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PAPER

New cyclometallated precursors of unsubstituted N-phenylpyrazole [{Pd(phpz)(μ-X)}$_2$] (X = AcO or OH) and study of their reactivity towards selected ligands†

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A new acetate-bridged dinuclear palladacycle with unsubstituted N-phenylpyrazole [{Pd(phpz)(μ-AcO)}$_2$] **1** has been isolated and characterised, including an X-ray diffraction study. A survey of the Cambridge Structural Database (CSD) v. 5.31 looking for analogous dimeric CˆN cyclopalladated complexes has been done, exploring the incidence of *cisoid*/*transoid* arrangements, the preferred conformation of the eight-membered ring formed in the double bridge, the Pd–Pd distance and the main factors that affect it. The reaction of **1** with NBu_4OH yielded [{Pd(phpz)(μ-OH)}$_2$] **2** that has shown to be a complementary precursor of **1** in terms of acid/base reactivity. In this sense, both **1** and **2** are also well differentiated from halide precursors available to date. The preparation of selected complexes with potential applications in several fields, [Pd(phpz)(OˆN)] OˆN = N-*p*-chlorophenylsalycilaldiminate (N-*p*Clsal) **3**, picolinic acid (pic) **4**; 8-hydroxiquinolinate (oxin) **5**; 2-pyrrole-carboxaldeydate (2-pcal) **6**, [Pd(phpz)(OˆO)] OˆO = salycilaldehydate (sal) **7** acetylacetonate (acac) **8**, [{Pd(phpz)(μ-NˆS)}$_2$] NˆS = 2-mercapto-1-methylimidazolate (SMeimz) **11**; [{Pd(phpz)(μ-NˆO)}$_2$] NˆO = succinimidate (succ) **12**; [{Pd(phpz)(μ-NˆN)}$_2$] (NˆN = pyrazolate (pz) **13**, has been achieved using **1** or **2** as starting materials in acid/base reactions. Dithiocarbamate [Pd(phpz)(S_2CNEt_2)] **9** and dithiophosphate [Pd(phpz){S(S)P($OEt)_2$}] **10** derivatives have been synthesised in related reactions, and the reactivity of **1** against neutral phoshine ligands has also been tested with the preparation of [Pd(phpz)(AcO)(PPh_3)] **14**. The crystal structures of compounds **7**, **9**, **11**, **12** and **13** (this one obtained from a powder sample using synchrotron radiation) have also been established, and together with **1** are the first examples of complexes containing unsubstituted N-phenylpyrazole as cyclometallated backbone that have been deposited to date on the Cambridge Structural Database.

Introduction

Since the description of the easy cyclopalladation of azobenzene upon reaction with tetrachloropalladate in 1965,[1] several related organopalladium compounds that incorporated an intramolecular nitrogen atom were soon reported.[2] The chloride-bridged compounds were generally insoluble, and at that time their characterisation usually included the conversion to soluble mononuclear derivatives with phosphine, pyridine or acetilacetonato ligands.[3] Initial synthetic interest led to explore the more reactive palladium acetate as the source of the metal, which proved to be a more useful starting material than $PdCl_4^{2-}$ to achieve cyclopalladation in some cases, and especially since the resulting acetato-bridged dimers were conveniently soluble in common organic solvents.[4] Thus the availability of both halide and acetate-bridged dinuclear precursor, of for example unsubstituted orthometallated backbones such as 2-(2-pyridyl)phenyl or 7,8-benzoquinolyl, owing differentiated properties and reactivity has revealed to be a powerful synthetic tool extensively employed to obtain mono- and dinuclear cyclometallates.[5,6] Indeed, in our hands, the use of chloro-, acetate- or hydroxo- bridged dimers of those CˆN systems even promoted different coordination modes in phosphine–amide ligands.[7] Nowadays the initial synthetic interest that the cyclometallation reaction[3a,8] with Pd(II) salts attracted has been surpassed by the wide variety of applications found by cyclometallated compounds acting as mesogenic and luminescent agents or in different fields like organic synthesis, organometallic catalysis, medicinal and biological chemistry.[9]

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Regarding unsubstituted N-phenylpyrazole, its chloride-bridged and a few derivatives were reported in the early 70s,[10] but surprisingly the analogous acetate complex has not been synthesised and its chemistry has not been further explored apart from the excellent NMR study carried out by Caygill and Steel[11] on those derivatives previously reported. In fact not even a crystal structure has been deposited to date on the Cambridge Structural Database (CSD) v. 5.31 (November 2009 and three updates) and only a few containing substituted N-phenylpyrazoles have been reported so far.[11b,12]

On the other hand, in addition to their interest related to applied fields such as antitumour activity[13] or catalytic processes,[14] the synthetic value of palladium(II) and platinum(II) di-μ-hydroxo-complexes is a subject of continuous study.[15] For example, Sharp[16] and later others,[17] have employed several such complexes as precursors in the preparation of scarce oxo- and imido- derivatives that are also relevant to C–O and C–N bond forming reactions in catalytic processes. The reactivity towards protic substrates of dinuclear compounds $[Pd(\mu\text{-}OH)L^n]_2$ (L^n = orthometallated imine-based ligands) provides a general route to obtain mesomorphic mono- and dinuclear complexes.[18] In this sense, during the last few years we have also been developing the usefulness of binuclear hydroxo complexes of palladium, some of them with a cyclometallated backbone,[7,19] in the preparation of a wide variety of new compounds by means of a simple acid–base reaction.[20]

In this paper we present the synthesis of the cyclopalladated acetate dimer $[\{Pd(phpz)(\mu\text{-}AcO)\}_2]$ (phpz = N-phenylpyrazole) and its characterisation, including the X-ray structure determination and a comparative structural study with related compounds previously reported. The easy transformation to the corresponding di-μ-OH precursor is also described. Apart from their intrinsic interest, the acetate- and hydoxo-complexes of palladium whose reactivity we present here can offer a convenient and fastest route in the preparation of compounds that may even not be accessible using classical halide precursors. Specifically we explore here the reactivity of $[\{Pd(phpz)(\mu\text{-}X)\}_2]$ (X = AcO or OH) towards several protic electrophiles, related reactions like that against amines in the presence of carbon disulfide or also neutral ligands, all selected to yield complexes that have shown interesting structural features/physical properties with other orthometallated backbones similar to N-phenylpyrazole.

Results and discussion

Synthesis and characterisation

The acetato-bridged cyclometallated dimer $[\{Pd(phpz)(\mu\text{-}AcO)\}_2]$ **1** was readily prepared in good yield by the classical method that involves reacting N-phenylpyrazole with $Pd(AcO)_2$ in hot acetic acid. The infrared spectra of **1** displayed the characteristic absorptions around 1512 and 750 cm^{-1} corresponding to C=N absorption of the cyclometallated ligand and the out-of-plane C–H bending in disubstituted arenes, respectively. A strong broad band of carbonyl stretching centered in 1561 cm^{-1} is the main feature of the spectra that allows fast monitoring of the reactions explored with this precursor. Support for the proposed dinuclearity of complex **1** comes from the mass spectrometry, as can be implied by the *m*/*z* values for the observed fragments $[M^+$-acetate$]^+$ and $[Pd(phpz)]^+$. The abundances of the signals around the pattern ion are consistent with the natural isotopic ones.

The expected solubility of the new precursor allowed its NMR characterisation. In the experimental section are the two sets of signals observed in the $(CD_3)_2CO$ spectra attributed to a 1 : 3 mixture of *cis*- and *trans*-isomers. The presence of these isomers in acetato-bridged cyclometallated dimers is well known,[12a,21] and their distinction has been made on the basis of the methyl-AcO resonances that appear as one or two singlets for the *trans*- or *cis*-isomer, respectively. In our case the major isomer corresponds to a *trans*-arrangement and the assignment has been done by comparison with reported data for the free ligand and the acetylacetonate derivative.[11a] As it was also possible to grow single crystals of complex **1** suitable for X-ray diffraction, we were able to unambiguously confirm the molecular structure and the mentioned conformation, presented in Fig. 1. As mentioned above, this and the other X-ray structures presented in this paper are the first examples of complexes containing simple cyclometallated N-phenylpyrazole reported to date. Selected bond distances and angles are displayed in Table 1.

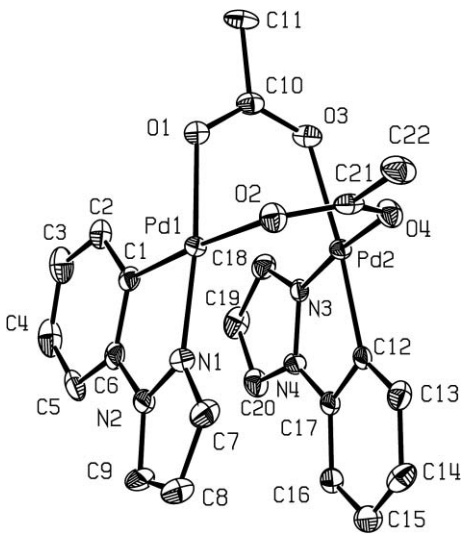


Fig. 1 ORTEP diagram of complex **1** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level.

A survey of the Cambridge Structural Database (CSD) v. 5.31 (November 2009 and three updates) reveals that the *trans*-arrangement is also preferred in the solid state and that a folded shape, commonly known as *open-book* structure, is always adopted. The CSD was searched for all the structures of dimeric C^N cyclopalladated complexes containing a double carboxylate bridge with a total of 86 *refcodes* matching the search, 15 of them have a six membered cyclopalladated C^N ring and the resting 71 have a five membered ring. It was not until 2002 that the first crystal structure of a *cisoid*-acetate bridged dinuclear cyclometallated complex was reported (refcode XUHVAX).[22] A selected iminic backbone $2,3,4\text{-}(MeO)_3C_6H_2C(H)=NCH_2CH_2OH$ with small steric hindrance at the N-atom was claimed to direct the adoption of this conformation, that can be determined without ambiguity due to the geometry of the iminic ligand itself. Since then only two structures with refcodes NOGKUG[23] and XEMQIQ01[24] and simple unsubstituted backbones have appeared as *cisoid* at the

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**, **11**, **12** and **13** (structure solved by powder X-ray diffraction)

1				**11**			
Pd(1)–C(1)	1.966(3)	Pd(2)–C(12)	1.963(3)	Pd(1)–C(1)	1.999(3)	Pd(2)–C(14)	2.006(3)
Pd(1)–N(1)	1.983(3)	Pd(2)–N(3)	1.999(3)	Pd(1)–N(1)	2.042(3)	Pd(2)–N(3)	2.121(3)
Pd(1)–O(1)	2.040(2)	Pd(2)–O(3)	2.132(2)	Pd(1)–N(7)	2.118(3)	Pd(2)–N(5)	2.031(3)
Pd(1)–O(2)	2.120(2)	Pd(2)–O(4)	2.037(2)	Pd(1)–S(1)	2.2985(9)	Pd(2)–S(2)	2.2925(10)
C(1)–Pd(1)–N(1)	80.86(13)	C(12)–Pd(2)–N(3)	81.44(12)	C(1)–Pd(1)–N(1)	80.84(13)	C(14)–Pd(2)–N(3)	173.86(13)
C(1)–Pd(1)–O(1)	94.33(12)	C(12)–Pd(2)–O(3)	175.02(11)	C(1)–Pd(1)–N(7)	174.18(13)	C(14)–Pd(2)–N(5)	81.03(14)
C(1)–Pd(1)–O(2)	175.70(12)	C(12)–Pd(2)–O(4)	93.49(12)	C(1)–Pd(1)–S(1)	92.85(10)	C(14)–Pd(2)–S(2)	92.11(11)
N(1)–Pd(1)–O(1)	173.91(10)	N(3)–Pd(2)–O(3)	95.46(10)	N(1)–Pd(1)–N(7)	93.82(12)	N(3)–Pd(2)–N(5)	95.05(12)
N(1)–Pd(1)–O(2)	94.86(11)	N(3)–Pd(2)–O(4)	174.92(10)	N(1)–Pd(1)–S(1)	173.49(9)	N(3)–Pd(2)–S(2)	91.74(9)
O(1)–Pd(1)–O(2)	89.96(9)	O(3)–Pd(2)–O(4)	89.61(9)	N(7)–Pd(1)–S(1)	92.55(8)	N(5)–Pd(2)–S(2)	173.12(9)
Pd(1)–Pd(2) 2.8421(3)				**Pd(1)–Pd(2) 2.9621(4)**			
12				13			
Pd(1)–C(1)	1.974(3)	Pd(2)–C(14)	1.968(3)	Pd(1)–C(1)	1.966	Pd(2)–C(10)	2.079
Pd(1)–N(1)	2.010(3)	Pd(2)–N(4)	1.994(3)	Pd(1)–N(1)	2.058	Pd(2)–N(3)	2.087
Pd(1)–N(3)	2.037(3)	Pd(2)–N(6)	2.026(3)	Pd(1)–N(5)	2.064	Pd(2)–N(6)	2.063
Pd(1)–O(2)	2.165(2)	Pd(2)–O(1)	2.151(2)	Pd(1)–N(7)	2.060	Pd(2)–N(8)	2.154
C(1)–Pd(1)–N(1)	81.31(12)	C(14)–Pd(2)–N(4)	81.56(13)	C(1)–Pd(1)–N(1)	79.35	C(10)–Pd(2)–N(3)	76.73
C(1)–Pd(1)–N(3)	94.10(12)	C(14)–Pd(2)–N(6)	94.21(13)				
C(1)–Pd(1)–O(2)	172.49(11)	C(14)–Pd(2)–O(1)	175.23(12)				
N(1)–Pd(1)–N(3)	175.24(11)	N(4)–Pd(2)–N(6)	175.77(11)				
N(1)–Pd(1)–O(2)	93.67(10)	N(4)–Pd(2)–O(1)	93.67(11)	N(5)–Pd(1)–N(7)	92.83	N(6)–Pd(2)–N(8)	82.69
N(3)–Pd(1)–O(2)	91.02(10)	N(6)–Pd(2)–O(1)	90.56(11)				
Pd(1)–Pd(2) 2.9106(4)				**Pd(1)–Pd(2) 3.569**			

CSD, although the authors have not even commented it in the articles. A survey of the data available at the CSD for NOGKUG and XEMQIQ01, paying special attention to the *trans* influence associated with an aromatic carbon and with an aromatic nitrogen, that produce bond distances *trans* to C significantly longer than *trans* to N, revealed a mistake in the assignment of C/N atoms around one palladium that would make these structures also *transoid*. It seems that the differentiated *trans* influence would favour the preferred *trans* geometric isomer in solid state, in which alternated long/short Pd–O distances are found in the double bridge (C_2), formed in this case by two identical units of bridge. *Cisoid*-isomer would involve two different units instead that fit worse, a side of the bridge with short Pd–O distances opposite to a side with long Pd–O distances (C_s).

The geometric isomer does not affect the conformation of the eight-membered ring formed in the double bridge. We have developed methods for the conformational classification of these rings.[25] From this perspective the Pd1–O1–C10–O3–Pd2–O4–C21–O2 ring in complex **1** displays a *boat–boat* conformation (BB = 0.9864; S = 0.0136 for σ = 10°) deformed 39°. The same distribution appears in 66 from 182 total fragments.

The surrounding of the Pd atoms in **1** may be described as planar and their deviation from the planar coordination has been quantified by measures of improper torsion angles, with values of w_1 = –0.06° and w_2 = –2.44° for Pd(1) and w_1 = –2.62° and w_2 = 0.05° for Pd(2).[26] These values correspond respectively to a tetrahedral and pyramidal square distortion from the ideal square-plane. The N–Pd–C angle, 80.86(13)° and 81.44(12)°, is similar to that found in related complexes with substituted N-phenylpyrazoles.[11b,12] Pd(1)–Pd(2) distance of 2.8421(3) Å is well in the generally accepted range for a Pd–Pd intramolecular interaction (< 3.00 Å). Some authors[27] claimed that this interaction should not be considered a bond up to 2.62 Å (taking it as the sum of square planar palladium covalent radius),[28] which would exclude all the structures surveyed here (mean Pd–Pd distance = 2.924; min. = 2.823; max. = 3.281 Å, 55 refcodes once excluded those with errors, disorder or not availability of 3D coordinates). When working with the more recent data set[29] the value of 1.39(6) Å for Pd covalent radius takes the complexes of the low part of the list close to a single bond. The distance in **1** is quite short, as it is for the 11 complexes that contain a cyclometallated backbone formed by a set of 6 (including the C bonded to Pd) and 5 membered rings like N-phenylpyrazole (mean Pd–Pd distance = 2.874, min. = 2.831; max. = 3.159 Å). In fact only the complex JEPVEF,[30] that has the maximum distance of 3.159 Å with the hindering 2-(4′,4′-dimethyl-2-oxazolinyl)phenyl backbone, is up to 2.88 Å in this group. Other planar backbones with a set of two 6 membered rings like 2-phenylpyridine produce 8 complexes in the similar range of Pd–Pd distances, all below 2.90 Å. Azobencenes and imine based ligands (23 refcodes: mean Pd–Pd distance = 2.980; min. = 2.834; max. = 3.281 Å) that bear freely rotating groups on the N atom bonded to Pd, together with N,N dimethyl benzylamine and related systems are the cyclometallating ligands prone to give Pd–Pd distances up to 2.90 Å in the family of complexes under study. We grouped separately complexes with a palladacycle of six members that have longer Pd–Pd distances (mean Pd–Pd distance = 2.987; min. = 2.888; max. = 3.113 Å). Thus, in complexes with a double carboxylate bridge, it seems that the number of atoms in the palladacycle, the bulky substituents on key positions and the planarity of the cyclometallated ligands (with potential interactions between faced groups) are the main factors that would control the Pd–Pd distance.

Complex **1** displays an interesting arrangement of the two phpz ligands, nearly parallel but not eclipsed with *centroid*-plane and *centroid–centroid* distances compatible with a face-to-face sliced intramolecular π–π interaction. (Fig. 2)

The cyclometallated precursor [{Pd(phpz)(μ-OH)}$_2$] **2** was conveniently prepared by the smooth reaction of the acetate-bridged complex with NBu_4OH in acetone. The IR spectrum of the new complex exhibited a clean carbonyl region and the expected

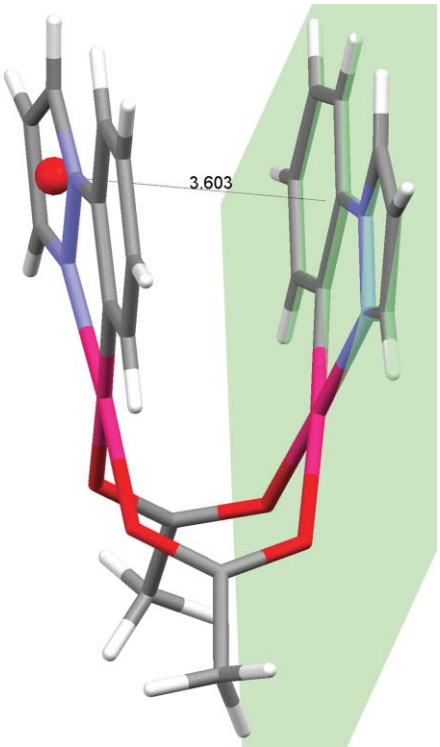


Fig. 2 Intramolecular arrangement in **1** displaying *centroid*-plane distances.

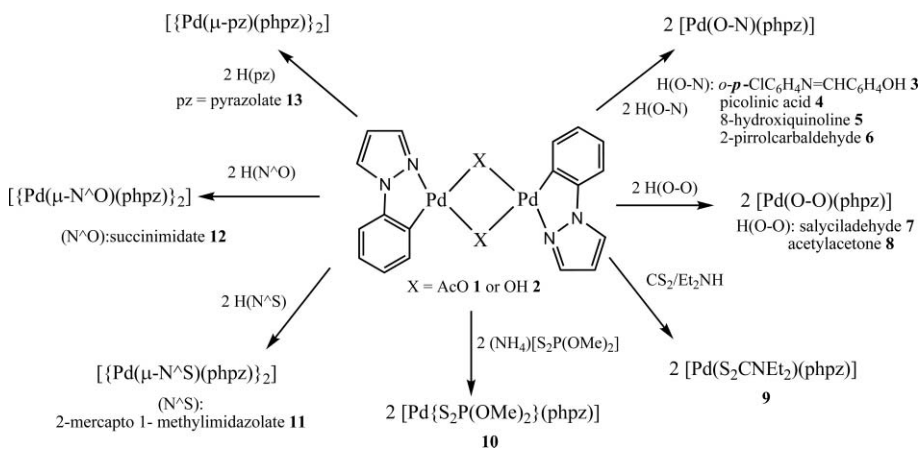
bands for the cyclometallated backbone, together with a 3371 cm^{-1} absorbance due to the ν(OH) stretching. The ^{1}H NMR data of **2** are collected in the experimental section and include a conclusive high field resonance characteristic of palladium hydroxo-complexes.[19] Further evidence of the proposed coordination is obtained with mass spectrometry, with a fragmentation pattern similar to that shown by **1**.

As mentioned above, complexes containing the $\{Pd(\mu\text{-}X)\}_2$ (X = AcO or OH) core are good synthetic precursors, as their reactions towards protic electrophiles have allowed the isolation of numerous compounds in good yields. The reactions explored in this paper using **1** and **2** as precursors against a selection of ligands are displayed in Scheme 1 and specific conditions followed for each of them are collected in the Experimental.

In the excellent review carried out by Ghedini and coworkers,[9a] they have pointed out the relationship between molecular geometries, types of ligands and important physical properties of dinuclear and mononuclear cyclometallated derivatives containing OˆO or OˆN complementary ligands. Thus, the authors have studied the effects exerted by different bridging groups on the spectroscopic and liquid-crystal properties of complexes type $[\{Pd(C\hat{}N)(\mu\text{-}X)\}_2]$ (X = halide, azido, thiocyanate, oxalate or acetate),[31] or the presence of an asymmetric coordination around palladium as a key aspect for photophysical properties, well exemplified by complexes [Pd(phpy)(oxin-R)] that emit in solution at room temperature.[32] Cyclopalladated acetylacetonate complexes have also been thoroughly studied, showing again the importance of the orthometallated backbone and the substituents on the *acac* moiety in the fine tuning of properties.[33] As a whole these results suggest that related complexes can be candidates for the above mentioned practical applications.

Our new precursors react with weak protic acids H(LˆL) to give mono- or binuclear species depending on whether the deprotonated acid $(L\hat{}L)^-$ is *exo*- or *endo*-bidentate. These reactions can be viewed as an initial proton abstraction by **1–2** that provides $(L\hat{}L)^-$ and the metal substrate, subsequently trapped by the anion to form the new complexes of general formula [Pd(phpz)(LˆL)] (**3–10**) or $[\{Pd(phpz)(\mu\text{-}N\hat{}X)\}_2]$ (**11–13**) respectively. It is worth noting that the synthesis of the *acac* complex **8** has been previously reported by reacting $[\{Pd(phpz)(\mu\text{-}Cl)\}_2]$ with an excess of Na(acac) prepared in advance.[11b] Longer reaction times (24 h) and a different work-up in the reported procedure in comparison with the straightforward route that we present here, allow one to envisage the general usefulness of our precursors when reacting with other substrates.

Thus a 30 min reaction at room temperature with selected H(OˆO) or H(OˆN) ligands was enough to obtain mononuclear complexes **3–8** when the hydroxo-complex **2** was employed as starting material. With the exception of **6** and **7**, that even under reflux and excess of ligand produced mixtures with **1**, the new compounds can be prepared from the di μ-acetate precursor in the same smooth conditions. The derivatives are air-stable yellow or white solids and their infrared spectra show the characteristic absorptions of the cyclometallated ligand, partially overlapped



Scheme 1 Reactivity of the acetato and hydroxo-complexes under study.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **7** and **9**

7				**9**	
Pd(1)–C(1)	1.967(5)	Pd(2)–C(17)	1.961(5)	Pd(1)–C(1)	2.004(3)
Pd(1)–N(1)	1.984(4)	Pd(2)–N(3)	1.996(4)	Pd(1)–N(1)	2.045(2)
Pd(1)–O(1)	2.088(4)	Pd(2)–O(3)	2.105(4)	Pd(1)–S(1)	2.2906(7)
Pd(1)–O(2)	1.992(3)	Pd(2)–O(4)	2.005(4)	Pd(1)–S(2)	2.3961(7)
C(1)–Pd(1)–N(1)	80.91(19)	C(17)–Pd(2)–N(3)	81.16(19)	C(1)–Pd(1)–N(1)	80.77(10)
C(1)–Pd(1)–O(1)	174.43(17)	C(17)–Pd(2)–O(3)	175.23(17)	C(1)–Pd(1)–S(1)	98.55(8)
C(1)–Pd(1)–O(2)	92.52(17)	C(17)–Pd(2)–O(4)	91.72(17)	C(1)–Pd(1)–S(2)	172.88(8)
N(1)–Pd(1)–O(1)	93.63(16)	N(3)–Pd(2)–O(3)	94.37(16)	N(1)–Pd(1)–S(1)	178.68(7)
N(1)–Pd(1)–O(2)	172.61(16)	N(3)–Pd(2)–O(4)	171.98(16)	N(1)–Pd(1)–S(2)	105.14(7)
O(1)–Pd(1)–O(2)	92.86(14)	O(3)–Pd(2)–O(4)	92.63(14)	S(1)–Pd(1)–S(2)	75.46(2)

in some cases with those of the incoming ligands. However the disappearance of hydroxo or carbonyl stretching gives unequivocal monitoring of the reaction, in agreement with the ^{1}H NMR spectra that show no methyl (reactions with **1**) or high field (reactions with **2**) resonances.

Although mononuclear complexes can exist as two isomers depending on the relative positions of the CˆN/OˆO or CˆN/OˆN chelating systems, the presence of only one isomer was observed by ^{1}H NMR except for **4** that displayed two sets of resonances with 1 : 3 relative proportion. M^+ and/or $M^+ + 23$ signals in the mass spectra support the proposed formulation.

The preparation of the dithiocarbamate complex **9** should involve a first step of amine deprotonation, followed by nucleophilic attack of Et_2N^- to carbon disulfide to form the dithiocarbamate anion in a well known reactivity of hydroxo complexes[34,19d,20c] that have allowed the preparation of new mesomorphic mononuclear orthometallated palladium complexes.[18b] Characteristic dithiocarbamate vibrations were found in the ν(CN) and ν(CS) regions. The presence of only one band in the latter at 1075 cm^{-1} supports the bidentate coordination of the dithio- ligand.[35] As found in other cyclopalladated systems, the alkyl groups on the dithiocarbamate are equivalent and give one set of NMR resonances for NEt_2 protons.[19d] The considerable nucleophilicity of the bridging groups of **1** and **2** make them also reactive towards ammonium O,O′-dimethyldithiophosphate, yielding complex **10** with the concomitant release of NH_3 and H_2O. The ^{31}P NMR of **10** shows a single resonance for the coordinated dithiophosphate ligand at the usual range.

Suitable crystals of **7** (two molecules in the asymmetric unit) and **9** were grown from CH_2Cl_2–hexane, enabling their molecular structures to be confirmed by X-ray single crystal diffraction (Fig. 3 and 4, respectively, and Table 2).

The deviation from the planar coordination has been quantified by measurements of improper torsion angles.[26] The values are 0.99° (C1O2O1Pd1), –2.36° (N1O1O2Pd1), 1.37° (C17O4O3Pd2), –2.62° (N3O3O4Pd2) in **7**, while they are 2.39° (C1S1S2Pd1) and –0.68° (N1S2S1Pd1) in **9**. Thus, the coordination around Pd is essentially planar in the two complexes, with a slight square pyramidal distortion. The bite angle that involves the CˆN ligand is also close to 81°.

The planar molecules of **7** are packed in pairs with the salicylate of one of them in front of the orthometallated ligand of the other. A distance of 3.419 Å between the planes defined by these ligands corresponds to intermolecular π–π face to face sliced interaction.[36] Furthermore the planes of a pair of molecules are located at 71°

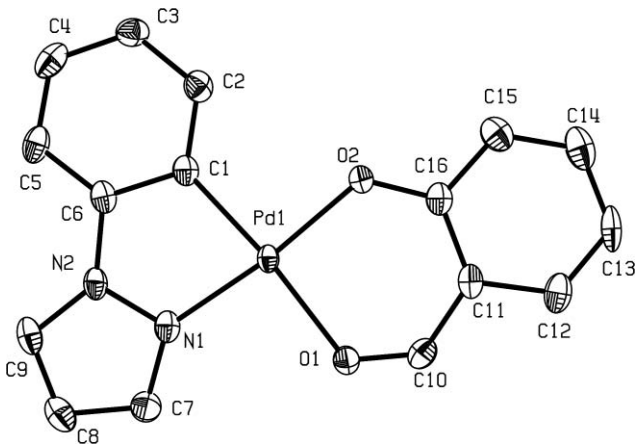


Fig. 3 ORTEP diagram of complex **7** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level.

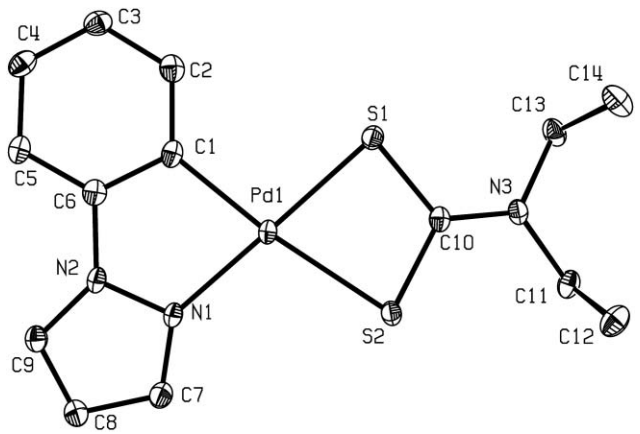


Fig. 4 ORTEP diagram of complex **9** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level.

from neighbour pairs associated by means of CH-π interaction. This packing can be observed in Fig. 5(a), and also the very similar one found in complex **9** (Fig. 5(b)).

As mentioned in the introduction, the reactivity of di-μ hydroxo complexes towards protic substrates has provided a general route to other dinuclear complexes with double and mixed bridges. An interesting reaction explored here has been that of **1** or **2** against 2-mercapto-1-methyl imidazole that yields dinuclear complex **11**. We have recently prepared[37] cyclometallated palladium complexes with heterocyclic thiones that exhibited an exceptional behaviour

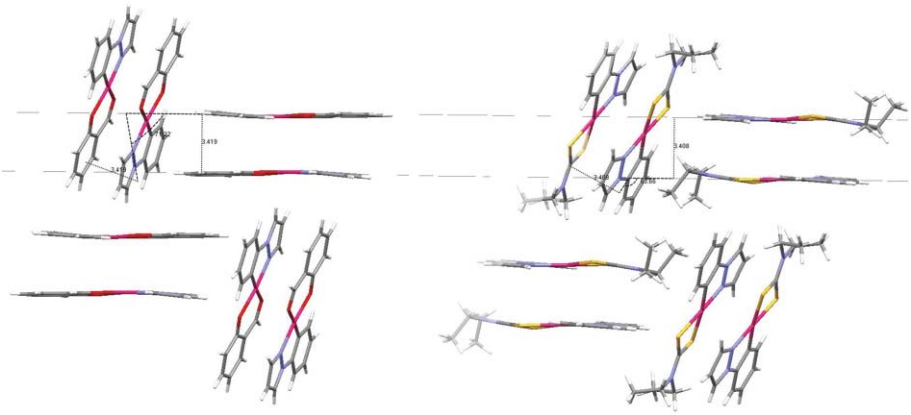


Fig. 5 Crystal packing found in **7** (a) and **9** (b).

since intense photoluminescence was found in both solid state and in solution, at room temperature or 77 K, supporting the crucial role played for those auxiliary ligands in the luminescent properties of palladacycles suggested by other authors.[9a] Characterisation data of the new complex **11** in solid state and solution are collected in the Experimental section. In this case its dinuclear *head to tail* nature, the most common arrangement in this type of complexes,[38] has also been confirmed by single crystal X-ray analysis. It is noticeable that no equilibrium in solution with the *head to head* configuration was detected by ^{1}H NMR, and only one sharp singlet for the *–Me* protons was observed.

The corresponding ORTEP drawing is shown in Fig. 6, while the relevant bond lengths and angles are reported in Table 1.

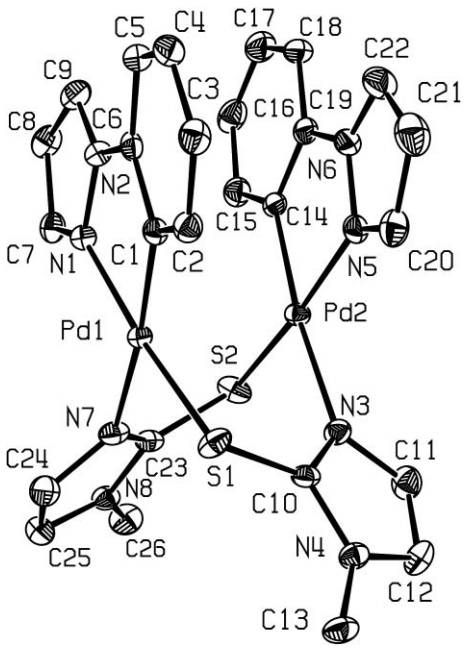


Fig. 6 ORTEP diagram of complex **11** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level.

The influence of the N–C–S bond angle on the stability of heterocyclic-2-thiolate dipalladium complexes has been studied. Complexes containing a five-membered heterocyclic ring such **11** have larger angles than those of six-membered ones and are expected to be stabilised as dimers.[39] Complex **11** exhibits S1–C10–N3 and S2–C23–N7 angles of 128.2(3)° and 129.6(3)° respectively, in the range of those previously reported for related Pd complexes. Regarding the cyclometallated ligands, an *anti*-arrangement of identical donor atoms is found with bite angles again close to 81° and this time the conformation of the eight-membered ring Pd1–S1–C10–N3–Pd2–S2–C23–N4 is *twist-boat* deformed 41°. Like in complex **1** an *open-book* geometry is adopted, accompanied by a Pd(1)–Pd(2) distance of 2.962(4) Å, within the generally accepted value for a Pd–Pd intramolecular interaction although longer than that found in **1**. The geometry around the palladium centres is almost planar with values of $w_1 = 1.41°$ and $w_2 = 0.90°$ for Pd(1) (tetrahedral distortion) and $w_1 = -3.11$ and $w_2 = 0.76°$ for Pd(2) (pyramidal square distortion). Also in common with complex **1** is the arrangement of the two phpz ligands described above, that suggest a face to face sliced intramolecular π–π interaction. In complex **11** we have also found relevant intermolecular CH/π interactions (with short H···C distances in the range 2.413–2.792 Å) and bond lengths and angles that suggest likely H···Pd anagostic interactions[40,41] and weak hydrogen bonding (Fig. 7).

On the other hand, during the last few years we have devoted our effort to understand, control and exploit the diverse functions and role of imidate anionic ligands (rather unusual pseudohalides with a subtle blend of σ-donating and π-accepting ability)[42] in topical and important Pd-catalysed cross-coupling reactions.[43] From the discovery of the useful precatalyst[44] [Pd(Br)(N-succ)(PPh_3)$_2$] (Sigma-Aldrich; Cat. No. 643742) for Stille reaction to its recent application for Suzuki–Miyaura cross-couplings of benzylic halides,[45] we have explored different synthetic routes to get second generation imidato precatalysts. Among them, binuclear cyclometallated palladium(II) complexes and mononuclear phosphine adducts have been evaluated in Stille,[46] Suzuki and Sonogashira reactions,[47] and later phosphine-free anionic dinuclear imidate complexes[48] containing a palladacyclopentadiene backbone have shown superb performance in Stille couplings. We decided then to prepare a sample imidate complex **12** that suggests that a new chemistry of phenylpyrazole complexes in the fields above mentioned could be explored. Again important differences were found between precursors **1** and **2** when reacted against succinimide. Thus straightforward reaction with **2** takes place at room temperature in 30 min while the acetate precursor could not deprotonate succinimide even in excess of it and keeping

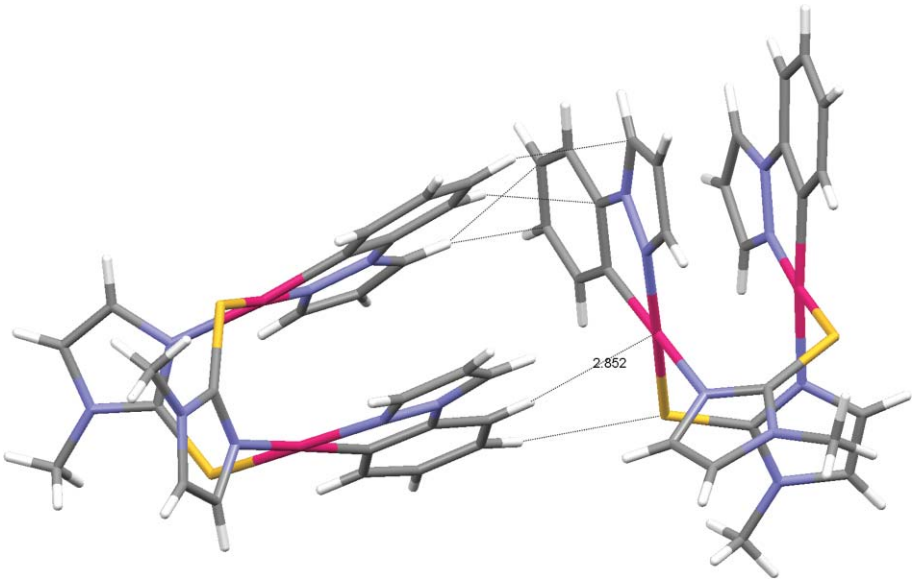


Fig. 7 Details of the interactions in **11**.

the reaction under continued reflux. The IR spectra of the new complex exhibited the expected bands for the cyclometallated backbone, together with two strong bands in the carbonyl region characteristic of a bridging –NCO– coordination of the imidate ligand. Also mass spectrometry and X-ray analysis support the proposed dinuclearity of complex **12**, whose structure is displayed in Fig. 8 and selected bond lengths and angles are collected in Table 1.

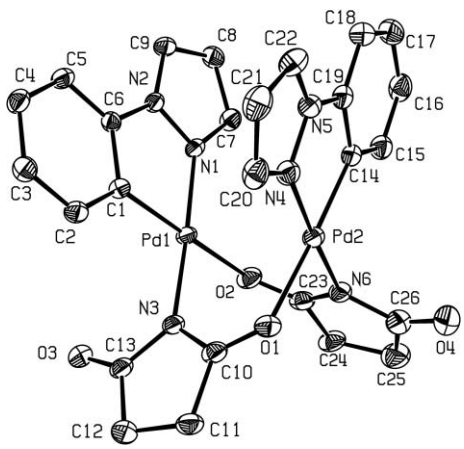


Fig. 8 ORTEP diagram of complex **12** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level.

In accordance with all the dinuclear imidate compounds reported to date, an *anti*-arrangement of identical donor atoms, and an *open-book* geometry is found in **12**.[42,49]

A slightly shorter Pd(1)–Pd(2) distance of 2.9106(4) Å than those found in the analogous di-μ-succinimidate compounds with N-phenylbenzaldimine (2.9793 Å)[42] phenylpyridine (2.9544 Å)[49a] or the bulkier 2-dimethylaminomethyl(ferrocenyl) (3.040 Å)[49d] as orthometallated backbones should give account of its different steric requirements and the interactions established between the faced cyclometallates. In **12** molecules the atoms of the orthometallated rings overlap in major extent than in **1** or **11** and the angle of phpz planes opens to 29°. Fig. 9 shows the packing of molecules with parallel intermolecular phpz planes separated in alternating 3.424 and 3.440 Å. Both Pd atoms display a tetrahedral distortion ($w_1 = 3.67°$ and $w_2 = 0.55°$ for Pd(1) and $w_1 = 0.07°$ and $w_2 = 0.11°$ for Pd(2)) and the conformation of the eight-membered ring Pd1–N3–C10–O1–Pd2–N6–C23–O2 is *twist-boat* deformed 42°.

Our last test of reactivity against acidic ligands of **1** and **2** allowed the preparation of the di-μ-pyrazolate complex **13** from both precursors. A large area of coordination and supramolecular chemistry has been developed around pyrazole and pyrazolate anions.[50] As an example, homoleptic pyrazolate complexes have been widely studied because of their potential use as liquid crystals,[51] antimicrobial drugs[52] or phosphorescent materials.[53] The bridging pyrazolate in cyclometallated Pt(II) complexes have shown to control the degree of metal–metal interaction and thus the nature of excited states.[54]

We have recently reported the similar solid state arrangement of "interlocked dimers" following a herringbone-like pattern found in all neutral dinuclear square-planar complexes having μ-pz or related bridges and planar aromatic ligands completing the coordination spheres.[40] There we confirmed this extent with the crystal structures of three pseudopolymorphs of the 2-phenylpyridine complex [{Pd(ppy)(μ-pz)}$_2$], two of which were elucidated by powder X-ray diffraction, and the support of DFT-based calculations. Due to the scarce solubility of **13**, that nevertheless allowed spectroscopic characterisation (see Experimental), and also to avoid the perturbation of the crystallisation process, we have elucidated its structure by powder diffraction using synchrotron radiation. Fig. 10 shows the expected packing of "dimers" where the N-phenylpyrazole ligands overlap with a distance between planes of 3.577 Å, and Table 1 collects selected crystallographic data.

The Pd···Pd separation shows a value of 3.569 Å within the range of related compounds.[40] The central six-membered ring

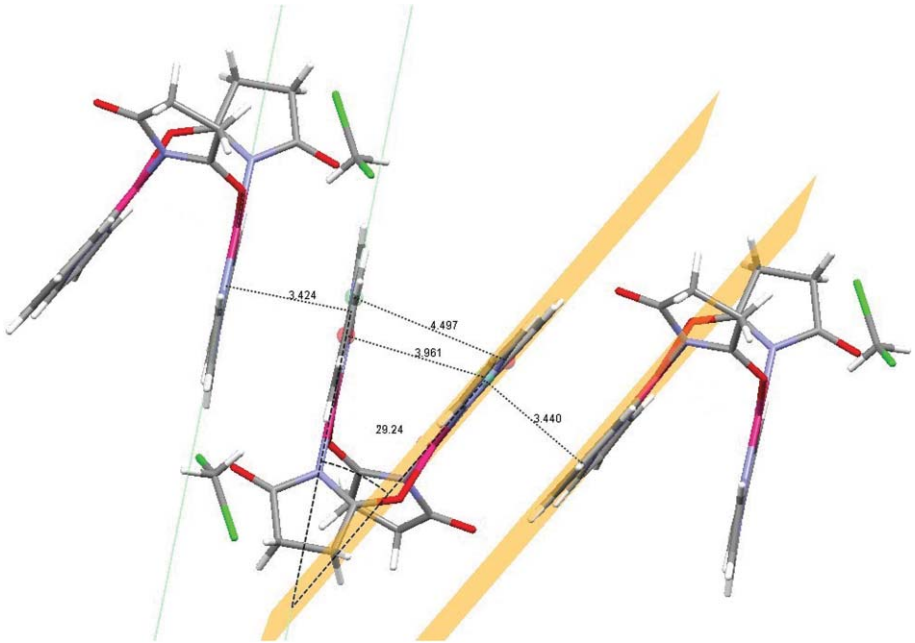


Fig. 9 Crystal inter- and intramolecular packing in succinimidate complex **12**.

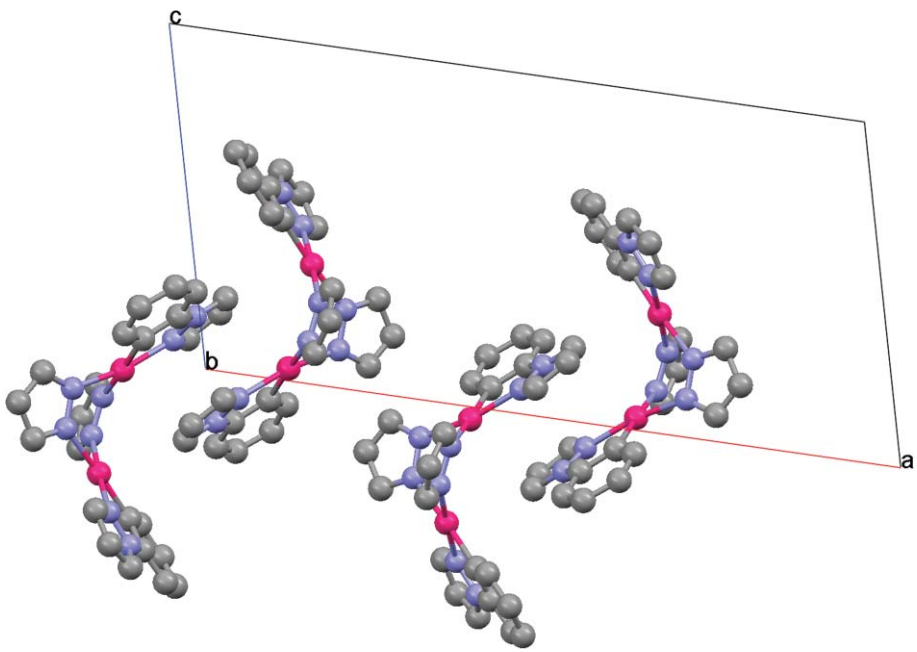


Fig. 10 "Dimers" of [{Pd(phpz)(μ-pz)}$_2$], **13**.

consisting of the two Pd atoms and the four pyrazolyl N atoms has a boat-shaped conformation with mean Pd–N_{pz} distances of 2.085 Å and N–Pd–N mean angle of 87.76° between the two pyrazolate groups. This conformation creates an "open book" disposition for the square-planar environment of the two Pd atoms, the (phpz)Pd_1 and (phpz)Pd_2 planes forming a dihedral angle of 81.35°.

As mentioned in the introduction, the conversion to soluble mononuclear derivatives with phosphine or pyridine has been a typical reaction of dinuclear precursor since the early advances in this field. In our case, the triphenylphosphine adduct **14** was synthesised in good yield by reaction of this ligand and the parent dinuclear acetate precursor **1** in dichloromethane. The reaction against such neutral ligands has been explored with other cyclometallated backbones to prepare mononuclear derivatives that improve the catalytic activity of the starting materials in cross-coupling reactions.[55] The presence of phosphine ligands in monomeric cyclometallated halo-complexes has also revealed crucial to increase growth inhibitory activity against murine leukaemias.[56] The IR spectra of the new complex exhibited the bands for the cyclometallated backbone, together with those attributed to the incoming phosphine ligand and one strong carbonyl band around 1600 cm^{-1}. The ^{31}P NMR spectrum of the

complex shows characteristic singlet resonance at 43.60 ppm, in the expected range for Pd(II) complexes.

Conclusion

We have synthesised two new versatile precursors bearing AcO or OH bridges with simple N-phenylpyrazole acting as an orthometallated backbone. The exploration of their reactivity against selected ligands to yield twelve new complexes with potential applications is also presented. The scarcity of complexes with this orthometallated ligand is stated by the fact that the six crystal structures reported here, one of them elucidated from a powder sample using X-ray synchrotron radiation, are the first to be deposited at the CSD. A survey of this database about dimeric CˆN cyclopalladated complexes with a carboxylate bridging core like **1** reveals the most frequent ligands that produce them, the preferred conformations adopted in complexes and the main factors that seem to control the Pd–Pd distance.

Experimental

Materials and physical techniques

All chemicals were of reagent grade and were used without further purification. Solvents were dried and distilled by general methods before use. C, H, and N analyses were carried out with a microanalyzer Carlo Erba model EA1108. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. ESI-MS analyses were performed on an Agilent VL mass spectrometer. The ionization mechanism used was electrospray in positive and negative ion full scan mode using acetonitrile as solvent and nitrogen gas for desolvation. The NMR spectra of $CDCl_3$ solutions were recorded on a Bruker spectrometer (AC 200E or AC 300E).

Synthesis of precursors [{Pd(phpz)(μ-AcO)}$_2$] and [{Pd(phpz)(μ-OH)}$_2$] (1 and 2)

[{Pd(phpz)(μ-AcO)}$_2$] 1. Palladium acetate (500 mg (2.22 mmol) and excess phenylpyrazol (0.3 mL) were suspended in glacial acetic acid (80 mL) and the mixture was heated on oil bath (50 °C, 4 h). Still hot it was filtered through Celite to remove palladium black and the solution was then concentrated under vacuum to *ca.* 3 mL, layered with 15 mL acetone and stored at 5 °C for 24 h. The yellow product was then isolated by filtration, washed with acetone and air dried. (0.445 g, 65%). Anal. calc. for $C_{22}H_{20}N_4O_4Pd_2$: C, 42.8; H, 3.3; N, 9.1. Found: C, 42.9; H, 3.4; N, 9.2%). IR (cm^{-1}): ν(CO) 1561 s, ν(phpz) 1512 m, 750 m. ^{1}H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.07 (d, $H_{5'cis}$, J = 2.7 Hz), 7.95 (d, 2H, $H_{5'}$, J = 2.7 Hz), 7.36 (d, $H_{3'cis}$, J = 2.1 Hz), 7.09 (d, 2H, $H_{3'}$, J = 2.1 Hz), 6.95 (d, 2H, H_6, J = 1.8 Hz), 6.91 (m, 4H, H_5, H_3, H_{6cis}), 6.78 (m, 2H, H_4, H_{5cis}), 6.68 (d, H_{3cis}, J = 1.2 Hz), 6.59 (m, H_{4cis}), 6.31 (m, $H_{4'cis}$), 6.03 (m, 2H, $H_{4'}$), 2.10 (s, 6H, CH_3). Positive MS: m/z: 640 [{Pd (phpz) (μAcO)}$_2$]$^+$ + 23, 558 [Pd_2(phpz)$_2$(AcO)]$^+$, 249 [{Pd(phpz)]$^+$.

[{Pd(phpz)(μ-OH)}$_2$] 2. To a solution of [{Pd(phpz)(μ-AcO)}$_2$] (70 mg, 0.114 mmol) in 10 mL acetone was added 20% NBu_4OH (aq.) (0.3 mL, 0.227 mmol). After 1 h stirring at room temperature the solvent was partially evaporated under reduced pressure. Addition of water followed by vigorous stirring and filtration afforded a white solid which was air dried. (0.041 g, 68%). Anal. calc. for $C_{18}H_{16}N_4O_2Pd_2$: C, 40.6; H, 3.0; N, 10.5. Found: C, 40.6; H, 3.1; N, 10.6%). IR (cm^{-1}): ν(OH) 3371, ν(phpz) 1515 m, 750m. ^{1}H NMR (300 M Hz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.02 (d, 2H, $H_{5'}$, J = 2.1 Hz), 7.62 (d, 2H, $H_{3'}$, J = 2.1 Hz), 7.56 (m, 1H, H_6), 7.41 (m, 2H, H_5), 7.13 (m, 4H, H_3, H_4), 6.06 (m, 2H, $H_{4'}$), –0.15 (s, 2H, OH). Positive MS: m/z: 516 [Pd_2 (phpz)$_2$ (OH)]$^+$.

Preparation of complexes [Pd(phpz)(OˆN)] OˆN = N-*p*-chlorophenylsalycilaldiminate (N-*p*Clsal) 3, picolinic acid (pic) 4; 8-hydroxiquinolinate (oxin) 5; 2-pyrrole-carboxaldeydate (2-pcal) 6, [Pd(phpz)(OˆO)] OˆO = salycilaldehydate (sal) 7 and acetylacetonate (acac) 8; [{Pd(phpz)(μ-NˆS)}$_2$] (NˆS = 2-mercapto- 1 methylimidazolate (SMeimz) 11; [{Pd(phpz) (μ-NˆN)}$_2$] NˆO = succinimidate (succ) 12; [{Pd(phpz)(μ-NˆN)}$_2$] (NˆN = pyrazolate (pz) 13. With the exception of complexes **6**, **7** and **12** that require the use of di-μ-hydroxo complex **2** as starting material, the new complexes were obtained by treating an acetone solution (20 mL) of the precursor **1** (0.07 g; 0.136 mmol) with the corresponding protic ligand (HLˆL) (molar ratio 1 : 2). The reaction was stirred at room temperature for 30 min and then it was concentrated under reduced pressure until *ca.* one fifth of the initial volume. Slow addition of diethyl ether caused the formation of the complexes, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane–diethyl ether.

[Pd(phpz)(NpClphsal)] 3. (0.087 g, 79%). Anal. calc. for $C_{22}H_{16}ClN_3OPd$: C, 55.0; H, 3.4; N, 8.8. Found: C, 55.0; H, 3.4; N, 8.7%). IR (cm^{-1}): ν(NpClphsal) 1610 vs, 1530 vs, ν(phpz) 1515 br, 753 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.38 (d, 1H, $H_{5'}$, J = 2.7 Hz), 8.26 (s, 1H, CH-iminic), 7.87 (m, 1H, $H_{3'}$), 7.44 (m, 4H, NpClphsal), 7.13 (m, 2H, NpClphsal), 7.06 (d, 1H, H_6, J = 8.7 Hz), 6.56 (m, 4H, NpClphsal), 6.31 (m, 1H, H_4), 5.67 (m, 1H, $H_{4'}$). Positive MS: m/z: 503 [Pd (phpz) (NpClphsal)]$^+$ + 23, 249 [Pd (phpz)]$^+$.

[Pd(phpz)(pic)] 4. (0.069 g, 81%). Anal. calc. for $C_{15}H_{11}N_3O_2Pd$: C, 48.5; H, 3.0; N, 11.3. Found: C, 48.6; H, 3.0; N, 11.3%). IR (cm^{-1}): ν(pic) 1649 vs, 1602 s, ν(phpz) 1515 s, 750 m. ^{1}H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.94 (d, 1H, pic, J = 5.6 Hz), 8.62 (d, 1H, $H_{5'}$, J = 2.8 Hz), 8.29 (d, 1H, $H_{3'}$, J = 2.4 Hz), 8.25 (m, 1H, pic), 8.14 (d, 1H, pic, J = 7.6 Hz), 7.84 (m, 1H, pic), 7.64 (dd, 1H, H_3, J = 1.6 Hz, J* = 7.4 Hz), 7.44 (dd, 1H, H_6, J = 1.2 Hz, J* = 7.8 Hz), 7.16 (m, 1H, H_5), 7.05 (m, 1H, H_4), 6.75 (m, 1H, $H_{4'}$). Positive MS: m/z: 395 [Pd (phpz) (pic)]$^+$ + 23, 249 [Pd (phpz)]$^+$.

[Pd(phpz)(oxin)] 5. (0.072 g, 80%). Anal. calc. for $C_{18}H_{13}N_3OPd$: C, 54.9; H, 3.3; N, 10.7. Found: C, 54.9; H, 3.3; N, 10.8%). IR (cm^{-1}): ν(oxin) 1571 s, 1501 s, ν(phpz) 1512 m, 750 m. ^{1}H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.29 (dd, 1H, oxin, J = 1.2 Hz, J* = 4.6 Hz), 8.60 (d, 1H, $H_{5'}$, J = 2.8 Hz), 8.41 (dd, 1H, oxin, J = 1.6 Hz, J* = 8.4 Hz), 8.30 (d, 1H, $H_{3'}$, J = 2.0 Hz), 7.82 (dd, 1H, H_6, J = 1.2 Hz, J* = 7.4 Hz), 7.57 (m, 1H, H_5), 7.43 (m, 1H, H_3), 7.38 (d, 1H, oxin, J = 8.0 Hz), 7.14 (m, 1H, oxin), 7.06 (m, 1H, H_4), 6.97 (m, 2H, oxin), 6.74 (m, 1H, $H_{4'}$). Positive MS: m/z: 416 [Pd (phpz) (oxin)]$^+$ + 23, 393 [Pd (phpz) (oxin)]$^+$ + 249 [Pd (phpz)]$^+$.

[Pd(phpz)(2pcal)] 6. The general procedure was followed, using 0.07 g, 0.131 mmol of the di-μ-hydroxo complex **2** as starting material instead of **1**. (0.049 g, 62%). Anal. calc. for $C_{14}H_{11}N_3OPd$: C, 48.9; H, 3.2; N, 12.2. Found: C, 48.9; H, 3.2; N, 12.2%). IR (cm^{-1}): ν(2pcal) 1570 vs, ν(phpz) 1512 m, 765 m. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.77 (d, 1H, CH), 8.56 (d, 1H, $H_{5'}$, J = 2.6 Hz), 7.95 (d, 1H, $H_{3'}$, J = 1.2 Hz), 7.62 (m, 2H, 2pcal), 7.49 (m, 1H, H_6), 7.22 (m, 2H, H_3, H_5), 7.11 (m, 1H, H_4), 6.69 (s, 1H, $H_{4'}$), 6.36 (d, 1H, 2pcal, J = 3.2 Hz). Positive MS: m/z: 366 [Pd (phpz) (2pcal)]$^+$ + 23, 249 [Pd (phpz)]$^+$.

[Pd(phpz)(sal)] 7. The general procedure was followed, using 0.07 g, 0.131 mmol of the di-μ-hydroxo complex **2** as starting material instead of **1**. (0.059 g, 60%). Anal. calc. for $C_{16}H_{12}N_2O_2Pd$: C, 51.8; H, 3.3; N, 7.6. Found: C, 51.8; H, 3.2; N, 7.5%). IR (cm^{-1}): ν(CO) 1610 s, 1547 vs, ν(phpz) 1512 s, 745 m. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 9.36 (s, 1H, CH), 8.52 (d, 1H, $H_{5'}$, J = 0.9 Hz), 7.89 (s, 1H, $H_{3'}$), 7.61 (m, 2H, H_6, H_3), 7.40 (m, 2H, sal), 7.14 (m, 1H, H_5), 7.06 (m, 1H, H_4), 6.96 (d, 1H, sal, J = 8.7 Hz), 6.65 (m, 1H, $H_{4'}$), 6.59 (m, 1H, sal). Positive MS: m/z: 392 [Pd (phpz) (sal)]$^+$ + 23, 249 [Pd (phpz)]$^+$.

[Pd(phpz)(acac)] 8. (0.045 g, 56%). Anal. calc. for $C_{14}H_{14}N_2O_2Pd$: C, 48.2; H, 4.1; N, 8.0. Found: C, 48.2; H, 4.0; N, 8.0%). IR (cm^{-1}): ν(acac) 1577 vs, 1547 vs, ν(phpz) 1518 s, 767 s. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.50 (d, 1H, $H_{5'}$, J = 2.7 Hz), 7.82 (d, 1H, $H_{3'}$, J = 1.8 Hz), 7.47 (dd, 1H, H_6, J = 1.2 Hz, J* = 7.35 Hz), 7.40 (d, 1H, H_3, J = 7.5 Hz), 7.15 (m, 1H, H_5), 7.03 (m, 1H, H_4), 6.64 (m, 1H, $H_{4'}$), 5.44 (s, 1H, CH), 2.04 (s, 3H, CH_3), 2.09 (s, 3H, CH_3). Positive MS : m/z: 598 [$Pd_2(phpz)_2(acac)$]$^+$, 372 [Pd (phpz) (acac)]$^+$ + 23, 249 [Pd (phpz)]$^+$.

[Pd(phpz)(S_2CNEt_2)] 9. To an acetone solution (20 mL) of the different precursors (**1** or **2**) (0.07 g) was added Et_2NH, (molar ratio 1 : 2) and a slight excess of carbon disulfide. Once the suspension was dissolved (*ca.* 30 min) it was concentrated under reduced pressure until *ca.* one fifth of the initial volume. Slow addition of diethyl ether caused the formation of the complexes, which were filtered off, washed with water, diethyl ether and air-dried. The compound was recrystallised from dichloromethane–diethyl ether. (0.068 g, 75%). Anal. calc. for $C_{14}H_{17}N_3S_2Pd$: C, 42.3; H, 4.3; N, 10.5; S, 16.1. Found: C, 42.2; H, 4.3; N, 10.7, S, 16.2%). IR (cm^{-1}): ν(S_2CNEt_2) 1580 s, 1075 s. ν(phpz) 1503 s, 753 s. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 7.96 (d, 1H, $H_{5'}$, J = 2.4 Hz), 7.63 (d, 1H, $H_{3'}$, J = 2.0 Hz), 7.16 (m, 3H, H_6, H_3, H_5), 7.01 (m, 1H, H_4), 6.46 (m, 1H, $H_{4'}$), 3.85 (q, 4H, CH_2, J = 7.2 Hz), 1.35 (m, 6H, CH_3). Positive MS: m/z: 397 [Pd(phpz)(S_2CNEt_2)]$^+$, 249 [Pd(phpz)]$^+$.

[Pd(phpz){$S_2P(OMe)_2$}] 10. The new complex was obtained by treating an acetone solution (20 mL) of the different precursors (**1** or **2**) (0.07 g) with the corresponding amount of [NH_4][S(S)P($OMe)_2$] (molar ratio 1 : 2). Once the suspension was dissolved (*ca.* 30 min) it was concentrated under reduced pressure until *ca.* one fifth of the initial volume. Slow addition of diethyl ether caused the formation of the complexes, which were filtered off, washed with water, diethyl ether and air-dried. The compound was recrystallised from dichloromethane–diethyl ether. (0.059 g, 64%). Anal. calc. for $C_{11}H_{13}N_2O_2PS_2Pd$: C, 32.5; H, 3.2; N, 6.9; S, 15.7. Found: C, 32.7; H, 3.3; N, 7.1, S, 15.9%). IR (cm^{-1}): ν($S_2P(OMe)_2$) 1020 vs, 811 vs. ν(phpz) 1509 s, 749 s. ^1H NMR (200 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 7.96 (d, 1H, $H_{5'}$, J = 2.6 Hz), 7.70 (d, 1H, $H_{3'}$, J = 2.0 Hz), 7.29 (m, 1H, H_6), 7.16 (m, 2H, H_3, H_5), 7.01 (m, 1H, H_4), 6.49 (m, 1H, $H_{4'}$), 3.89 (s, 3H, CH_3), 3.81 (s, 3H, CH_3). ^{31}P NMR (200 MHz, $CDCl_3$): δ (H_3PO_4)(ppm): 111.85. Positive MS: m/z: 406 [Pd(phpz){$S_2P(OMe)_2$}]$^+$, 249 [Pd(phpz)]$^+$.

[{Pd(phpz)(μ-SMeimz)}$_2$] 11. (0.069 g, 83%). Anal. calc. for $C_{26}H_{24}N_8Pd_2S_2$: C, 43.0; H, 3.3; N, 15.5. Found: C, 42.9; H, 3.4; N, 15.4%). IR (cm^{-1}): ν(CS) 1585 s, ν(phpz) 1516 m, 746 m. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 7.88 (d, 2H, $H_{5'}$, J = 2.4 Hz), 7.29 (dd, 2H, SMeimz, J = 1.2 Hz, J* = 7.8 Hz), 7.04 (d, 2H, $H_{3'}$, J = 1.5 Hz), 6.87 (dd, 2H, H_6, J = 1.2 Hz, J* = 7.8 Hz), 6.75 (m, 6H, H_5, H_3, SMeimz), 6.56 (m, 2H, H_4), 6.32 (m, 1H, $H_{4'}$), 3.55 (s, 6H, CH_3) Positive MS: m/z: 613 [$Pd_2(phpz)_2$(SMeimz)]$^+$.

[{Pd(phpz)(μ-suc)}$_2$] 12. The general procedure was followed, using 0.07 g, 0.131 mmol of the di-μ-hydroxo complex **2** as starting material instead of **1**. (0.054 g, 68%). Anal. calc. for $C_{26}H_{22}N_6O_4Pd_2$: C, 44.9; H, 3.2; N, 12.1. Found: C, 45.0; H, 3.3; N, 12.1%). IR (cm^{-1}): ν(suc) 1742 s, 1610 vs, ν(phpz) 1515 s, 745 m. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 7.88 (d, 2H, $H_{5'}$, J = 2.8 Hz), 7.14 (d, 2H, $H_{3'}$, J = 2 Hz), 6.95 (d, 2H, H_6, J = 6 Hz), 6.82 (m, 1H, H_3), 6.60 (m, 4H, H_4, H_5), 6.00 (m, 2H, $H_{4'}$), 2.80 (m, 8H, succ). Positive MS: m/z: 717 [{Pd(phpz)(suc)}$_2$]$^+$ + 23, 696 [{Pd(phpz)(suc)}$_2$]$^+$, 598 [$Pd_2(phpz)_2$(suc)]$^+$.

[{Pd(phpz)(μ-pz)}$_2$] 13. (0.051 g, 70%). Anal. calc. for $C_{24}H_{20}N_8Pd_2$: C, 45.5; H, 3.2; N, 17.7. Found: C, 45.5; H, 3.3; N, 17.6%). IR (cm^{-1}): ν(pz) 1590 s, ν(phpz) 1515 s, 753 m. ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 8.51 (d, 2H, $H_{5'}$, J = 2.8 Hz), 7.63 (m, 4H, $H_{3'}$, pz), 7.44 (d, 2H, pz, J = 2.4 Hz), 7.43 (m, 2H, H_6), 7.11 (m, 2H, H_5), 7.06 (m, 2H, H_4), 6.93 (m, 2H, H_3), 6.58 (m, 2H, $H_{4'}$), 6.34 (m, 2H, pz). Positive MS: m/z: 633 [{Pd(phpz)(pz)}$_2$]$^+$, 566 [$Pd_2(phpz)_2(pz)$]$^+$, 317 [Pd(phpz)(pz)]$^+$.

[Pd(phpz)(AcO)(PPh_3)] 14. To a dichloromethane (20 mL) solution of **1** (0.07 g; 0.136 mmol) was added triphenylphosphine in 1 : 2 ratio. The solution was stirred for 30 min at room temperature, then concentrated until *ca.* one fifth of the initial volume. Slow addition of diethyl ether completed the precipitation of the complex, which was filtered off, washed with ether and air-dried. (0.083 g, 64%). Anal. calc. for $C_{29}H_{25}N_2O_2PPd$: C, 61.1; H, 4.4; N, 4.9. Found: C, 61.3; H, 4.6; N, 5.1%). IR (cm^{-1}): ν(AcO) 1600 vs. ν(PPh_3) 534 s, 517 s, 490 s. ν(phpz) 1514 s, 755 s. ^1H NMR (200 MHz, $CDCl_3$): δ ($SiMe_4$)(ppm): 7.97 (d, 1H, $H_{5'}$, J = 2.2 Hz), 7.83 (m, 6H, Ph), 7.66 (m, 1H, $H_{3'}$), 7.40 (m, 8H, H_6, H_5 + Ph), 7.09 (m, 1H, H_3), 6.94 (m, 1H, H_4), 6.46 (m, 4H, $H_{4'}$ + Ph), 1.42 (s, 3H, CH_3). ^{31}P NMR (200 MHz, $CDCl_3$): δ (H_3PO_4)(ppm): 43.60. Positive MS: m/z: 511 [Pd(phpz)(PPh_3)]$^+$, 249 [Pd(phpz)]$^+$.

Crystallographic data and structure determination

Crystals of **1**, **7**, **9**, **11** and **12** suitable for a single crystal diffraction study were prepared by slow diffusion of dichloromethane into hexane. Diffraction data were measured on a Bruker SMART APEX using Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods[57] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-hydrogen atoms.

For **13**, high resolution X-ray powder diffraction patterns were collected at the SpLine beamline (BM25A) of the Spanish CRG at

Table 3 Crystal data and structure refinement for complexes **1**, **7**, **9**, **11**, **12** and **13**

	1	**7**	**9**	**11**	**12**·CH_2Cl_2	**13**
Empirical formula	$C_{22}H_{20}N_4O_4Pd_2$	$C_{16}H_{12}N_2O_2Pd$	$C_{14}H_{17}N_3PdS_2$	$C_{26}H_{24}N_8Pd_2S_2$	$C_{27}H_{24}Cl_2N_6O_4Pd_2$	$C_{24}H_{20}N_8Pd_2$
M	617.22	370.68	397.83	725.45	780.22	633.2
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	298
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	
Crystal system	Trigonal	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P3121$	$P21/a$	$P21/n$	$Pbca$	$P\bar{1}$	$P21/a$
a/Å	11.7292(3)	14.4947(10)	8.8527(7)	11.1797(5)	8.9145(4)	23.3603(5)
b/Å	11.7292(3)	12.1565(9)	12.4569(10)	17.5215(7)	10.8879(4)	8.95252(17)
c/Å	27.8342(13)	15.8097(11)	13.7577(11)	26.8062(11)	15.3871(8)	11.5684(2)
α/°	90	90	90	90	103.0790(10)	90
β/°	90	99.4880(10)	95.1880(10)	90	90.5410(10)	104.0736(14)
γ/°	120	90	90	90	107.2350(10)	90
V/Å^3	3316.2 (2)	2747.6(3)	1510.9(2)	5250.9(4)	1384.71(11)	2346.74(8)
Z	6	8	4	8	2	4
D_c/Mg m^{-3}	1.854	1.792	1.749	1.835	1.871	1.797
μ/mm^{-1}	1.663	1.356	1.497	1.562	1.538	
$F(000)$	1824	1472	800	2880	772	
θ range for data collection/°	2.00 to 28.23	1.31 to 28.68	2.21 to 28.61	2.29 to 28.17	1.36 to 28.23	
Reflections collected	38 625	32 760	18 234	57 537	15 980	
Independent reflections	5225	6649	3674	6240	6209	
Goodness-of-fit on F^2	1.064	1.217	1.096	1.209	0.911	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0260$	$R_1 = 0.0590$	$R_1 = 0.0336$	$R_1 = 0.0419$	$R_1 = 0.0343$	
	w$R_2 = 0.0578$	w$R_2 = 0.1362$	w$R_2 = 0.0816$	w$R_2 = 0.0901$	w$R_2 = 0.0856$	
R indices (all data)	$R_1 = 0.0267$	$R_1 = 0.0627$	$R_1 = 0.0338$	$R_1 = 0.0451$	$R_1 = 0.0368$	
	w$R_2 = 0.0582$	w$R_2 = 0.1385$	w$R_2 = 0.0817$	w$R_2 = 0.0915$	w$R_2 = 0.0876$	
Max/min $\Delta\rho$/e Å^{-3}	0.714 and –0.396	6.025 and –0.864	3.652 and –0.956	1.325 and –0.597	3.154 and –0.620	

the European Synchrotron Radiation Facility (ESRF, Grenoble) with a fixed wavelength of 0.826924 Å at room temperature. Powdered samples were placed inside a 0.5 mm-diameter capillary, which was rotated during exposure. Data collection was done in a continuous 2θ-scan mode with 0.015° step and 2 s acquisition time per point. The diffracted beam was detected using a scintillation counter. The incoming beam was also monitored to normalise the decay of the primary beam.

The peak positions were identified using a derivative-based algorithm that is implemented in the peak search utility of the *WINPLOTR* software package.[58] The indexing was carried out using the commonest indexing programs: *ITO*, *TREOR90*, *DICVOL*, *KOHL*, *TAUP*, *FJZN*, and *LZON*. To estimate the shape and width of the Bragg reflections as well as the instrumental shifts, we performed the Le Bail fit[59] implemented as the profile matching option in the *FULLPROF* program.[60] A first approximation to the crystal structure was obtained by Monte Carlo methods, using the parallel tempering algorithm implemented in the *FOX* software package.[61] The atomic coordinates obtained by Monte Carlo methods were used to initialise the Rietveld refinements, which were performed using the *FULLPROF* program.[61]

Hydrogen atoms were added at theoretical positions in all the structures. Crystallographic data are summarised in Table 3. The structural data have been deposited with the Cambridge Crystallographic Data Center. CCDC reference numbers CCDC 783647 – 783652.

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