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Synthesis and reactivity of new functionalized Pd(II) cyclometallated complexes with boronic esters

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ABSTRACT

Treatment of the functionalized Schiff base ligands with boronic esters **1a**, **1b**, **1c** and **1d** with palladium (II) acetate in toluene gave the polynuclear cyclometallated complexes **2a**, **2b**, **2c** and **2d**, respectively, as air-stable solids, with the ligand as a terdentate [C,N,O] moiety after deprotonation of the –OH group. Reaction of **1j** with palladium (II) acetate in toluene gave the dinuclear cyclometallated complex **5j**. Reaction of the cyclometallated complexes with triphenylphosphine gave the mononuclear species **3a**, **3b**, **3c**, **3d** and **6j** with cleavage of the polynuclear structure. Treatment of **2c** with the diphosphine $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) in 1:2 molar ratio gave the dinuclear cyclometallated complex **4c** as an air-stable solid.

Deprotection of the boronic ester can be easily achieved; thus, by stirring the cyclometallated complex **3a** in a mixture of acetone/water, **3e** is obtained in good yield. Reaction of the tetrameric complex **2a** with *cis*-1,2-cyclopentanediol in chloroform gave complex **2c** after a transesterification reaction. Under similar conditions complexes **3a** and **3d** behaved similarly: with *cis*-1,2-cyclopentanediol, pinacol or diethanolamine complexes **3c**, **3b**, **3g** and **3f**, were obtained. The pinacol derivatives **3b** and **3g** experiment the Petasis reaction with glyoxylic acid and morpholine in dichloromethane to give complexes **3h**, and **3i**, respectively.

1. Introduction

In past decades the chemistry of cyclometallated transition metal complexes has attracted much attention, being the five-membered palladacycles the most widely studied [1]. Cyclometallated complexes present applications in catalytic and synthetic processes [2], as chiral auxiliaries [3] or as building blocks for molecular architectures of higher complexity [4]. They also show interesting mesogenic [5] and luminescent and electronic properties [6] and potential applications in medicine and biology [7].

On the other hand, boronic acids and boronic esters have found numerous applications in organic and medicinal chemistry [8]. In particular, boronic esters have proven to be of great importance in asymmetric synthesis [9]; the facile introduction and recovery of chiral auxiliaries is the key step, and transesterification is the one of the simplest procedures by which chiral auxiliaries may be introduced to, and recovered from, an ester. Another important application of boronic acids is the Petasis multicomponent reaction of aryl- and vinylboronic acids with aldehydes and amines, sometimes referred to as the boronic acid Mannich reaction, which is a powerful and convenient method for the one-pot formation of unnatural amino acid derivatives [10,11].

Although the synthesis and reactivity of boronic acids and esters is well studied, few complexes in which this group is part of a coordinated ligand are known [12–14].

With this in mind we reasoned that combining the properties of cyclometallated complexes and of boronic acids could be of great interest and we therefore decided to examine functionalized Schiff bases with boronic esters as ligands in the cyclometallation reaction with palladium(II). As a result herein we present the synthesis of, to the best of our knowledge, the first functionalized cyclometallated complexes with boronic acids and boronic esters. Their reactivity towards the transesterification and the Petasis reaction is also described.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1–3. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR

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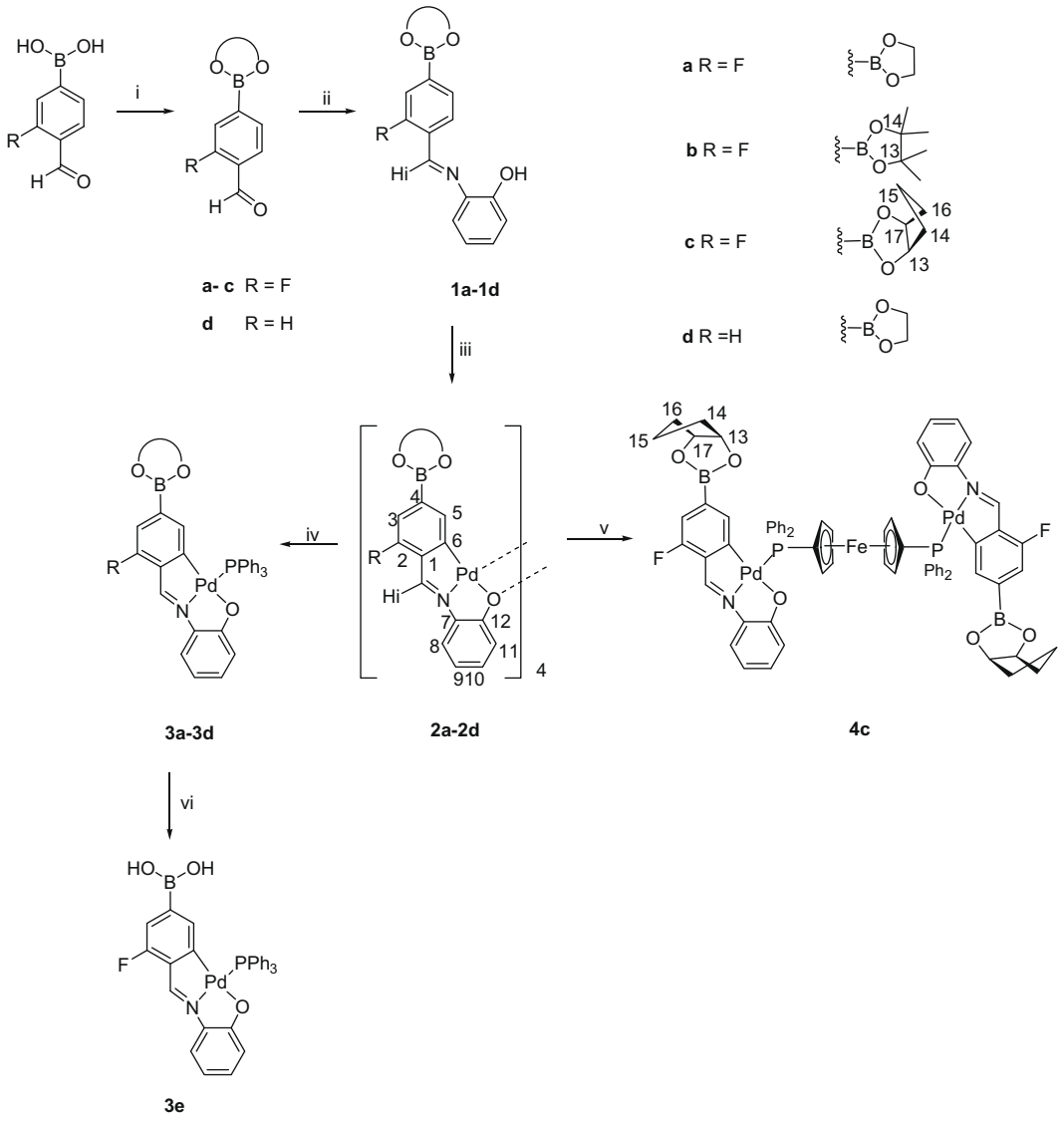
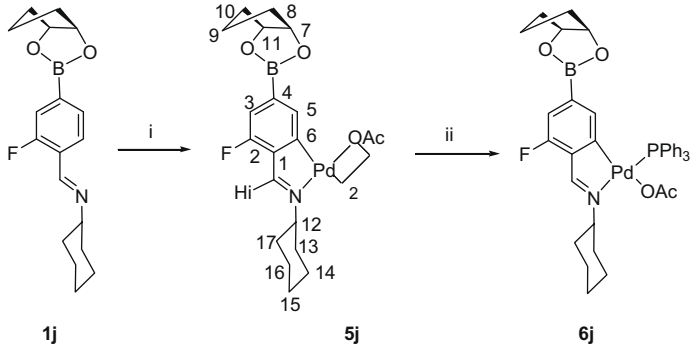


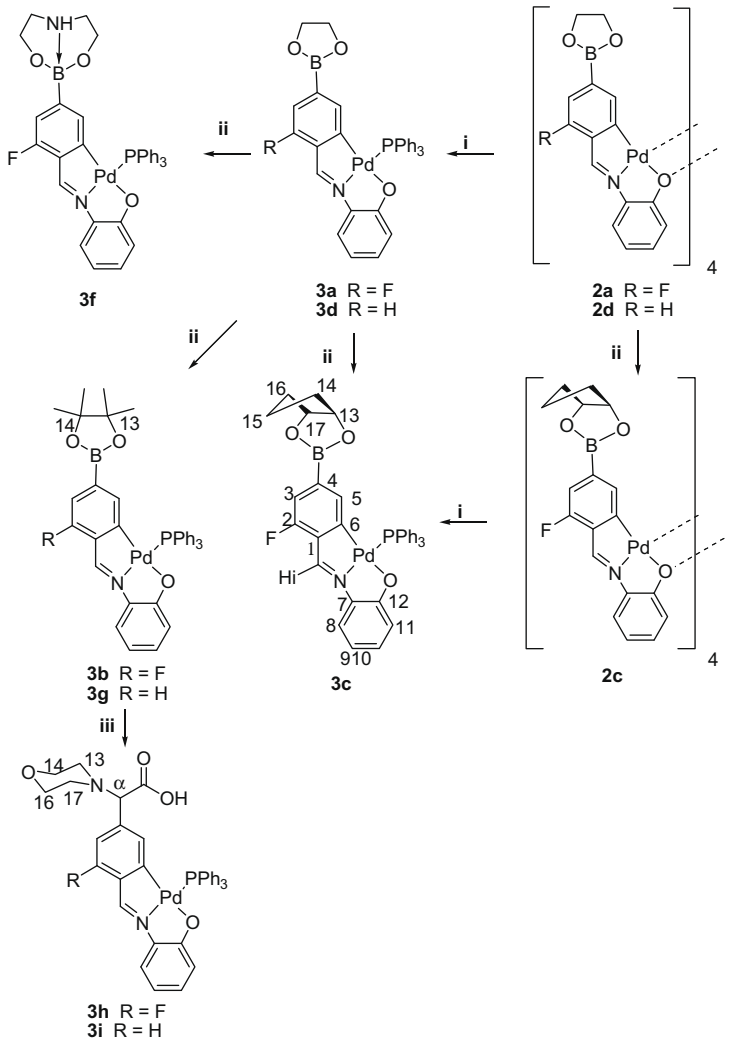
Scheme 1. (i) 1,2-Diol, toluene, reflux; (ii) aminophenol, chloroform, reflux; (iii) $Pd(OAc)_2$, toluene, 60 °C; (iv) PPh_3, chloroform; (v) dppf, chloroform; (vi) acetone/water.



Scheme 2. (i) $Pd(OAc)_2$, toluene, 60 °C; (ii) PPh_3, acetone.

spectroscopy and by ^1H, $^{31}P-\{^1H\}$ and, in part, $^{13}C-\{^1H\}$ NMR spectroscopy and mass spectrometry (see Section 4).

Reaction of ligands **1a–1d** with palladium (II) acetate in toluene at 60 °C gave the cyclometallated complexes **2a–2d**, as air-stable solids which were fully characterized. The IR spectra showed the shift of the *ν*(C═N) stretch toward lower wavenumbers, from the free ligand value, due to nitrogen coordination of the imine [15,16], and the absence of the *ν*(O–H) stretch, in accordance with loss of the –OH proton. This observation was confirmed by absence of the O*H* signal in the ^1H NMR spectra. The *HC*═N and *H*5 resonances in the ^1H NMR spectra were highfield shifted, as compared to the uncoordinated ligands, by *ca.* 1.5 and 0.9 ppm, respectively;



Scheme 3. (i) PPh_3, chloroform; (ii) diol, chloroform; (iii) $HCOCO_2H$, morpholine, dichloromethane.

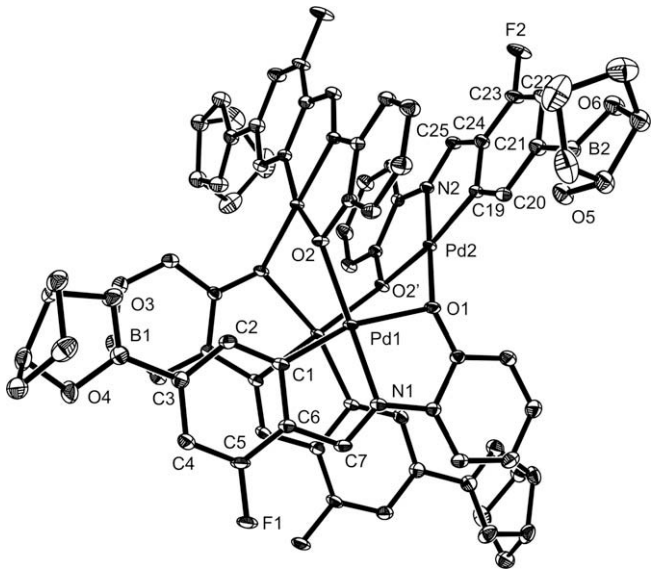


Fig. 1. Molecular structure of $[Pd\{2\text{-}F\text{-}4\text{-}(\text{-}OCH(CH_3)_3CHO\text{–}B)C_6H_2C(H)\text{=}N[2'\text{-}(O)C_6H_4]\}]_4$ **2c**, with labelling scheme. Hydrogen atoms have been omitted for clarity.

the low δ values were in agreement with the structure of the complexes which puts the *H*C=N and *H*5 protons in the proximity of the shielding zone of the phenyl rings of a neighbouring metallated ligand [17–20].

Complex **2c** was also characterized by $^{13}C\text{–}\{^1H\}$ NMR spectroscopy. The most noticeable feature was the shift to higher frequency of the C6, C=N, and C1 resonances, as compared to their value in the spectrum of the uncoordinated ligand, confirming that metallation had occurred [17,18,20]; the smallest shift was observed for the *C*=N carbon resonance of only 2.7 ppm. The resonance assigned to the C–O carbon was also shifted to higher frequency (15.7 ppm) consequent upon Pd–O bond formation.

The mass-FAB spectra showed the cluster of peaks characteristic of the tetranuclear $[Pd(L\text{-}2H)]_4^+$ fragments (see Section 4); the isotopic patterns were in good agreement with a tetrameric formulation.

Complex **2b** was insoluble in the common deuterated solvents; however the IR and mass-FAB spectra as well as the spectroscopic data for its derivative **3b**, allowed us to propose a similar formulation as for the other tetranuclear complexes.

2.1. Crystal structure of *2c*

Suitable crystals were grown by slowly evaporating a chloroform/*n*-hexane solution of the complex. The molecular structure

Table 1
Crystal and structure refinement data.

	2c	3c	5j
Formula	$C_{77}H_{65}B_4Cl_{15}F_4N_4O_{12}Pd_4$	$C_{38}H_{34}BCl_4FNO_3PPd$	$C_{40}H_{52.50}B_2F_2N_2O_{9.25}Pd_2$
M_r	2314.92	861.64	981.76
T (K)	100(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Trigonal
Space group	*Pccn*	$P2_1/c$	$R\bar{3}$
Cell dimensions			
a (Å)	13.912(5)	17.720(5)	25.928(1)
b (Å)	24.195(5)	13.219(5)	25.928(1)
c (Å)	26.160(5)	17.282(5)	39.404(1)
α (°)			
β (°)		113.102(5)	
γ (°)			
V (Å^3)	8805(4)	3724(2)	22940.5(7)
Z	4	4	18
μ (mm^{-1})	1.746	0.872	0.759
Crystal size (mm)	0.25 × 0.20 × 0.12	0.50 × 0.18 × 0.04	0.15 × 0.12 × 0.04
$2\theta_{max}$ (°)	56.6	56.6	50.1
Reflections:			
Collected	83 395	33 796	70 897
Unique	10 937 (R_{int} = 0.028)	9049 (R_{int} = 0.064)	8911 (R_{int} = 0.099)
Transmissions	0.86, 0.72	0.96, 0.67	0.95, 0.88
R [F, $I > 2\sigma(I)$]	0.0362	0.0806	0.0486
wR [F^2, all data]	0.1336	0.2204	0.1769

Table 2
Selected bond distances (Å) and angles (°) for complexes **2c** and **3c**.

	2c	3c		2c	3c
Pd(1)–C(1)	1.968(3)	2.017(6)	C(1)–Pd(1)–N(1)	82.8(1)	81.7(2)
Pd(1)–N(1)	1.963(3)	2.021(6)	C(1)–Pd(1)–O(2)	98.1(1)	
Pd(1)–O(1)	2.131(2)	2.094(5)	N(1)–Pd(1)–O(1)	81.1(1)	81.0(2)
Pd(1)–O(2)	2.059(2)		O(2)–Pd(1)–O(1)	98.0(1)	
B(1)–O(3)	1.357(5)	1.367(9)	C(1)–Pd(1)–P(1)	82.8(1)	97.2(2)
B(1)–O(4)	1.363(5)	1.374(10)	O(1)–Pd(1)–P(1)	82.8(1)	100.1(1)
B(1)–C(3)	1.555(5)	1.553(11)	C(19)–Pd(2)–N(2)	83.11(1)	
Pd(2)–C(19)	1.965(3)		C(19)–Pd(2)–O(1)	95.7(1)	
Pd(2)–N(2)	1.959(3)		N(2)–Pd(2)–O(2′)	81.4(1)	
Pd(2)–O(1)	2.030(2)		O(1)–Pd(2)–O(2′)	99.8(1)	
Pd(2)–O(2′)	2.156(2)		Pd(2)–O(1)–Pd(1)	113.4(1)	
B(2)–O(5)	1.358(5)		Pd(1)–O(2)–Pd(2′)	118.0(1)	
B(2)–O(6)	1.365(5)				
B(2)–C(21)	1.574(5)				
Pd(1)–P(1)		2.268(2)			
C(9)–O(1)	1.351(4)				
C(27)–O(2)	1.349(4)				
C(13)–O(1)	1.325(9)				

Symmetry transformations used to generate equivalent atoms: $-x + 3/2, -y + 1/2, z$.

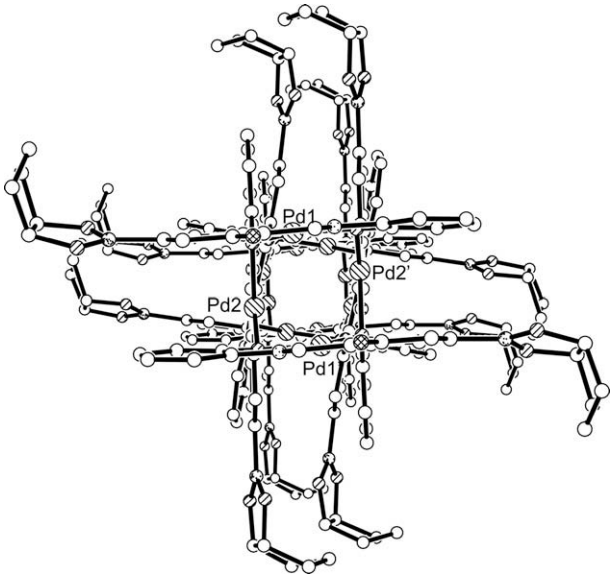


Fig. 2. View of the crystal of **2c** along the *c* axis.

is illustrated in Fig. 1. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The asymmetric unit is formed by one half molecule of **2c** and 2.5 severely disordered molecules of chloroform. The entire molecule is generated by a crystallographic C2 axis which is perpendicular and bisecting Pd(1)–Pd(1′) and Pd(2)–Pd(2′).

Each palladium is bonded in a slightly distorted square–planar disposition to the ligand through an aryl carbon, a C=N nitrogen, and a phenoxy oxygen atom, and to a bridging oxygen atom of a neighbouring cyclometallated ligand monomer. Therefore, the core of the tetrameric molecule consists of an eight-membered ring of alternating palladium and oxygen atoms. The Pd–C [1.968(3) and 1.965(3) Å], Pd–N [1.963(3) and 1.959(3) Å] and Pd–O bond lengths are within the expected values, with the Pd–O (*trans* to carbon) showing the larger *trans* influence of the carbon atom as compared to nitrogen [20,19,21–23]. The B–O and B–C distances are similar to previously reported values [12].

The Pd(1)···Pd(1′) and Pd(2)···Pd(2′) bond distances of 3.354(1) and 3.357(1) Å, respectively, preclude any Pd–Pd interactions. Two of the *quasi*-planar Pd-ligand units are parallel and almost orthogonal to the other two parallel monomer moieties, with the distance between the parallel Pd-ligands units approximately 3.3 Å. The crystallographic C2 axis of the tetrameric molecules is parallel to the unit cell *c* axis forming channels along this direction (see Fig. 2).

Reaction of the ligands with the unprotected –$B(OH)_2$ group and palladium (II) acetate were carried out under analogous reaction conditions, however, instead of the expected cyclometallated complexes, large amounts of reduced black palladium were obtained. The use of different reaction times and temperatures and/or change of solvent (glacial acetic acid, reflux; chloroform, room temperature) gave similar results.

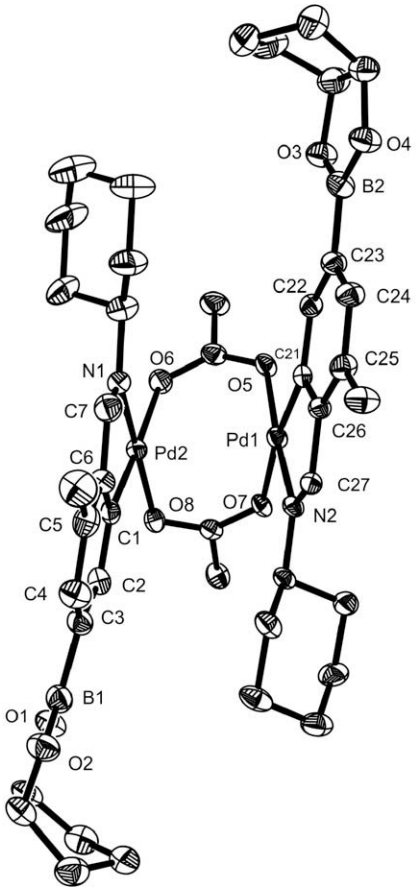


Fig. 3. Molecular structure of [Pd{2-F-4-(-OCH$(CH_2)_3$CHO–B)C_6H_2C(H)=N-[C_6H_{11}]}$(CH_3COO)]_2$ **5j**, with labelling scheme. Hydrogen atoms have been omitted for clarity.

Treatment of ligand **1j** with palladium (II) acetate in dry toluene at 60 °C yielded the dinuclear cyclometallated complex **5j** as an air-stable yellow solid. The resonance corresponding to the *HC*=N proton appeared as a singlet at δ 7.62 ppm shifted to lower frequency consequent upon coordination of the imine group to the palladium atom via the lone pair of the nitrogen atom [24]. The *H*5 resonance also appeared as a singlet, confirming metallation of the C6 carbon. The ^{1}H NMR spectrum showed the signal of the acetate *Me*COO protons as a singlet at δ 2.16, in agreement with the presence of the anti isomer in the solution [25]. The IR spectrum showed the ν(C=N) stretch at 1614 cm^{-1}, shifted to lower wavenumbers (as compared to the free ligand) due to N-coordination of the imine [15,16]. The ^{13}C–{^{1}H} spectrum showed the characteristic lowfield shift of the signals corresponding to the *C*=N, *C*1and *C*6 carbons consequent upon metallation (*vide supra* and experimental). The IR spectrum also showed strong bands assigned to the symmetric and asymmetric ν(COO) vibrations, in agreement with bridging acetate ligands [25,26]. The mass-FAB spectrum showed the cluster of peaks centered at 959 amu, corresponding to the dinuclear fragment $[Pd(L\text{-}H)(OCOCH_3)]_2$, with the expected isotopic pattern.

2.2. Crystal structure of **5j**

Suitable crystals of the title compound were grown by slowly evaporating a dichloromethane solution of the complex. The molecular structure is illustrated in Fig. 3. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 3.

The crystals consist of discrete molecules separated by normal van der Waals distances. The asymmetric unit for **5j** comprises one molecule of the complex and several molecules of water.

The molecular configuration of complex **5j** is a dimeric form with the cyclopalladated moieties in an "open book" arrangement linked by two acetate bridging ligands, as observed in related dimers [27–29]. As a result, the chelating *C,N* bonded Schiff bases are forced to lie above one another in the dimeric molecule. This leads to interligand repulsions on the "open" side of the molecule and results in the coordination planes of the palladium atoms being tilted at an angle of 27.0°. The coordination sphere around each cyclometallated palladium atom consists of a nitrogen atom of the imine group, the *ortho* carbon of the phenyl ring, and two oxygen atoms (one from each of the bridging acetate ligands). The most noticeable distortion of the ideal coordination sphere corresponds to the C–Pd–N bite angle of 80.7(4)° and 81.7(3)°.

The palladium–palladium distance is 2.869(1) Å and may be regarded as nonbonding [27–29]. The palladium–nitrogen bond lengths [2.019(8) and 1.999(6) Å] and the palladium carbon [1.946(9), 1.942(8) Å] bond distances are in agreement with values previously reported for similar complexes [27–29]. The *trans* influence of σ-bonded carbon is clearly illustrated by the lengthening of the palladium–oxygen distance *trans* to carbon (*ca.* 2.13 Å), relative to that *trans* to oxygen (*ca.* 2.04 Å) [28,29].

Treatment of the cyclometallated complexes **2a–2d** with triphenylphosphine gave the mononuclear species **3a–3d** in which the polynuclear structure has been opened due to P–$O_{bridging}$ bond cleavage. The ^{1}H NMR spectra showed the resonances due to the *H*5 and *HC*=N protons lowfield shifted (as compared to the free ligands), however the *HC*=N shift was smaller than in the parent tetranuclear complexes, in agreement with opening of the polynuclear structure. The *H*5 resonance showed large shifts due to shielding of the phosphine phenyl rings, as we have observed before in related complexes [17,18,20]. The *H*5 and *HC*=N signals showed the coupling to the ^{31}P nucleus of the phosphine ligand (3.6 and *ca.* 10 Hz, respectively), and in the ^{31}P–{^{1}H} spectra the phosphorus resonance was a singlet *ca.* δ 35 ppm; these findings were in agreement with a phosphorus *trans* to nitrogen arrangement [20,30–33].

Complexes **3b** and **3c** were also characterized by ^{13}C–{^{1}H} spectroscopy and their spectra were similar to those of the tetranuclear **2b** and **2c** complexes with the shift to higher frequency of the C6, and C1 resonances (as compared to the uncoordinated ligand) [17,18,20] and the lowfield shift of the C=N carbon resonance; with the resonance assigned to the C–O carbon showing a greater high frequency shift (*ca.* 22 ppm). In the mass spectra the clusters of peaks corresponding to the molecular ions were correctly assigned.

Table 3
Selected bond lengths (Å) and angles (°) for complex **5j**.

Pd(1)–C(1)	1.946(9)	Pd(1)–Pd(2)	2.869(1)
Pd(1)–N(1)	2.019(8)	B(1)–O(1)	1.360(13)
Pd(1)–O(5)	2.141(6)	B(1)–O(2)	1.374(12)
Pd(1)–O(7)	2.033(6)	B(1)–C(3)	1.557(15)
Pd(2)–C(21)	1.942(8)	B(2)–O(3)	1.355(12)
Pd(2)–N(2)	1.999(6)	B(2)–O(4)	1.345(12)
Pd(2)–O(6)	2.037(5)	B(2)–C(23)	1.525(14)
Pd(2)–O(8)	2.135(5)		
C(1)–Pd(1)–N(1)	80.7(4)	C(21)–Pd(2)–N(2)	81.7(3)
N(1)–Pd(1)–O(5)	97.2(3)	N(2)–Pd(2)–O(8)	95.9(2)
O(5)–Pd(1)–O(7)	88.5(2)	O(8)–Pd(2)–O(6)	89.4(2)
C(1)–Pd(1)–O(7)	93.6(3)	C(21)–Pd(2)–O(6)	92.8(3)
C(1)–Pd(1)–O(5)	177.6(3)	C(21)–Pd(2)–O(8)	173.5(3)
N(1)–Pd(1)–O(7)	173.8(3)	N(2)–Pd(2)–O(6)	174.3(2)

2.3. Crystal structure of **3c**

Suitable crystals of the title compound were grown by slowly evaporating a dichloromethane solution of the complex. The molecular structure is illustrated in Fig. 4. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The crystal structure comprises one molecule of **3c** and two dichloromethane molecules per asymmetric unit. The palladium (II) atom is bonded to the aryl carbon C(1), the imine nitrogen N(1) and the oxygen O(1) of the Schiff base ligand and to a phosphorus atom of the triphenylphosphine ligand, P(1). The Pd–N(1), 2.021(6) Å, Pd–C(1), 2.017(6) and Pd(1)–P(1), 2.268(2), bond distances are within the range found earlier [17,18,20,34] The Pd–O(1) bond distance (2.094(5) Å) reflects the *trans* influence of the aryl carbon atom. The Pd–C and Pd–N bond distances are longer than the values found in the parent complex **2c**; however the Pd–O (*trans* to carbon) length is somewhat shorter. The sum of angles about the palladium atom is *ca.* 360° with the only noteworthy deviations being the somewhat reduced N(1)–Pd(1)–C(1) and N(1)–Pd(1)–O(1) bond angles of 82.8(1) and 81.1(1)°, respectively, consequent upon chelation.

An unusual characteristic of the coordinated ligand is the shortening of the O(4)–C(13) bond distance as compared to values reported previously for uncoordinated phenols [35] [1.325(9) vs. 1.411(5) Å in N-(2-hydroxyphenyl)-2-hydroxyaniline]. This value is also shorter than those found in complex **2c** [1.351(4) and 1.349(4)].

Reaction of the cyclometallated tetramer **2c** with the diphosphine dppf in 1:2 molar ratio gave the dinuclear cyclometallated complex **4c**, as an air-stable solid, which was fully characterized (see Section 4). The IR and ^{1}H NMR spectra of the complex showed similar features for the cyclometallated moiety as those of the mononuclear compound **3c**. Only one singlet (24.31 ppm) was observed in the ^{31}P–{^{1}H} NMR spectrum for the two equivalent nuclei in accordance with a symmetric nature of the dinuclear complex. The mass-FAB spectrum showed the set of peaks corresponding to the molecular ion with the isotropic patter characteristic of the dinuclear formulation.

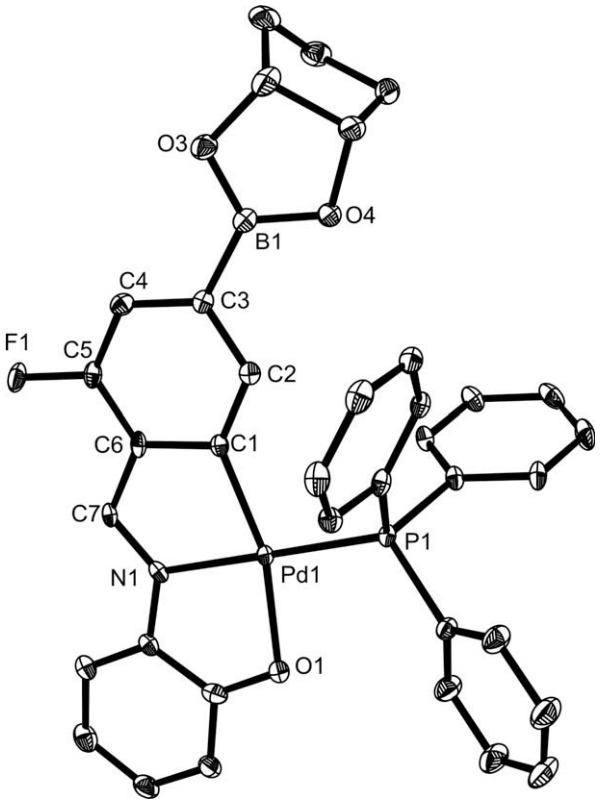


Fig. 4. Molecular structure of [Pd{2-F-4-(-OCH(CH$_3$)$_3$CHO–B)C$_6$H$_2$C(H)=N[2′-(O)C$_6$H$_4$]}(PPh$_3$)] **3c**, with labelling scheme. Hydrogen atoms have been omitted for clarity.

Reaction of **5j** with PPh_3 gave complex **6j**, as an air-stable solid which was fully characterized (see Section 4). The IR spectrum of **6j** showed strong bands at 1300 and 1555 cm^{-1} assigned to the symmetric and asymmetric ν(COO) vibrations, respectively, in agreement with those expected for mono-coordinate acetate ligands [26]. The ^{1}H NMR spectrum showed the *H*C=N and *H*5 resonances coupled to the phosphorus nucleus [δ 8.33 (J_{PH} = 9.7) and δ 5.48 (J_{PH} = 6.0 Hz), respectively], with the *H*5 resonance shifted towards lower frequency due to the shielding effects of the phosphine phenyl ring [17–20]. In the ^{31}P–{^{1}H} spectrum the resonance of the coordinated phosphine was a singlet at δ 42.04 ppm in agreement with a phosphorus *trans* to nitrogen arrangement (*vide supra*).

2.4. Reaction at the boronic ester sites

Deprotection of the boronic ester can be easily achieved by stirring the cyclometallated complex **3a** in a mixture of acetone/water from which complex **3e** is recovered in good yield. The ^{1}H NMR spectrum of **3e** showed the absence of the resonances corresponding to the OC*H*$_2$C*H*$_2$O protons and the mass-FAB spectrum the cluster of peaks, centered at 626 amu, corresponding to the molecular ion.

Boronic esters are known to readily experiment transesterification reactions [36] with a wide variety of diols. Similarly the reaction of the tetrameric complex **2a** with *cis*-1,2-cyclopentanediol in chloroform gave complex **2c** after column chromatography.

The cyclometallated monomers also experiment the reaction using similar conditions; consequently, the esters of 1,2-ethanediol, **3a** and **3d**, undergo transesterification with *cis*-1,2-cyclopentanediol, 2,3-dimethyl-2,3-butanediol (pinacol) or diethanolamine with moderate yields, being the latter the most favourable. Therefore, the transesterification reaction can be carried out in the cyclometallated ligands using similar conditions to those used with uncoordinated boronic esters and constitute an easy method to functionalize cyclometallated ligands.

The pinacol derivatives **3b** and **3g** react with glyoxylic acid and morpholine in dichloromethane to give complexes **3h**, and **3i**, respectively. The boronic group was replaced by the amino acid, through the formation of a C–C and a C–N bonds. This shows that the cyclometallated aryl boronic esters can easily take part in the multicomponent Petasis reaction. In the ^{1}H NMR spectra of the complexes the signals corresponding to the pinacol group disappeared. The resonance assigned to the *H*α appeared as a singlet at *ca.* 3.3 ppm and the protons of the morpholine ring as multiplets at *ca.* 3.7 and 2.2 ppm. The ^{13}C–{^{1}H} spectra showed the signal of the *C*OOH carbon at *ca.* 172 ppm, the *C*α at *ca.* 75 ppm and the resonances corresponding to the morpholine moiety at 64.6 and 51.0 ppm. The ESI-mass spectra showed the peaks corresponding to the molecular ions at 725 and 707 amu form **3h** and **3i**, respectively.

3. Conclusions

We have shown that Schiff bases bearing boronic esters may undergo cyclometallation to give the corresponding tetranuclear, mono- and dinuclear palladium complexes; however, it was not possible to metallate the imines having the unprotected –B(OH)$_2$ group. This may be due to deactivation of the phenyl ring rather than to low stability of the resulting complexes. Thus, when the boronic ester group on a palladacycle suffers water hydrolysis

the expected product with the unprotected group is obtained in good yield as an air-stable solid. Also, transesterification reactions may be carried out at the boronic esters site to give new functionalized cyclometallated palladium(II) complexes.

4. Experimental

4.1. General remarks

Solvents were purified by standard methods [37]. Chemicals were reagent grade. Microanalyses were carried out using a Carlo Erba Elemental Analyser, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs Nujol mulls or KBr discs on a Satellite FTIR. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C–{^1H}) or 85% H_3PO_4 (^{31}P–{^1H}) and were recorded on a Bruker AV-300F or AV-500F spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a FISONS Quatro mass spectrometer with a Cs ion gun using matrixes of 3-nitrobenzyl alcohol or 3-nitrophenyl octyl ether (NOPE). The ESI-mass spectra were recorded using a QSTAR Elite mass spectrometer, using dichloromethane/acetonitrile or dichloromethane/ethanol as solvents.

4.2. Preparation of 2-F-4-(-OCH_2CH_2O–B)$C_6H_3C(H)$=O (**a**)

4-{$B(OH)_2$}$C_6H_3FC(H)$=O (0.304 g, 1.81 mmol) and 1,2-ethanediol (0.112 g, 1.80 mmol) were added to 50 cm^3 of toluene. The mixture was heated under reflux for 8 h. After cooling to room temperature, the solvent was evaporated to give a yellow pale solid. Yield: 81%. IR: ν(C=N) 1622sh, w, ν(HCO) 1687 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 10.40 [s, 1H, –CHO]; 7.88 [t, 1H, H6, ^3J(H5H6) = 7.6 Hz, ^3J(H6F) = 6.9]; 7.67 [d, 1H, H5, ^3J(H5H6) = 7.6]; 7.58 [d, 1H, H3, ^3J(H3F) = 10.8]; 4.42 [s, 4H,–OCH_2-CH_2O–].

Compounds **b–d** were obtained as yellow pales solid following a similar procedure.

4.3. 2-F-4-(-$O(CH_3)_2CC(CH_3)_2O$–B)$C_6H_3C(H)$=O (**b**)

Yield: 82%. IR: ν(C=N) 1626sh, w, ν(HCO) 1697 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 10.41 [s, 1H, –CHO]; 7.85 [t, 1H, H6, ^3J(H5H6) = 7.5, ^3J(H6F) = 6.9]; 7.68 [d, 1H, H5, ^3J(H5H6) = 7.5]; 7.58 [d, 1H, H3, ^3J(H3F) = 10.8]; 1.37 [s, 12H, –$OC(CH_3)_2C(CH_3)_2O$–].

4.4. 2-F-4-(-$OCH(CH_2)_3CHO$–B)$C_6H_3C(H)$=O (**c**)

Yield: 73%. IR: ν(C=N) 1620sh, m, ν(HCO) 1695 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 10.39 [s, 1H, –CHO]; 7.84 [t, 1H, H6, ^3J(H5H6) = 7.5, ^3J(H6F) = 6.9]; 7.65 [d, 1H, H5, ^3J(H5H6) = 7.5]; 7.56 [d, 1H, H3, ^3J(H3F) = 10.8]; 5.03 [s, 2H, H7, H11]; 2.03 [m, 2H, H8, H10]; 1.65 [s, 4H, H8′/H10′, H9, H9′].

4.5. 4-(-OCH_2CH_2O–B)$C_6H_4C(H)$=O (**d**)

Yield: 43%. IR: ν(C=N) 1679sh, m, ν(HCO) 1698 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 10.05 [s, 1H, –CHO]; 7.98 [d, 2H, H2/H6 ó H3/H5,^3J(H2H3) = 8.1]; 7.87 [d, 2H, H2/H6 ó H3/H5,^3J(H2H3) = 8.1]; 4.41 [s, 4H,–OCH_2CH_2O–].

4.6. Preparation of 2-F-4-(-OCH_2CH_2O–B)$C_6H_3C(H)$=N[2′-$(OH)C_6H_4$] (**1a**)

4-(-OCH_2CH_2O–B)$C_6H_3FC(H)$=O (0.188 g, 0.97 mmol) and 2-aminophenol (1.026 g, 0.97 mmol) were added to 50 cm^3 of chloroform. The mixture was heated under reflux in a modified Dean-Stark apparatus for 8 h. After cooling to room temperature, the solvent was evaporated to give an orange solid. Yield: 90%. IR: ν(C=N) 1620 m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 9.03 [s, 1H, Hi]; 8.17 [t, 1H, H6, ^3J(H5H6) = 7.5, ^3J(H6F) = 7.2]; 7.68 [d, 1H, H5, ^3J(H5H6) = 7.5]; 7.58 [d, 1H, H3, ^3J(H3F) = 10.8]; 7.36 [dd, 1H, H8, ^3J(H8H9) = 8.0, ^4J(H8H10) = 1.4]; 7.24 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.0, ^4J(H8H10) = 1.4]; 7.04 [dd, 1H, H11, ^3J(H10H11) = 8.0, ^4J(H9H11) = 1.4]; 6.93 [td, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.0, ^3J(H9H11) = 1.4]; 4.43 [s, 4H, –OCH_2-CH_2O–].

Compound **1b** was obtained as a yellow solid and compounds **1c–1d** were prepared as orange solids following a similar procedure.

4.7. 2-F-4-(-$O(CH_3)_2CC(CH_3)_2O$–B)$C_6H_3C(H)$=N[2′-$(OH)C_6H_4$] (**1b**)

Yield: 74%. IR: ν(C=N) 1621sh, m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 9.02 [s, 1H, Hi]; 8.13 [t, 1H, H6, ^3J(H5H6) = 7.5, ^3J(H6F) = 7.2]; 7.66 [d, 1H, H5, ^3J(H5H6) = 7.5]; 7.57 [d, 1H, H3, ^3J(H3F) = 10.8]; 7.34 [dd, 1H, H8, ^3J(H8H9) = 7.8, ^4J(H8H10) = 1.2]; 7.25 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 7.8, ^4J(H8H10) = 1.2]; 7.03 [dd, 1H, H11, ^3J(H10H11) = 7.8, ^4J(H9H11) = 1.2]; 6.90 [td, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 7.8, ^3J(H9H11) = 1.2]; 1.37 [s, 12H, –$OC(CH_3)_2C(CH_3)_2O$–]. ^{13}C–{^1H} NMR (75.47 MHz, $CDCl_3$, δ ppm, J Hz): δ = 163.92 [s, C2]; 160.54 [s, C4]; 152.47 [s, C12], 149.79 [d, Ci, ^3J(Ci,F) = 5.1]; 135.17 [s, C7]; 130.26 [d, C5, ^4J(C5,F) = 3.5]; 129.37 [s, C10]; 126.62 [d, C6, ^3J(C6F) = 1.7]; 125.61[d, C1, ^2J(C1,F) = 9.0]; 121.64 [d, C3, ^2J(C3,F) = 19.4]; 119.99 [s, C9]; 115.77 [s, C8]; 115.00 [s, C11]; 84.23 [s, C13, C14], 24.70 [s, $4CH_3$].

4.8. 2-F-4-(-$OCH(CH_2)_3CHO$–B)$C_6H_3C(H)$=N[2′-$(OH)C_6H_4$] (**1c**)

Yield: 82%. IR: ν(C=N) 1622 m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 9.03 [s, 1H, Hi]; 8.15 [t, 1H, H6, ^3J(H5H6) = 7.5, ^3J(H6F) = 7.2]; 7.65 [d, 1H, H5, ^3J(H5H6) = 7.5]; 7.56 [d, 1H, H3, ^3J(H3F) = 10.8]; 7.35 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.2]; 7.23 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.1, ^4J(H8H10) = 1.2]; 7.04 [dd, 1H, H11, ^3J(H10H11) = 8.1, ^4J(H9H11) = 1.2]; 6.93 [td, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1, ^3J(H9H11) = 1.2]; 5.04 [br, 2H, H13, H17]; 2.03 [m, 2H, H14, H16]; 1.69 [br, 4H, H14′/H16′, H15, H15′]. ^{13}C–{^1H} NMR (75.47 MHz, $CDCl_3$, δ ppm, J Hz): δ = 164.10 [s, C2]; 160.72 [s, C4]; 152.67 [s, C12], 149.90 [d, Ci, ^3J(Ci,F) = 5.1]; 135.32 [s, C7]; 130.57 [d, C5, ^4J(C5,F) = 3.5]; 129.62 [s, C10]; 126.91 [d, C6, ^3J(C6F) = 1.7]; 125.92 [d, C1, ^2J(C1,F) = 9.0]; 121.93 [d, C3, ^2J(C3,F) = 19.5]; 120.21 [s, C9]; 115.98 [s, C8]; 115.21 [s, C11]; 83.22 [s, C13, C17]; 34.66 [s, C14, C16]; 21.59 [s, C15].

4.9. 4-(-OCH_2CH_2O–B)$C_6H_4C(H)$=N[2′-$(OH)C_6H_4$] (**1d**)

Yield: 82%. IR: ν(C=N) 1622 m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.72 [s, 1H, Hi]; 7.94 [s, 4H, H2, H3, H5, H6]; 7.33 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.4]; 7.22 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.1, ^4J(H8H10) = 1.4]; 7.04 [dd, 1H, H11, ^3J(H10H11) = 8.1, ^4J(H9H11) = 1.4]; 6.92 [td, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1, ^3J(H9H11) = 1.4]; 4.43 [s, 4H, –OCH_2-CH_2O–].

4.10. Preparation of [Pd{2-F-4-(-OCH_2CH_2O–B)$C_6H_2C(H)$=N[2′-$(O)C_6H_4$]}]$_4$ (**2a**)

A pressure tube containing 4-(-OCH_2CH_2O–B)$C_6H_3FC(H)$=N[2′-$(OH)C_6H_4$] (0.167 g, 0.59 mmol), palladium(II) acetate (0.132 g,

0.59 mmol) and 20 cm^3 of dry toluene was sealed under argon. The mixture was heated for 24 h at 60 °C. After cooling to r.t. the red precipitate formed was filtered off and dried under vacuum. Yield: 69%. Anal. Calc. for $C_{60}H_{44}N_4O_{12}F_4B_4Pd_4$: C, 46.3; H, 2.8; N, 3.6. Found: C, 46.4; H, 2.8; N, 3.5%. IR: ν(C=N) 1590 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 7.57 [s, 1H, Hi]; 7.46 [d, 1H, H11, ^3J(H10H11) = 8.1]; 6.92 [m, 2H, H3, H10]; 6.56 [s, 1H, H5]; 6.49 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.2]; 6.24 [td, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1, ^4J(H9H11) = 1.2]; 4.30 [s, 4H, –OCH_2CH_2O–]. MS-FAB: m/z = [{(L-H_2)Pd}$_2H_2$]$^+$ = 779.95; [{(L-H_2)Pd}$_3$H]$^+$ = 1167.98; [(L-H_2)Pd]$_4^+$ = 1557.02.

Compounds **2b** and **2d** were obtained as red solids following a similar procedure.

4.11. [Pd{2-F-4-(-O(CH_3)$_2$CC(CH_3)$_2$O–B)C_6H_2C(H)=N[2′-(O)C_6H_4]}]$_4$

(2b) Yield: 79%. Anal. found: C, 51.3; H, 4.4; N, 3.2; $C_{76}H_{76}N_4O_{12}B_4F_4Pd_4$ requires C, 51.2; H, 4.3; N, 3.1%. IR: ν(C=N) 1573sh, m cm^{-1}. MS-FAB: m/z = [(L-H_2)Pd]$_4^+$ = 1782.0.

4.12. [Pd{4-(-OCH_2CH_2O–B)C_6H_3C(H)=N[2′-(O)C_6H_4]}]$_4$. (**2d**)

Yield: 63%. Anal. Calc. for $C_{60}H_{48}N_4O_{12}B_4Pd_4$: C, 48.5; H, 3.3; N, 3.8. Found: C, 48.6; H, 3.4; N, 3.7%. IR: ν(C=N) 1590 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 7.49 [d, 1H, H3, ^3J(H10H11) = 8.4]; 7.25 [d, 1H, H2, ^3J(H2H3) = 8.4]; 7.12 [s, 1H, Hi]; 6.96–6.87 [m, 2H, H10, H11]; 6.80 [s, 1H, H5]; 6.38 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.2]; 6.21 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1]; 4.29 [s, 4H, –OCH_2CH_2O–]. MS-FAB: m/z = [(L-H_2)Pd]$_4^+$ = 1485.7.

4.13. Preparation of [Pd{2-F-4-(-OC(CH_3)$_3$CHO–B)C_6H_2C(H)=N[2′-(O)C_6H_4]}]$_4$ (**2c**)

Method 1: a pressure tube containing 4-(-OCH_2CH_2O–B)C_6H_3FC(H)=N[2′-(OH)C_6H_4] (0.167 g, 0.59 mmol), palladium(II) acetate (0.132 g, 0.59 mmol) and 20 cm^3 of dry toluene was sealed under argon. The mixture was heated for 24 h at 60 °C. The solvent was removed under vacuum, and the residue obtained was recrystallized from dichloromethane/hexane. The red precipitate formed was filtered off and dried under vacuum. Yield: 62%.

Method 2: cis-1,2-cyclopentanediol (0.027 g, 0.26 mmol) was added to a solution of **2a** (0.102 g, 0.070 mmol) in dry chloroform under argon and stirred at room temperature for 10 min. The solvent was removed under vacuum to give a red residue which was chromatographed on a column packed with silica gel. Elution with ethyl acetate/hexane (1:1) afforded the final product as a red solid after solvent removal. Yield: 37%.

Anal. Calc. for $C_{72}H_{60}N_4O_{12}F_4Pd_4B_4$: C, 50.3; H, 3.5; N, 3.3. Found: C, 50.4; H, 3.6; N, 3.4%. IR: ν(C=N) 1592 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 7.61 [s, 1H, Hi]; 7.44 [d, 1H, H11, ^3J(H10H11) = 8.1]; 6.91 [m, 2H, H3, H10]; 6.51 [s, 1H, H5]; 6.48 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.2]; 6.21 [td, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1, ^4J(H9H11) = 1.2]; 4.92 [br, 2H, H13, H17]; 1.99 [m, 2H, H14, H16]; 1.67 [br, 4H, H14′/H16′, H15, H15′]. ^{13}C–{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ ppm, J Hz): δ = 168.35 [s, C12]; 159.73 [s, C2]; 157.66 [s, C4], 155.31 [s, C7]; 152.62 [s, Ci]; 139.43 [d, C1, ^2J(C1,F) = 6.5 Hz]; 135.93 [s, C6]; 133.9 [s, C5]; 131.40 [s, C10]; 124.41 [s, C9]; 117.03 [s, C8]; 115.90 [d, C3, ^2J(C3,F) = 17.5]; 115.19 [s, C11]; 82.82 [s, C13, C17]; 34.65 [s, C14, C16]; 21.69 [s, C15]. MS-FAB: m/z = [(L-H_2)Pd]$_4^+$ = 1717.9.

4.14. Preparation of [Pd{2-F-4-(-OCH_2CH_2O–B)C_6H_2C(H)=N[2′-(O)C_6H_4]}(PPh_3)] (**3a**)

PPh_3 (0.099 g, 0.38 mmol) was added to a suspension of **2a** (0.147 g, 0.09 mmol) in dry chloroform (15 cm^3). The mixture was stirred for 24 h at room temperature and the solvent removed to give a violet solid which was recrystallized form dichloromethane/hexane. Yield: 56%. Anal. Calc. for $C_{33}H_{28}NO_3PdFPB$: C, 60.6; H, 4.3; N, 2.1. Found: C, 60.6; H, 4.2; N, 3.4%. IR: ν(C=N) 1575 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.20 [d, 1H, Hi, ^4J(PHi) = 9.9]; 7.12 [dd, 1H, H8, ^3J(H8H9) = 7.8, ^4J(H8H10) = 1.5]; 6.96 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 7.8, ^4J(H8H10) = 1.5]; 6.88 [d, 1H, H3, ^3J(H3F) = 10.2]; 6.53 [d, 1H, H11, ^3J(H10H11) = 7.8]; 6.36 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 7.8]; 6.30 [d, 1H, H5, ^4J(PHi) = 3.6]; 4.11 [s, 4H, –OCH_2CH_2O–]. ^{31}P–{^{1}H} NMR (121.50 MHz, $CDCl_3$, δ ppm, J Hz): δ = 34.01 [s]. MS-FAB: m/z = [(L-H_2)Pd(PPh_3)]$^+$ = 651.1.

Compounds **3b–3d** were obtained as violet (**3b** and **3c**) or garnet (**3d**) solids following a similar procedure.

4.15. [Pd{2-F-4-(-O(CH_3)$_2$CC(CH_3)$_2$O–B)C_6H_2C(H)=N[2′-(O)C_6H_4]}(PPh_3)] (**3b**)

Method 1: similar procedure to that used in the synthesis of **3a**. Yield 29%.

Method 2: compound **3b** was also prepared by treating a solution of **3a** in dry chloroform (0.115 g, 0.18 mmol) with pinacol (0.022 g, 0.18 mmol) at room temperature under argon for 10 min. The solvent was then removed under vacuum to give a residue which was chromatographed on a column packed with silica gel. Elution with ethyl acetate/hexane (1:1) followed by recrystallization from dichloromethane/hexane afforded the final product as a violet solid. Yield: 55%.

Anal. Calc. for $C_{37}H_{34}NO_3PdFBP$: C, 62.8; H, 4.8; N, 1.9%. Found: C, 62.6; H, 4.7; N, 1.8%. IR: ν(C=N) 1573 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.18 [d, 1H, Hi, ^4J(PHi) = 9.9]; 7.11 [dd, 1H, H8, ^3J(H8H9) = 7.8, ^4J(H8H10) = 1.5]; 6.95 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 7.8, ^4J(H8H10) = 1.5]; 6.88 [d, 1H, H3, ^3J(H3F) = 10.5]; 6.55 [d, 1H, H11, ^3J(H10H11) = 7.8]; 6.37 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 7.8]; 6.31 [d, 1H, H5, ^4J(PH5) = 3.6]; 1.13 [s, 12H, –OC(CH_3)$_2$C(CH_3)$_2$O–]. ^{31}P–{^{1}H} NMR (121.50 MHz, $CDCl_3$, δ ppm, J Hz): δ = 37.77 [s]. ^{13}C–{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ ppm, J Hz): δ = 174.24 [s, C12]; 160.15 [s, C2]; 158.08 [s, C4]; 156.45 [s, C7]; 150.74 [s, Ci]; 143.82 [s, C1]; 139.08 [dd, ^3J(C5,P) = 7.3, ^4J(C5,F) = 2.4]; 135.59 [s, C6]; 134.97 [d, C-*ortho*, ^2J(C-*ortho*,P) = 12.6]; 132.28 [s, C10]; 130.85 [d, C-*para*, ^4J(C-*para*,P) = 2.4]; 129.45 [d, C-*ipso*, ^1J(C-*ipso*,P) = 48.3]; 128.56 [d, C-*meta*, ^3J(C-*meta*,P) = 10.8]; 122.14 [s, C9]; 117.22 [d, C3, ^2J(C3,F) = 18.2]; 116.22 [s, C8]; 114.15 [s, C11]; 83.61 [s, C13, C14], 24.76 [s, 4CH_3]. MS-FAB: m/z = [(L-H_2)Pd(PPh_3)]$^+$ = 707.1.

4.16. Preparation of [Pd{2-F-4-(-OC(CH_3)$_3$CHO–B)C_6H_2C(H)=N[2′-(O)-C_6H_4]}(PPh_3)] (**3c**)

Method 1: similar procedure to that used in the synthesis of **3a**. Yield 48%.

Method 2: To a solution of compound **3a** in dry chloroform (0.131 g, 0.20 mmol) *cis*-1,2-cyclopentanediol (0.030 g, 0.29 mmol) was added under argon and the resulting solution stirred for 10 min. The solvent was removed to give a violet solid, which was recrystallized from dichloromethane/hexane. Yield: 50%.

Anal. Calc. for $C_{36}H_{30}NO_3PdFPB$: C, 62.5; H, 4.4; N, 2.0. Found: C, 62.6; H, 4.3; N, 1.9%. IR: ν(C=N) 1573 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.19 [d, 1H, Hi, ^4J(PHi) = 10.2]; 7.11 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.5]; 6.95 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.1, ^4J(H8H10) = 1.5]; 6.86 [d, 1H, H3,

^3J(H3F) = 10.5]; 6.53 [d, 1H, H11, ^3J(H10H11) = 8.1]; 6.37 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1]; 6.28 [d, 1H, H5, ^4J(PHi) = 3.6]; 4.74 [br, 2H, H13, H17]; 1.86 [m, 6H, H14/H16, H14′/H16′, H15, H15′]. ^{31}P–{^{1}H} NMR (121.50 MHz, $CDCl_3$, δ ppm, J Hz): δ = 34.02 [s]. ^{13}C–{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ ppm, J Hz): δ = 174.28 [d, C12, ^3J(C12,P) = 2.8]; 160.11 [s, C2]; 158.04 [s, C4], 156.64 [s, C7]; 150.69 [s, Ci]; 143.94 [s, C1]; 139.20 [dd, C5, ^3J(C5,P) = 7.3, ^4J(C5,F) = 2.5]; 135.59 [s, C6]; 135.00 [d, C-*ortho*, ^2J(C-*ortho*,P) = 12.7]; 132.33 [s, C10]; 130.86 [d, C-*para*, ^4J(C-*para*,P) = 2.4]; 129.95 [d, C-*ipso*, ^1J(C-*ipso*,P) = 48.5]; 128.56 [d, C-*meta*, ^3J(C-*meta*,P) = 10.8]; 122.15[s, C9]; 117.37 [d, C3, ^2J(C3,F) = 18.2]; 116.22 [s, C8]; 114.18 [s, C11]; 82.56 [s, C13, C17]; 34.56 [s, C14, C16]; 21.35 [s, C15]. MS-FAB: m/z = [(L-H_2)Pd(PPh_3)]$^+$ = 691.1.

4.17. [Pd{4-(-OCH_2CH_2O–B)$C_6H_3C(H)$=N[2′-(O)C_6H_4]}(PPh_3)] (**3d**)

Yield: 86%. Anal. Calc. for $C_{33}H_{27}NO_3PdBP$: C, 62.5; H, 4.3; N, 2.2. Found: C, 62.6; H, 4.4; N, 2.1%. IR: ν(C=N) 1581 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 7.93 [d, 1H, Hi, ^4J(PHi) = 9.9]; 7.24 [d, 1H, H2, ^3J(H2H3) = 8.4]; 7.10 [m, 2H, H3, H8]; 6.95 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H111) = 8.1, ^4J(H8H10) = 1.5]; 6.57–6.52 [m, 2H, H5, H11]; 6.35 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1]; 4.11 [s, 4H, –OCH_2CH_2O–]. ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ ppm, J Hz): δ = 34.38 [s]. MS-FAB: m/z = [(L-H_2)Pd(PPh_3)]$^+$ = 633.1.

4.18. Preparation of [Pd{2-F-4-(-$OCH(CH_2)_3CHO$–B)$C_6H_2C(H)$=N[2′-(O)C_6H_4]}(μ-PPh_2(η^5-C_5H_4)Fe(η^5-C_5H_4)PPh_2)] (**4c**)

PPh_2(η^5-C_5H_4)Fe(η^5-C_5H_4)PPh_2 (0.018 g, 0.033 mmol) was added to a solution of **2a** (0.028 g, 0.016 mmol) in dry chloroform (15 cm^3). The mixture was stirred for 24 h at room temperature and the solvent removed to give a violet solid which was recrystallized from chloroform/hexane. Yield: 71%. Anal. Calc. for $C_{70}H_{58}N_2O_6Pd_2B_2F_2FeP_2$: C, 59.5; H, 4.1; N, 1.9. Found: C, 59.6; H, 4.3; N, 2.0%. IR: ν(C=N) 1575 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.14 [d, 1H, Hi, ^4J(PHi) = 10.2]; 7.12 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.5]; 6.98 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.1 Hz, ^4J(H8H10) = 1.5]; 6.86 [d, 1H, H3, ^3J(H3F) = 10.2]; 6.58 [d, 1H, H11, ^3J(H10H11) = 8.1]; 6.37 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1]; 6.21 [d, 1H, H5, ^4J(PHi) = 3.9]; $(CH)_{ferrocene}$ = 5.19; 4.73 (br, 2H, H13, H17); $(CH)_{ferrocene}$ = 4.28. ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ ppm, J Hz): δ = 24.31 [s]. ^{13}C–{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ ppm, J Hz): δ = 174.52 [d, C12, ^3J(C12,P) = 3.0]; 160.15 [s, C2]; 159.20 [s, C4], 156.95 [s, C7]; 150.56 [d, Ci, ^3J(Ci,P) = 4.6]; 143.82 [s, C1]; 139.23 [d, C5, ^3J(C5, P) = 7.3]; 135.13 [s, C6]; 134.20 [d, C-*ortho*, ^2J(C-*ortho*,P) = 12.3]; 132.28 [s, C10]; 131.22 [d, C-*ipso*, ^1J(C-*ipso*,P) = 49.3]; 130.52 [d, C-*para*, ^4J(C-*para*,P) = 2.1]; 128.23 [d, C-*meta*, ^3J(C-*meta*,P) = 10.7]; 122.00 [s, C9]; 117.25 [d, C3, ^2J(C3,F) = 18.1]; 116.17 [s, C8]; 113.84 [s, C11]; 82.58 [s, C13, C17]; 34.53 [s, C14, C16]; 21.51 [s, C15]. MS-FAB: m/z = [{(L-H_2)$_2$$Pd_2$(dppf)}$H_2$]$^+$ = 1414.0.

4.19. Preparation of [Pd{[2-F-4-$(HO)_2$]$BC_6H_2C(H)$=N[2′-(O)C_6H_4]}(PPh_3)] (**3e**)

To a stirred solution of **3a** (0.179 g, 0.27 mmol) in acetone was added water until the apparition of a red precipitate and the resulting mixture stirred for a further 48 h. The red precipitate formed was filtered of and dried under vacuum. Yield: 84%. Anal. Calc. for $C_{31}H_{24}BNO_3FPPd$: C, 59.5; H, 3.9; N, 2.2. Found: C, 59.4; H, 3.7; N, 2.3%. IR: ν(C=N) 1574 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.51 [d, 1H, Hi, ^4J(PHi) = 10.5]; 7.41 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.5]; 6.95 [d, 1H, H3, ^3J(H3F) = 11.1]; 6.86 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.1, ^4J(H8H10) = 1.5]; 6.38 [d, 1H, H5, ^4J(PHi) = 3.9]; 6.26 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1]; 6.20 [d, 1H, H11, ^3J(H10H11) = 8.1]. ^{31}P–{^{1}H} NMR (121.50 MHz, $CDCl_3$, δ ppm, J Hz): δ = 34.69 [s]. MS-FAB: m/z = [{(L-H_2)Pd(PPh_3)}H]$^+$ = 626.07.

Compounds **4d** and **1e** were obtained as violet solids following a similar procedure to the one described for the synthesis of **3c** (method 2; *vide supra*).

4.20. [Pd{4-(-$O(CH_3)_2C$-$C(CH_3)_2O$–B)$C_6H_3C(H)$=N[2′-(O)C_6H_4]}(PPh_3)]-(**3g**)

Yield: 42%. Anal. Calc. for $C_{37}H_{35}BNO_3PdP$: C, 64.4; H, 5.1; N, 2.0. Found: C, 64.3; H, 5.2; N, 1.9%. IR: ν(C=N) 1573 m. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 7.90 [d, 1H, Hi, ^4J(PHi) = 9.9]; 7.23 [d; 1H, H2, ^3J(H2H3) = 8.4]; 7.09–7.06 [m, 2H, H3, H8]; 6.94 [ddd, 1H, H10, ^3J(H9H10) = 7.1, ^3J(H10H11) = 8.4, ^4J(H8H10) = 1.5]; 6.57 [d, 1H, H5, ^3J(PH5) = 3.9]; 6.54 [d, 1H, H11, ^3J(H10H11) = 8.4] 6.34 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 7.1]; 1.13 [s, 12H, –$OC(CH_3)_2C(CH_3)_2O$–]. ^{13}C–{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ ppm, J Hz): δ = 173.65 [d, C12, ^3J(C12,P) = 3.3]; 157.21 [s, C4]; 156.25 [s, C2]; 154.50 [d, C7, ^3J(C7,P) = 7.5]; 143.46 [d, Ci, ^3J(Ci,P) = 7.4]; 135.33 [s, C6]; 134.91 [d, C-*ortho*, ^2J(C-*ortho*,P) = 12.7]; 131.96 [s, C5]; 130.92 [s, C10]; 130.67 [d, C-*para*, ^4J(C-*para*,P) = 2.3]; 130.19 [d, C-*ipso*, ^1J(C-*ipso*,P) = 47.9]; 128.44 [d, C-*meta*, ^3J(C-*meta*,P) = 10.8]; 126.75 [s, C3]; 122.04 [s, C9]; 115.87 [s, C8]; 113.77 [s, C11]; 83.27 [s, C13, C14], 24.69 [s, 4CH_3]; $C1_{ocl}$. ^{31}P–{^{1}H} NMR (121.50 MHz, $CDCl_3$, δ ppm, J Hz): δ = 34.20 [s]. MS-FAB: m/z = [(L-H_2)Pd(PPh_3)]$^+$ = 689.1.

4.21. [Pd{2-F-4-(-$O(CH_2)_2NH(CH_2)_2O$–B)$C_6H_2C(H)$=N[2′-(O)C_6H_4]}(PPh_3)] (**3f**)

Yield: 70%. Anal. Calc. for $C_{35}H_{31}N_2O_3PdBFP$: C, 60.5; H, 4.5; N, 4.0. Found: C, 60.4; H, 4.3; N, 4.1%. IR: ν(C=N) 1589 m. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ =8.20 [d, 1H, Hi, ^4J(PHi) = 10.2]; 7.11 [dd, 1H, H8, ^3J(H8H9) = 7.8, ^4J(H8H10) = 1.5]; 6.92 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 7.8, ^4J(H8-H10) = 1.5]; 6.74 [d, 1H, H3, ^3J(H3F) = 10.8]; 6.47 [d, 1H, H11, ^3J(H10H11) = 7.8]; 6.35 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 7.8]; 6.14 [d, 1H, H5, ^4J(PH5) = 3.9]. ^{31}P–{^{1}H} NMR (12- 1.50 MHz, $CDCl_3$, δ ppm, J Hz): δ = 35.26 [s]. MS-FAB: m/z = [(L-H_2)P-d(PPh_3)]$^+$ = 694.1

4.22. Preparation of 2-F-4-(-$OCH(CH_2)_3CHO$–B)$C_6H_3C(H)$=N[C_6H_{11}] (**1j**)

Compound **c** (0.296 g, 1.27 mmol) and cyclohexylamine (0.126 g, 1.27 mmol) were added to 50 cm^3 of dry chloroform. The mixture was heated under reflux in a modified Dean-Stark apparatus for 10 h. After cooling to room temperature, the solvent was evaporated to give a white solid. Yield: 85%. IR: ν(C=N) 1621sh, w cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 8.63 [s, 1H, Hi]; 7.98 [t, 1H, H6, ^3J(H5H6) = 7.5, ^3J(H6F) = 6.9]; 7.56 [d, 1H, H5, ^3J(H5H6) = 7.5]; 7.47 [d, 1H, H3, ^3J(H3F) = 10.8]; 5.01 [br, 2H, H7, H11]; 3.26 [m, 1H, H12], 2.01 [m, 2H, H8, H10]; 1.36 [br, 4H, H8′/H10′, H9, H9′]. ^{13}C–{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ ppm, J Hz): δ = 163.37 [s, C2]; 160.03 [s, C4]; 152.03 [d, Ci, ^3J(CiF) = 7.9]; 130.36 [d, C5, ^4J(C5F) = 5.6]; 127.11 [d, C6, ^3J(C6F) = 4.0]; 126.49 [d, C1, ^2J(C1F) = 16.0]; 121.49 [d, C3, ^2J(C3F) = 32.7]; 83.04 [s, C7, C11]; 70.36 [s, C12]; 34.60 [s, C8, C10]; 34.26 [s, C13, C17]; 25.59 [s, C15], 24.72 [s, C14, C16]; 21.53 [s, C9].

*4.23. Preparation of [Pd{2-F-4-(-OCH(CH$_2$)$_3$CHO–B)C$_6$H$_2$C(H)=N[C$_6$H$_{11}$]}-(CH$_3$COO)]$_2$ (**5j**)*

A pressure tube containing 4-(-OCH(CH$_2$)$_3$CHO–B)C$_6$H$_3$FC(H)=N[C$_6$H$_{11}$] (**f**) (0.287 g, 0.91 mmol), palladium(II) acetate (0.204 g, 0.91 mmol) and 20 cm^3 of dry toluene was sealed under argon. The resulting mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the solution was filtered through celite to remove the black palladium formed. The solvent was removed under vacuum and the residue obtained was tritured with ether to give a yellow solid. Yield: 59%. Anal. Calc. for $C_{40}H_{50}N_2O_8Pd_2F_2B_2$: C, 50.0; H, 5.3; N, 2.9. Found: C, 49.9; H, 5.3; N, 2.8%. IR: ν(C=N) 1610sh, w cm^{-1}, ν_{as}(COO) 1580s; ν_s(COO) 1417s. ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 7.62 [s, 1H, Hi]; 7.24 [s, 1H, H5]; 7.03 [d, 1H, H3, ^3J(H3F) = 10.2]; 4.96 [br, 2H, H7, H11]; 3.02 [m, 1H, H12], 2.16 [s, 3H, –OAc]. ^{13}C–{^{1}H} NMR (125.76 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 181.08 [s, CH$_3$COO–]; 162.99 [s, Ci]; 159.07 [s, C2]; 156.99 [s, C4]; 155.60 [d, C1, ^2J(C1F) = 1.9]; 135.89 [d, C6, ^3J(C6F) = 7.0]; 133.57 [d, C5, ^4J(C5F) = 2.8]; 116.1 [d, C3, ^2J(C3F) = 17.7]; 82.91 [s, C7, C11]; 65.22 [s, C12]; [34.65 (s), 34.55 (s) (C8/C10, C13, C17)]; 30.14 [s, C13, C17]; [25.89 (s), 25.6 (s), 25.09 (s), (C14, C15, C16)], 24.41 [s, *C*H$_3$COO–]; 21.42 [s, C9]. MS-FAB: *m*/*z* = [{(L-H$_2$)$_2$Pd$_2$(CH$_3$COO)}-H]$^+$ = 900.0, [(L-H)Pd(OCOCH$_3$)]$_2^+$ = 958.9.

*4.24. Preparation of [Pd{2-F-4-(-OCH(CH$_2$)$_3$CHO–B)C$_6$H$_2$C(H)=N[C$_6$-H$_{11}$]}(CH$_3$COO)-(PPh$_3$)] (**6j**)*

PPh$_3$ (0.075 g, 0.28 mmol) was added to a suspension of **1f** (0.136 g, 0.14 mmol) in acetone (15 cm^3). The mixture was stirred for 6 h and solvent removed under vacuum to give an orange residue which was recrystallized form chloroform/hexane. The yellow solid obtained was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (2%) afforded the final product as a white solid after solvent removal. Yield: 12%. Anal. Calc. for $C_{38}H_{40}NO_4PdBFP$: C, 61.5; H, 5.4; N, 1.9. Found: C, 61.4; H, 5.3; N, 1.8%. IR: ν(C=N) 1600 m, ν_{as}(COO) 1555 m; ν_s(COO) 1300 m cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 8.33 [d, 1H, Hi, ^4J(PHi) = 8.7]; 6.08 [dd, 1H, H3, ^3J(H3F) = 11.4, ^4J(H3H5) = 2.1]; 5.48 [dd, 1H, H5, ^3J(PH5) = 6.0, ^4J(H3H5) = 2.1]; 4.59 [br, 1H, H7/H11]; 4.41 [m, 1H, H12], 2.26 [m, 2H, H8, H10], 2.18 [s, 3H, C*H*$_3$COO–]. ^{31}P–{^{1}H} NMR (121.50 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 42.04 [s].

*4.25. Preparation of [Pd{2-F-4-[(O(CH$_2$)$_4$N)C(H)(CO$_2$H)]C$_6$H$_2$C(H)=N-[2′-(O)C$_6$H$_4$]}-(PPh$_3$)] (**3h**)*

To a suspension of glyoxylic acid (4.0 mg, 0.04 mmol) in dry dichloromethane (10 cm^3) was added **3b** (30.5 mg, 0.04 mmol) and morpholine (3.7 mg, 0.04 mmol) under argon, and the resulting solution stirred at room temperature for 7 days. The solvent was then removed to give a pink solid, which was recrystallized from dichloromethane/hexane. Yield: 49%. Anal. Calc. for $C_{37}H_{32}N_2O_4PdFP$: C, 61.3; H, 3.9; N, 4.4. Found: C, 61.4; H, 3.7; N, 4.5%. IR: ν(CO$_2$H) = 1729w, ν(C=N) = 1579 m. ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 8.17 [d, 1H, Hi, ^4J(PHi) = 10.2]; 7.11 [dd, 1H, H8, ^3J(H8H9) = 8.1, ^4J(H8H10) = 1.5]; 6.96 [td, 1H, H10, ^3J(H9H10) = ^3J(H10H11) = 8.1, ^4J(H8H10) = 1.5]; 6.58 [d, 1H, H3, ^3J(H3F) = 10.8]; 6.50 [d, 1H, H11, ^3J(H10H11) = 8.1]; 6.39 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 8.1]; 5.81 [d, 1H, H5, ^4J(PH5) = 3.6]; 3.70 [br, 4H, H14, H14′, H16, H16′]; 3.32 [s, 1H, H$_\alpha$]; 2.15 [br, 4H, H13, H13′ H17, H17′]. ^{13}C–{^{1}H} NMR (125.76 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 173.69 [s, –COOH]; 171.01 [s, C12]; 160.24 [s, C2]; 158.17 [s, C4]; 157.92 [s, C7]; 150.45 [s, Ci]; 141.81 [s, C1]; 137.12 [s, C5]; 135.50 [s, C6]; 134.93 [d, C-*ortho*, ^2J(C-*ortho*,P) = 12.7]; 132.34 [s, C10]; 131.16 [d, C-*para*, ^4J(C-*para*,P) = 2.1]; 129.55 [d, C-*ipso*, ^1J(C-*ipso*,P) = 48.7]; 128.63 [d, C-*meta*, ^3J(C-*meta*,P) = 10.8]; 122.02 [s, C9]; 116.27 [s, C8]; 114.62 [s, C11]; 112.31 [d, C3, ^2J(C3,F) = 21.4]; 74.38 [s, Cα]; 64.69 [s, C14, C16], 51.03 [s, C13, C17]. ^{31}P–{^{1}H} NMR (121.50 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 34.43 [s]. ESI-MS: [(L-H$_2$)Pd(PPh$_3$)H]$^+$ = 725.12.

Compound **3i** was obtained as a violet solid following a similar procedure to the one described for **3h**.

*4.26. [Pd{4-[(O(CH$_2$)$_4$N)C(H)(CO$_2$H)]C$_6$H$_3$C(H)=N[2′-(O)C$_6$H$_4$]}(PPh$_3$)] (**3i**)*

Yield: 37%. Anal. Calc. for $C_{37}H_{33}N_2O_4PdP$: C, 62.9; H, 4.7; N, 3.9. found: C, 62.8; H, 4.6; N, 3.8%. IR: ν(CO$_2$H) = 1731w, ν(C=N) = 1581 m. ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 7.93 [d, 1H, Hi, ^4J(PHi) = 10.2]; 7.10 [m, 2H, H2, H8]; 6.99–6.92 [m, 2H, H3, H10]; 6.52 [d, 1H, H11, ^3J(H10H11) = 8.4]; 6.37 [t, 1H, H9, ^3J(H8H9) = ^3J(H9H10) = 7.4]; 6.03 [d, 1H, H5, ^4J(PH5) = 2.7]; 3.83 [br, 4H, H14, H14′, H16, H16′]; 3.35 [s, 1H, H$_\alpha$]; 2.23 [br, 4H, H13, H13′, H17, H17′]. ^{13}C–{^{1}H} NMR (125.76 MHz, CDCl$_3$, δ ppm, *J* Hz): δ= 172.05 [s, C12]; 156.5–153.6 [C2, C4, C7, Ci]; 139.63 [d, C5, ^3J(C5,P) = 3.5]; 137.5 [s, C1]; 135.20 [s, C6]; 134.97[d, C-*ortho*, ^2J(C-*ortho*,P) = 12.8]; 132.14 [s, C10]; 131.11 [s, C-*para*]; 129.87 [d, C-*ipso*, ^1J(C-*ipso*,P) = 48.2]; 128.65 [d, C-*meta*, ^3J(C-*meta*,P) = 10.7]; 121.97 [s, C3]; 118.64 [s, C9]; 116.18 [s, C8]; 114.39 [s, C11]; 75.32 [s, Cα]; 64.68 [s, C14, C16], 51.03 [s, C13, C17]; –COOH$_{ocl}$ ^{31}P–{^{1}H} NMR (121.50 MHz, CDCl$_3$, δ ppm, *J* Hz): δ = 34.88 [s]. ESI-MS: [(L-H$_2$)Pd(PPh$_3$)H]$^+$ = 707.13.

4.27. X-ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Bruker Smart 1k CCD and a Bruker X8 Apex diffractometers using graphite-monochromated Mo Kα radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods 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. Chloroform solvent molecules in the crystal of complex **2c** were poorly defined and all the chlorine atoms were disordered and, consequently, refined in two complementary positions with occupancies of approximately 50% for the chlorine atoms of two solvent molecules and 70–30% for the third. The chlorine atoms of the two dichloromethane solvent molecules found in the crystal of **3c** were also disordered and refined in two positions with occupancies of approximately 50%. Large solvent accessible [approximately 10% of the total volume] voids were found in the crystal of **5j**. The smeared electron density (maximum residual electron density 1.137 e A^3) found did not allow to identify the nature of the solvent. The program PLATON/SQUEEZE [38] was used to remove the effects of the disordered solvent but no significant improvements were observed and the original data were finally used. Refinement converged with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [39].

Supplementary material

CCDC 730624, 730625 and 730626 contain the supplementary crystallographic data for **2c**, **3c** and **5j**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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