 4-Me-piperidine in 1:2 molar ratio gave the Michael addition prod-

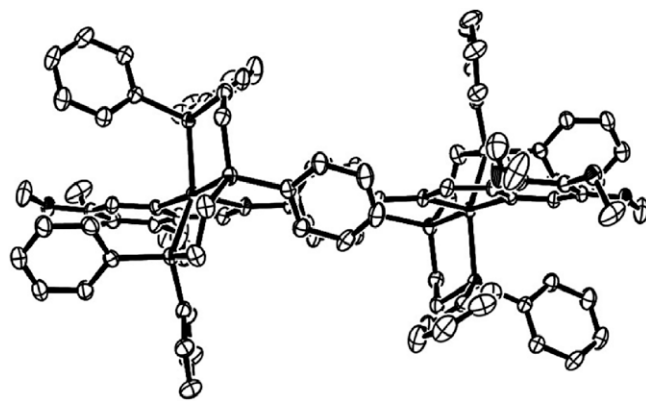


Fig. 4. The molecular structure of **7a** showing the  $\pi$ -stacking of the phenyl rings.

ucts **11–12(a–c)**, **13b**, **13c** and **14c** in good yield, as pure air-stable 1:2 electrolytes, which were fully characterized (see Section 4). The palladacycle activates the C=CH<sub>2</sub> double bond towards nucleophilic addition producing, in turn, a relief of strain in the P–C–P carbon atom of the four-membered PdP<sub>2</sub>C ring after addition, due to angle modification at carbon on going from sp<sup>2</sup> to sp<sup>3</sup> hybridization. Addition was sustained based on the absence of the PC(=CH<sub>2</sub>)P proton resonance and the appearance of the PCHP resonance *ca.* 4.5–5.0 ppm. The <sup>31</sup>P NMR spectra showed two doublets for the two inequivalent phosphorus nuclei; the  $\Delta\delta$ P difference with respect to the starting materials **9a–9c** was the same in the **b** series, slightly lower in the **a** compounds, and larger by *ca.* 5–10 ppm in the **c** derivatives. Although the P–C–P carbon atom in **9a–9c** shows sp<sup>2</sup> hybridization, as opposed to sp<sup>3</sup> hybridization in the addition materials (implying loss of the hybrid *s* character), the <sup>2</sup>J(PP) value in the latter species was higher than in the starting materials (*cf.* 45–60 and 14–18 Hz, respectively). We suggest this is due to a greater contribution of <sup>2</sup>J(PP) across the metal center (usually of negative sign) in the addition products, thus lowering the absolute value of the coupling constant. The H5 resonance was a doublet (<sup>4</sup>J<sub>trans–NH5</sub> *ca.* 10–12 Hz, <sup>4</sup>J<sub>cis–NH5</sub> *ca.* 8 Hz); in some complexes the HC=N nucleus showed coupling to both phosphorus nuclei (<sup>4</sup>J<sub>trans–NH</sub> 6.7–7.7 Hz, <sup>4</sup>J<sub>cis–NH5</sub> 0.4–1.2 Hz). In contrast to the starting materials, two resonances were observed for the phenylene protons, which were not equivalent in this case.

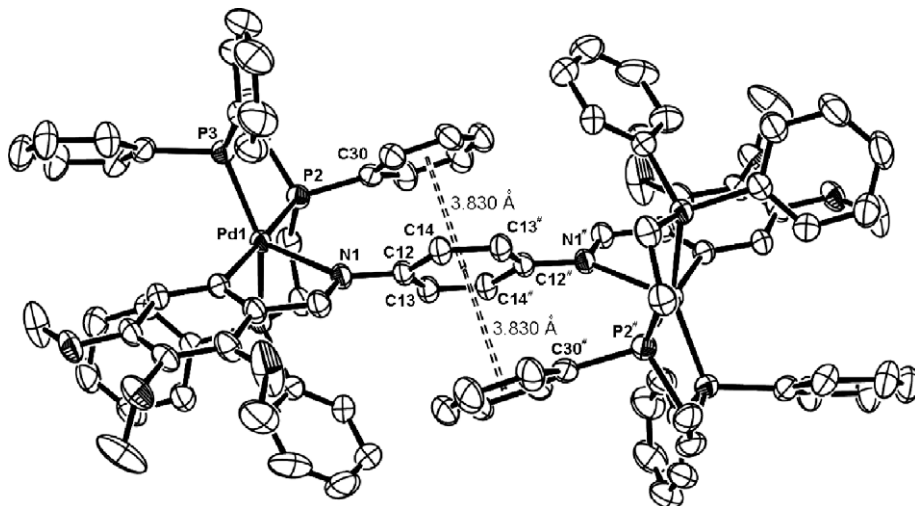


Fig. 3. Intramolecular  $\pi$ , $\pi$ -stacking interactions. Dashed lines link the centroids of the rings involved in each stacking interaction. Hydrogen atoms and counterions have been omitted for clarity.

## 4. Conclusions

We have shown that the chemistry of the *N*-benzylidene-1,4-phenylenediamine metallacycles can be further extended to enclose tetranuclear palladium complexes with bridging short-bite tertiary diphosphines, which deviate to a certain extent from full planarity in order to accommodate the phosphine bridging ligand consequent on the shorter span of the halogen atom; definite proof of which is the molecular structure given herein. Insight into other aspects of their chemistry stems from the preparation of the novel dinuclear five-coordinate palladacycles, for which the molecular structure shows there is intramolecular  $\pi$ -stacking, and from the Michael addition products that may be obtained in the case of the dinuclear species with the chelated diphosphine, vdpp.

## 5. Supplementary material

CCDC 697274 and 697275 contain the supplementary crystallographic data for compounds **4a** and **7a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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