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Reactivity Towards Acidic Protic Ligands of Cyclopalladated Di-μ-hydroxo Complexes

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The dinuclear hydroxo complexes [{Pd(μ-OH)(C^N)}$_2$] [C^N = 2-(2-pyridyl)phenyl (Phpy) (**I**), 7,8-benzoquinolyl (Bzq) (**II**) and 2-(2-oxazolinyl)phenyl (Phox) (**III**)] react in a 1:2 molar ratio with a wide variety of protic electrophiles H(L^L) bearing different sets of donor atoms (L^L = O^O or O^N) to give the mononuclear neutral palladium(II) derivatives with the general formula [Pd(L^L)(C^N)] [O^O = salicylaldehydate (sal) (**1**), acetylacetonate (acac) (**2**) and benzoylacetonate (bzac) (**3**); O^N = *N*-phenylsalicylaldiminate (*N*-Phsal) (**4**), *N*-*p*-chlorophenylsalicylaldiminate (*N*-pClPhsal) (**5**), 2-pyrrolecarbaldeydate (2-pcal) (**6**), 8-hydroxyquinolinate (oxin) (**7**)]. Structural characterisation of complexes **I1**, **I3**, **I6**, **II4**, **II5** and **III5** by X-ray diffraction confirmed the proposed formulae. Dinuclear complexes [{Pd(μ-N^S)(C^N)}$_2$] [N^S = 2-pyridinethiolate (spy)] (**8**) were obtained when treating complexes **I**–**III** with 2-mercaptopyridine in the same molar ratio. A related process takes place when the three precursors react with ammonium *O*,*O*′-diethyldithiophosphate under mild conditions and complexes [Pd{S(S)P(OEt)$_2$}(C^N)] (**I9**–**III9**) are obtained. Deprotonation of the secondary amine Et$_2$NH by complexes **I**–**III** in the presence of carbon disulfide leads to the corresponding dithiocarbamate complexes [Pd(S$_2$CNEt$_2$)(C^N)] (**I10**–**III10**). The new complexes were characterised by analytical and spectroscopic techniques (IR and ^{1}H NMR).

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Introduction

In addition to their interest relating to applied fields such as antitumour activity[1] or catalytic processes,[2] the synthetic value of palladium(II) and platinum(II) di-μ-hydroxo complexes is a subject of continuous study.[3] For example, Sharp et al.[4] and later others[5] 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(μ-OH)L^n]$_2$ (L^n = orthometalated imine-based ligands) provides a general route to obtaining dinuclear complexes with double and mixed bridges that have shown liquid crystal behaviour.[6] In this sense, during the last years we have also been developing the usefulness of dinuclear hydroxo complexes of palladium, some of them with a cyclometalated backbone,[7] in the preparation of a wide variation of new compounds by means of a simple acid–base reaction.[8]

With regard to the cyclopalladated systems whose reactivity we present here, the related acetate- or halide-bridged dimers have been extensively employed as convenient precursors of mononuclear and dinuclear cyclometalates.[9,10] Since 1970 to date several reviews have been dedicated to different aspects of their chemistry such as synthesis and structural characterization, their applications in organic synthesis, organometallic catalysis, their presence in medicinal and biological chemistry or their use as chiral auxiliaries, mesogenic and luminescent agents.[11] In their excellent review, Ghedini and coworkers[11a] have pointed out the relationship between molecular geometries, types of ligands and important physical properties of dinuclear and mononuclear cyclometalated derivatives containing O^O, N^N or O^N complementary ligands. Thus, the authors have studied the effects exerted by different bridging groups on the spectroscopic and liquid-crystalline properties of complexes of the type [{Pd(μ-X)(C^N)}$_2$] (X = halide, azido, thiocyanate, oxalate or acetate),[12]or the presence of an asymmetric coordination around the palladium atom as a key aspect for photophysical properties, which is well exemplified by complexes [Pd(oxin-R)(Phpy)] that emit in solution at room temperature.[13] Cyclopalladated acetylacetonate complexes have also been thoroughly studied, showing again the importance of the orthometalated backbone and the substituents on the acac moiety in the fine tuning of properties.[14] As a whole these results suggest that related

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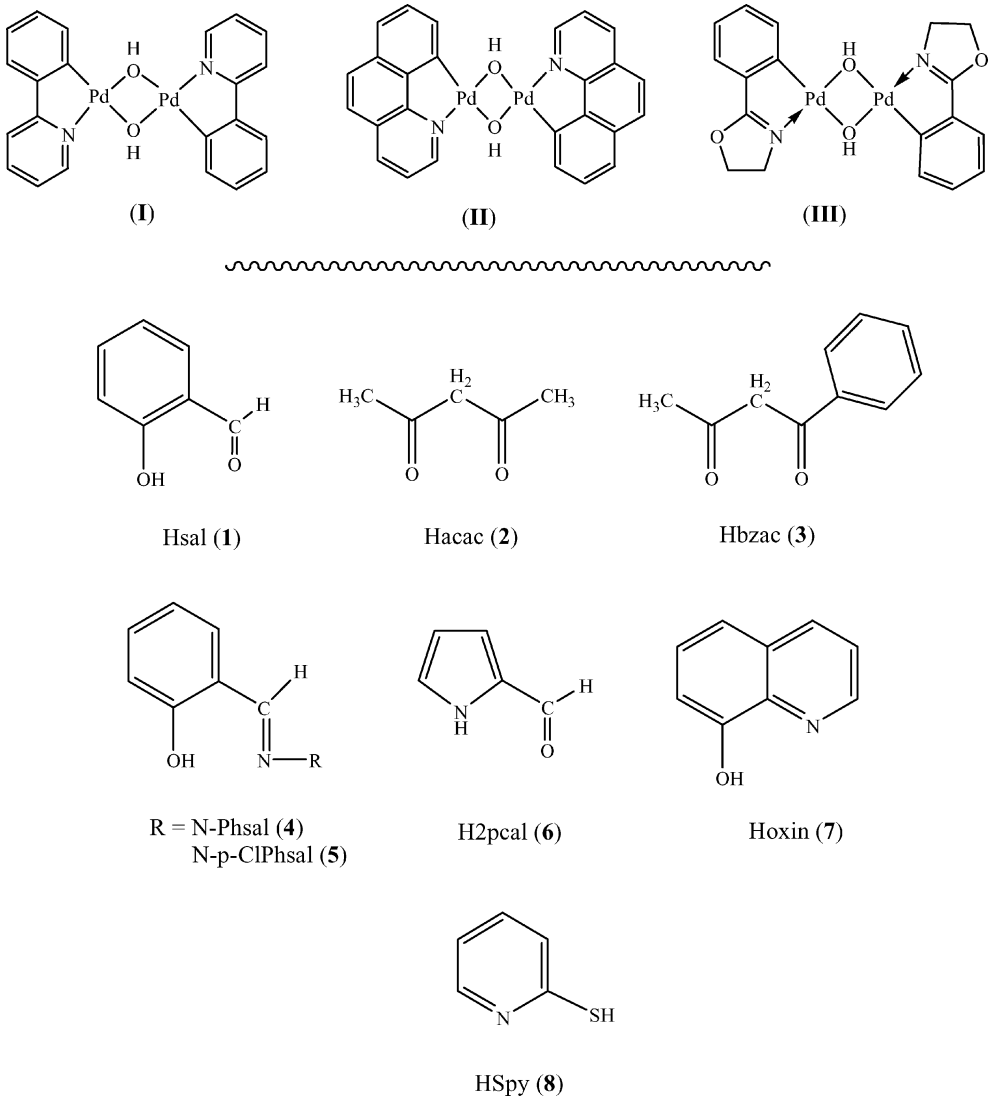
complexes can be candidates for the above-mentioned practical applications.

Apart from their intrinsic interest, the hydroxo complexes of palladium, whose reactivity we present here, can offer a convenient and faster route in the preparation of compounds that may not be accessible using classical halide or acetate precursors. In this paper we explore the reactivity of complexes [{Pd(μ-OH)(C^N)}$_2$] [C^N = 2-(2-pyridyl)-phenyl (Phpy) (**I**), 7,8-benzoquinolyl (Bzq) (**II**) and 2-(2-oxazolinyl)phenyl (Phox) (**III**)] towards several protic electrophiles and describe other related reactions, like those with amines in the presence of carbon disulfide.

Results and Discussion

The cyclometalated precursors [{Pd(μ-OH)(C^N)}$_2$] [C^N = (Phpy) (**I**), (Bzq) (**II**) and (Phox) (**III**)] were conveniently prepared by the treatment of the corresponding acetate-bridged complexes with NBu_4OH in acetone. The drawings of the dinuclear precursor together with the acidic ligands labelled with their abbreviations are shown in Scheme 1. The reactions explored in this paper and the specific conditions followed for each of them are collected in the Experimental Section.

The hydroxo complexes react with weak protic acids H(L^L) to give mono- or dinuclear species depending on whether the deprotonated acid (L^L)$^-$ is *exo*- or *endo*-bidentate. These reactions can be viewed as an initial proton abstraction by the complexes **I**–**III** that provides (L^L)$^-$ and the metal substrate, subsequently trapped by the anion to form the new complexes of the general formula [Pd(L^L)(C^N)] (**I**–**III/1**–**7**) or [{Pd(μ-N^S)(C^N)}$_2$] (**I8**–**III8**). It is worth noting that the syntheses of acac complexes **I2**, **II2** and **III2** has previously been reported by treating [{Pd(μ-OOCMe)(C^N)}$_2$] with an excess amount of K(acac), prepared in advance.[14,15] The complex [Pd(oxin)(Phpy)] (**I7**), which is a good emitter in solution,[13] has also been prepared in a similar manner. Longer reaction times (5–12 h) and successive filtration and extraction steps in the reported procedure, in comparison with the



Scheme 1. Precursors and acidic ligands under study.

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straightforward route that we present here, make our hydroxo complexes appropriate precursors in the preparation of such complexes, and allow one to envisage their general usefulness when treating them with other substrates. The considerable nucleophilicity of the bridging OH groups of the three precursors also makes them reactive towards ammonium *O*,*O'*-diethyldithiophosphate, yielding complexes **I9**–**III9** with the concomitant release of NH_3 and H_2O. The preparation of the dithiocarbamate complexes **I10**–**III10** should involve a first step of amine deprotonation, followed by nucleophilic attack of Et_2N^- to carbon disulfide to form the dithiocarbamate anion. It was impossible to prepare complex **III7** by this route. In all attempts made we have spectroscopic evidence of the bis(8-quinolinato)palladium(II) complex instead of the expected [Pd(oxin)(Phox)] complex.

The new palladium complexes are air-stable and their IR spectra show strong bands around 1600 cm^{-1}, characteristic of the corresponding cyclometalated backbone, and in some cases partly overlapped by the absorptions that are attributed to the incoming ligands (see Exp. Section). The absence of relevant bands in the region 3000–3500 cm^{-1} can be interpreted as both deprotonation of acidic ligands and complete reaction of the hydroxo-palladium precursors. This fact was also supported by the ^1H NMR spectra, where no high-field resonances are found. The ^1H NMR spectra also show the corresponding signals of the $(L^\wedge L)^-$ ligands, frequently overlapped in the aromatic region with those of the cyclometalated backbone (especially complexes **I** and **II**). In principle, new complexes containing the ligands **1**, **3**–**7** can exist as two isomers depending on the relative positions of the C^N/O^O (complexes labelled **1** and **3**) or C^N/O^N (complexes **4**–**7**) chelating systems. In the latter, the presence of only one isomer was observed by ^1H NMR spectroscopy. The determination of the molecular structures of **I6**, **II4**, **II5** and **III5** by X-ray analysis revealed a *N*,*N*-*trans* arrangement in complexes **I6**, **II4** and **II5**, while a *N*,*N*-*cis* disposition was found in the 2-(2-oxazolinyl)-phenyl derivative **III5**, suggesting a dependence on the specific cyclometalated system and that those isomers could also be predominant in solution. This dependence and the prevalence of the *N*,*N*-*trans* arrangement in C^N/O^N systems, where O^N is either the related Schiff base or the 8-hydroxyquinoline ligands, are also noted after a survey of the Cambridge Structural Database (CSD) v. 5.29 (updated to November 2007). On the other hand the ^1H NMR spectra of complexes **I1**–**III1** with salicylaldehydate as the co-ligand showed a mixture in solution with an isomer ratio of ca. 5:1 that did not change with time or the solvent used (deuterated chloroform or acetone). A crystal structure determination of **I1** shows that the carbonylic oxygen is placed *trans* to the orthometalated carbon atom. This disposition has also been found in related complexes with a C^P backbone,[16] for which the authors identified this complex as the major isomer in solution on the basis of steric requirements of substituents on the carbonylic carbon and the ability of the oxygen atoms to participate in hydrogen bonding. A different behaviour was displayed by benzoylacetonate derivatives with the ^1H NMR spectra consisting of a mixture of the two isomers in a variable ratio dependent on the cyclometalated backbone, the solvent and the time since the preparation. In fresh $CDCl_3$ solution spectra showed a mixture with a predominant isomer with low-field bzac signals ($I_I/I_{II} \approx 1.8$ for **I3**, 3.0 for **II3** and 1.4 for **III3**; average integrated peak ratio I_I/I_{II} taken from the corresponding two methine or methyl signals), and after three hours the ratio in all cases changed to $I_I/I_{II} \approx 1$. In deuterated acetone as the solvent this proportion was immediately reached and did not change with time. We were able to obtain crystals of **I3** from $CHCl_3$/hexane suitable for an X-ray diffraction study that revealed the presence of the isomer with the Ph-carbonylic oxygen placed *trans* to the orthometalated carbon atom. An unequivocal explanation for a specific isomer choice in the solid state is difficult to find, and it has been studied in the case of Rh(I) complexes with β-diketones.[17]

With regard to the rest of the complexes with a 2-(2-oxazolinyl)phenyl backbone (**III**), their spectra show just two triplets for the NCH_2 and OCH_2 protons in the 3.70–4.80 ppm region, except for complex [{Pd(μ-Spy)(Phox)}$_2$] (**III8**) in which a set of three unresolved multiplets (ratio 1:2:1) is observed. This observation supports the proposed coordination, as this behaviour has been reported for the related dinuclear complexes [{Pd(μ-X)(Phox)}$_2$] (X = acetate[15] or imidate[18]) in which each of two methylene protons of the oxazoline ring are nonequivalent as a consequence of the open-book structure of the complexes. The ^{31}P NMR spectra of complexes **I9**–**III9** show a single resonance for the coordinated dithiophosphate ligands at the usual range.

The mono- or dinuclearity of the new complexes is also supported by FAB mass spectrometry and the positive FAB-MS data of the complexes with the *m*/*z* values for the observed fragments (M^+ and $M^+ - L^\wedge L$ as a common pattern) are collected in the Experimental Section. The abundance of the signals around the parent ion is consistent in all cases with the natural isotopic abundances.

As mentioned above, the mononuclear nature of 2-(2-pyridyl)phenyl derivatives **I1**, **I3** and **I6** that contain chelating O^O and O^N donor ligands has also been confirmed by single-crystal X-ray analysis. The ORTEP drawings of the three complexes are shown in Figure 1, Figure 2 and Figure 3, while the relevant bond lengths and angles are reported in Table 1.

With regard to the salicylaldehydate complex **I1**, it has previously been reported for related complexes that an acac-type delocalization contributes to the overall structure, reducing the importance of delocalization within the aromatic ring.[16] This also applies for **I1** on the basis of quite close C12–C13 and C13–C18 distances [1.424(5) and 1.439(5) Å], despite the fact that there is an aromatic and a single bond in the parent ligand, and also the little difference between the C–O bond lengths (see Table 1). The unit cell of complex **I1** contains two molecules. The coordination around the Pd atoms based on measures of torsion angles is almost planar with a slight square-pyramidal dis-

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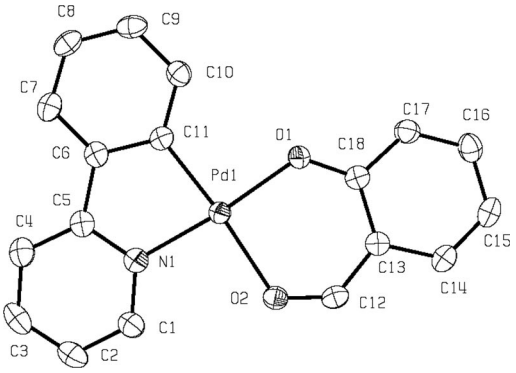

Figure 1. ORTEP diagram of complex **I1** with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

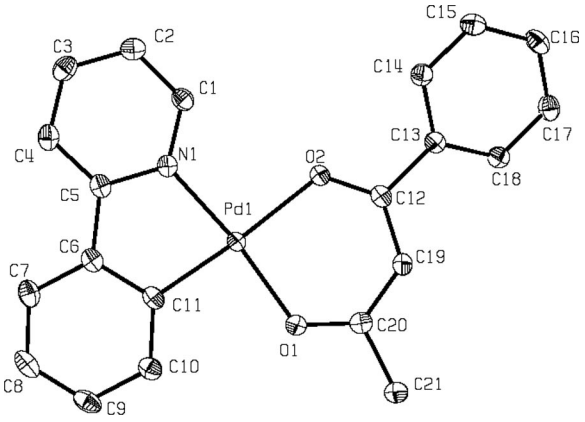

Figure 2. X-ray crystal structure of **I3**. Thermal ellipsoids are drawn at the 50% probability. Hydrogen atoms are omitted for clarity.

tortion[19] [w_1(O1–C11–N1–Pd1) = 2.25° and w_2(O2–N1–C11–Pd1) = –0.24; w_1(O3–C29–N2–Pd2) = 2.48° and w_2(O4–N2–C29–Pd2) = –0.01°]. The narrow N–Pd–C angle in the orthometalated moiety is similar to that found in other complexes containing the same ligand.[10a,10c]

We have recently developed methods for the conformational classification of eight-membered rings.[20] Using the so-called classification method, it can be concluded that the five-membered palladacycles Pd1–N1–C5–C6–C11 and Pd2–N2–C23–C24–C29 exhibit almost planar conformations [this method assigns the following probabilities for conformations when a standard deviation of σ = 10 is allowed: half-chair (HC) = 0.515; envelope (E) = 0.485 and HC = 0.514; E = 0.486, respectively]. The six-membered rings Pd1–O1–C18–C13–C12–O2 and Pd2–O4–C30–C31–C36–O3 are also nearly planar [screw-boat (SB) = 0.998; half-chair (HC) = 0.002 and SB = 0.999; HC = 0.001, respectively]. The same preferences regarding ring conformations were found for complex **I3** (HC = 0.514; E = 0.486 and SB = 0.996; HC = 0.004). In this case the coordination around the Pd atom is almost planar with slight tetrahedral distortion (w_1 = 1.11° and w_2 = 1.97°). As mentioned above, the isomer shown in Figure 2 with the relative C···O=C–Ph and N···O=C–Me *trans* disposition is the one found in the crystal. There is a notable difference between the distances Pd1–O2 = 2.0950(13) Å and Pd1–O1 = 2.0101(13) Å due to the larger *trans* influence exerted by the σ-bonded C atom.

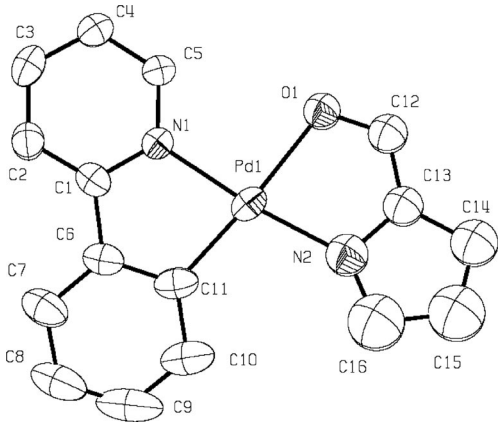

Figure 3. An ORTEP representation of **I6**. Thermal ellipsoids are drawn at the 50% probability.

Complex **I6** (Figure 4) also contains two molecules in the asymmetric unit. The coordination around the Pd atoms is almost planar with different distortions for each molecule: w_1 = 3.22° and w_2 = –0.53° (square pyramidal) and w_1 = 1.43° and w_2 = 1.81° (tetrahedral).

The four five-membered rings are almost planar with values for the half-chair and envelope conformations that are similar to those found for complexes **I1** and **I3**. This is the first X-ray crystal structure of a Pd complex containing

Table 1. Selected bond lengths [Å] and angles [°] for complexes **I1**, **I3** and **I6**.

I1				**I3**		**I6**			
Pd1–C11	1.965(3)	Pd2–C29	1.957(3)	Pd1–C11	1.9637(17)	Pd1–C11	1.977(5)	Pd2–C27	1.980(4)
Pd1–N1	2.012(3)	Pd2–N2	2.007(3)	Pd1–N1	2.0086(15)	Pd1–N1	2.013(3)	Pd2–N3	2.007(3)
Pd1–O1	2.018(2)	Pd2–O3	2.009(2)	Pd1–O1	2.0103(13)	Pd1–N1	2.026(4)	Pd2–N4	2.036(3)
Pd1–O2	2.116(2)	Pd2–O4	2.121(2)	Pd1–O2	2.0950(13)	Pd1–O1	2.170(3)	Pd2–O2	2.157(3)
C18–O1	1.293(4)	C36–O3	1.303(4)	C20–O1	1.274(2)	C12–O1	1.257(5)	C28–O2	1.253(5)
C12–O2	1.239(4)	C30–O4	1.239(4)	C12–O2	1.271(2)				
C11–Pd1–N1	81.48(13)	C29–Pd2–N2	81.33(13)	C11–Pd1–N1	81.77(7)	C11–Pd1–N1	81.11(16)	C27–Pd2–N3	81.74(14)
C11–Pd1–O1	93.09(11)	C29–Pd2–O3	92.39(12)	C11–Pd1–O1	91.43(6)	C11–Pd1–N2	104.12(19)	C27–Pd2–N4	103.90(14)
C11–Pd1–O2	175.15(11)	C29–Pd2–O4	175.72(12)	C11–Pd1–O2	175.47(6)	C11–Pd1–O1	175.97(16)	C27–Pd2–O2	175.33(13)
N1–Pd1–O1	173.69(10)	N2–Pd2–O3	172.80(10)	N1–Pd1–O1	172.66(6)	N1–Pd1–N2	172.78(17)	N3–Pd2–N4	173.68(13)
N1–Pd1–O2	93.68(10)	N2–Pd2–O4	94.39(10)	N1–Pd1–O2	93.99(6)	N1–Pd1–O1	94.90(12)	N3–Pd2–O2	94.05(12)
O1–Pd1–O2	91.72(9)	O3–Pd2–O4	91.88(9)	O1–Pd1–O2	92.88(5)	N2–Pd1–O1	79.81(15)	N4–Pd2–O2	80.40(12)

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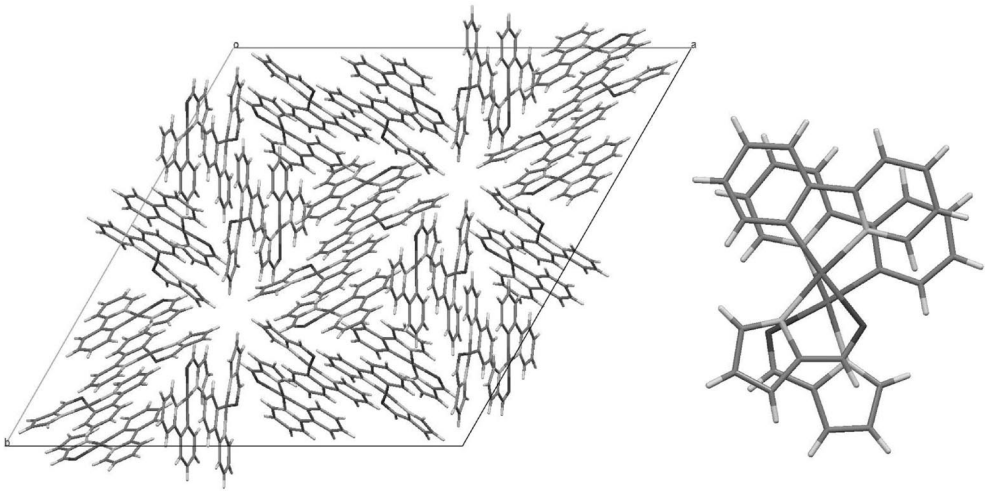

Figure 4. Molecular packing diagram of complex **I6** and perspective view of the alignment of the two molecules.

simple chelating 2-pyrrolecarbaldehydate as searched from the Cambridge Structural Database (CSD) v. 5.29 (updated to November 2007).

The three 2-(2-pyridyl)phenyl derivatives display groups of molecules stacked with plane-to-plane distances that are compatible with a π interaction (3.3–3.8 Å).[21] In complex **I1** a stacking of three parallel molecules is observed in the crystal structure with one of them placed between the other two with different distances and overlapping degrees. Distances between planes (measured as the Pd plane) are 3.264 and 3.447 Å, while Pd–Pd distances are 3.350 and 6.175 Å.

In complexes **I3** and **I6** a stacking of parallel molecules is also observed but is limited to two molecules (Pd···plane distances are 3.437 and 3.323 Å, respectively). The crystal packing in **I6** defines a narrow tunnel along the *c* direction with a diameter of about 2.8 Å. It is worth noting the high rate of alignment found in complex **I6**. A view of the crystal packing is shown in Figure 4.

The structures of two 7,8-benzoquinolyl derivatives **II4** (Figure 5) and **II5** (Figure 6) have been confirmed by X-ray diffraction analysis and selected bond lengths and angles are collected in Table 2.

The coordination around the Pd atoms is almost planar with slight tetrahedral distortion (w_1 = –2.11°; w_2 = –3.15° and w_1 = 1.88°; w_2 = 1.95°). The cyclometalated five-membered rings Pd1–N1–C12–C13–C1 are almost planar with values of probability for the conformations HC and E that are close to the former complexes. With regard to the six-membered rings Pd1–N2–C14–C15–C20–O1 in both **II4** and **II5**, similar values of probability (SB = 0.991; HC = 0.006; E = 0.003 and SB = 0.987; HC = 0.007; E = 0.006) to those of complex **I1** with salicylaldehydate were found. The chloride substituent in **II5** does not seem to influence the conformation of the ring, as it does not affect the N2–C14 bond length, 1.306(3) and 1.304(2) Å in **II4** and **II5**, respectively. Both complexes **II4** and **II5** stack forming chains (straight chains in the direction of the Pd atoms, see Figure 7), in which the planes defined by the metal and the orthometalated ligand are parallel, and show Pd···Pd and Pd···plane distances of 6.220 and 3.249 Å in **II4** and 6.351 and 3.105 Å in **II5**, respectively.

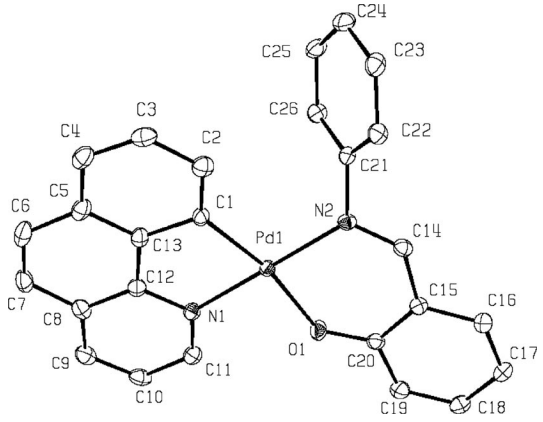

Figure 5. ORTEP diagram of **II4**. Thermal ellipsoids are drawn at the 50% probability level.

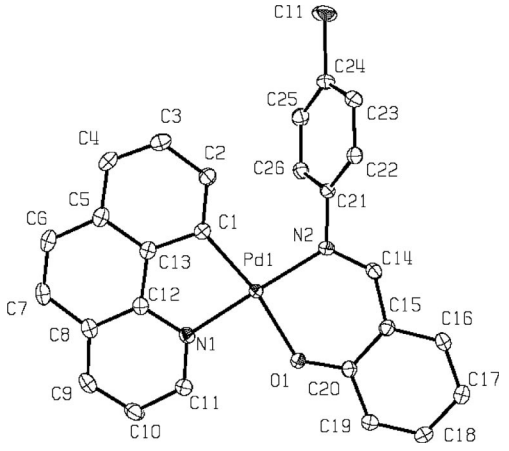

Figure 6. Molecular structure of **II5** with the labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

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Table 2. Selected distances [Å] and angles [°] of complexes **II4**, **II5** and **III5**.[a]

	II4	**II5**	**III5**		
Pd1–C1	2.026(5)	2.0157(15)	2.007(16)	2.003(15)	1.984(15)
Pd1–N1	2.037(2)	2.0373(13)	2.036(13)	2.083(14)	2.032(14)
Pd1–N2	2.031(2)	2.0373(13)	2.116(13)	2.104(12)	2.124(12)
Pd1–O1	2.052(3)	2.0568(11)	2.009(11)	2.027(11)	2.004(10)
C1–Pd1–N1	82.04(12)	82.06(6)	81.5(6)	78.6(6)	80.9(6)
C1–Pd1–N2	99.82(12)	99.93(6)	178.4(6)	176.6(5)	178.6(6)
C1–Pd1–O1	168.74(14)	169.48(5)	87.3(6)	88.0(6)	86.8(5)
N1–Pd1–N2	176.28(9)	176.50(5)	99.9(5)	102.5(5)	100.5(5)
N1–Pd1–O1	87.57(9)	87.77(5)	168.8(5)	166.5(5)	167.6(5)
N2–Pd1–O1	90.81(9)	90.36(5)	91.3(5)	91.0(5)	91.8(5)
C14[a]–N2	1.306(3)	1.304(2)	1.33(2)	1.301(19)	1.288(18)
C20[b]–O1	1.294(4)	1.2975(18)	1.329(18)	1.28(2)	1.298(17)
C24[c]–Cl1		1.7394(16)	1.770(16)	1.707(17)	1.752(17)

[a] C10 in **III5**. [b] C16 in **III5**. [c] C20 in **III5**.

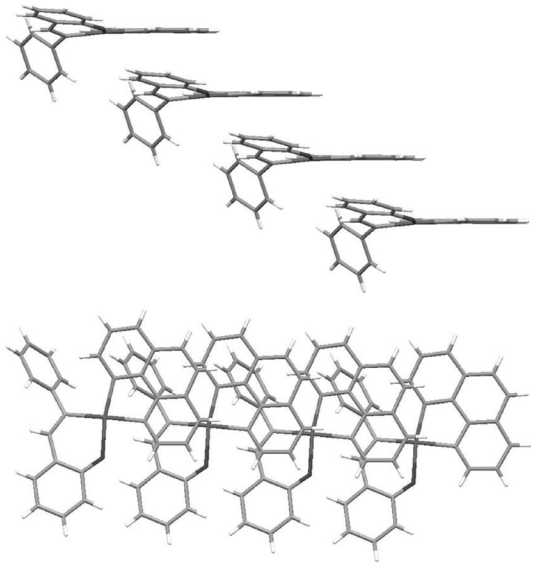

Figure 7. Packing diagram in **II4**.

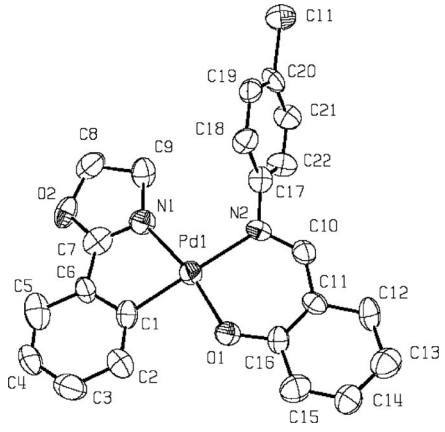

Figure 8. X-ray crystal structure of **III5**. Thermal ellipsoids are drawn at the 50% probability. Hydrogens are omitted for clarity.

The crystal structure of complex **III5** (Figure 8) has also been solved by X-ray diffraction analysis. It displays three molecules in the asymmetric unit and its selected geometrical features are given in Table 2. To date just three complexes containing an orthopalladated 2-phenyl-2-oxazoline ligand have been crystallographically characterised [searching the Cambridge Structural Database (CSD) v. 5.29 updated to November 2007].[7b,15]

The overall coordination geometry about the palladium atom is essentially square planar in the three molecules, with a slight square pyramidal distortion for Pd(1) (w_1 = –0.53°; w_2 = 0.16°) and Pd(3) (w_1 = –0.28°; w_2 = 1.18°) and a tetrahedral distortion for Pd(2) (w_1 = –2.07°; w_2 = –1.14°). The six-membered rings Pd–N–C–C–C–O in the three molecules are also nearly planar (for example SB = 0.996; HC = 0.004 for the ring Pd1–N2–C10–C11–C16–O1). The cyclometalated five-membered rings Pd1–N1–C7–C6–C1 and equivalent are also almost planar.

Conclusions

We have employed di-μ-hydroxo complexes containing a cyclometalated backbone as precursors in the preparation of new compounds when ligand deprotonation was required. Thus, stronger basic treatments were avoided reaffirming the unique characteristics of such hydroxo complexes as starting materials for simple acid–base reactions with protic electrophiles or related processes, like that of deprotonation of secondary amines in the presence of carbon disulfide to yield the corresponding dithiocarbamate complexes. Twenty nine palladium(II) complexes with 2-phenylpyridine, 7,8-benzoquinolyne or 2-phenyl-2-oxazoline have been prepared in this manner and characterised by spectroscopic techniques and single-crystal X-ray diffraction analysis. We present the first X-ray crystal structure of a Pd complex containing simple chelating 2-pyrrolecarbaldehydate as searched from the Cambridge Structural Database (CSD) v. 5.29 (updated to November 2007). Preliminary results show that most of the new complexes are good emitters in solution at room temperature. A comprehensive study exploiting their potential interest will be reported in due course.

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Experimental Section

General Remarks: C, H and N analyses were carried out with a Carlo–Erba instrument. IR spectra were recorded with a Perkin–Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR spectroscopic data (^1H, ^{31}P) were recorded with Bruker Avance 300 or 400 spectrometers. Mass spectrometric analyses were performed with a Fisons VG Autospec double-focusing spectrometer, operated in positive mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-KeV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000.

The cyclometalated precursors $[\{Pd(\mu\text{-}OOCMe)(C\text{^}N)\}_2]$[9h,15] and $[\{Pd(\mu\text{-}OH)(C\text{^}N)\}_2]$[7c] were prepared as described in the literature. The commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification, and all the solvents were dried by standard methods before use.

Synthesis

Preparation of complexes [Pd(O^O)(C^N)] C^N = (Phpy) (**I**), (Bzq) (**II**) or (Phox) (**III**), O^O = salicylaldehydate (sal) (**I1**–**III1**), acetylacetonate (acac) (**I2**–**III2**) and benzoylacetonate (bzac) (**I3**–**III3**); [Pd(O^N)(C^N)] O^N = *N*-phenylsalicylaldiminate (*N*-Phsal) (I4–III4), *N*-*p*-chlorophenylsalicylaldiminate (*N*-pClsal) (**I5**–**III5**), 2-pyrrolecarbaldehydate (2-pcal) (**I6**–**III6**), 8-hydroxyquinolinate (oxin) (**I7**–**III7**) and $[\{Pd(\mu\text{-}N\text{^}S)(C\text{^}N)\}_2]$ N^S = 2-pyridinthiolate (spy) (**I8**–**III8**).

The new complexes were obtained by treating a CH_2Cl_2 suspension (20 mL) of the different precursors (**I**–**III**) (0.100 g) with the corresponding protic ligand (HL^L) (molar ratio 1:2). The suspension was stirred at room temperature for 30 min until a clear solution was obtained 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(sal)(Phpy)] (I1): Yield 0.111 g (81%). $C_{18}H_{13}NO_2Pd$ (381.7): calcd. C 56.6, H 3.4, N 3.7; found C 56.7, H 3.5, N 3.6. IR (Nujol): $\tilde{\nu}$ = 1614 (vs), 1604 (s), 1578 (s), 1512 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.27 (s, 1 H, sal, CH=O), 8.76 (d, J = 5.4 Hz, 1 H, Phpy), 7.83 (m, 1 H, Phpy), 7.72 (d, J = 8.4 Hz, 1 H, sal), 7.62 (d, J = 8.0 Hz, 1 H, Phpy), 7.41 (m, 3 H, Phpy), 7.19 (m, 3 H, 2 Phpy + 1 sal), 7.05 (d, J = 8.8 Hz, 1 H, sal), 6.60 (m, 1 H, sal) ppm. FAB-MS (positive mode): m/z = 381 $[Pd(sal)(Phpy)]^+$.

[Pd(sal)(Bzq)] (II1): Yield 0.102 g (76%). $C_{20}H_{13}NO_2Pd$ (405.7): calcd. C 59.2, H 3.2, N 3.5; found C 59.3, H 3.3, N 3.4. IR (Nujol): $\tilde{\nu}$ = 1619 (br), 1600 (s), 1516 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.26 (s, 1 H, sal, CH=O), 8.88 (d, J = 5.1 Hz, 1 H, Bzq), 8.22 (d, J = 7.9 Hz, 1 H, Bzq), 7.75 (m, 2 H, sal + Bzq) 7.45 (m, 6 H, 5 Bzq + 1 sal), 7.11 (d, J = 8.6 Hz, 1 H, sal), 6.61 (m, 1 H, sal) ppm. FAB-MS (positive mode): m/z = 405 $[Pd(sal)(Bzq)]^+$.

[Pd(sal)(Phox)] (III1): Yield 0.073 g (53%). $C_{16}H_{13}NO_3Pd$ (373.5): calcd. C 51.4, H 3.5, N 3.8; found C 51.2, H 3.5, N 3.9. IR (Nujol): $\tilde{\nu}$ = 1610 (s), 1596 (vs), 1518 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.15 (s, 1 H, sal, CH=O), 7.70 (d, J = 7.9 Hz, 1 H, sal), 7.30–7.06 (m, 6 H, 4 Phox + 2sal), 6.57 (m, 1 H, sal), 4.74 (t, J = 9.4 Hz, 2 H, Phox, OCH_2), 4.00 (t, J = 9.4 Hz, 2 H, Phox, NCH_2) ppm. FAB-MS (positive mode): m/z = 373 $[Pd(sal)(Phox)]^+$.

[Pd(acac)(Phpy)] (I2): Yield 0.098 g (76%). $C_{16}H_{15}NO_2Pd$ (359.7): calcd. C 53.4, H 4.2, N 3.9; found C 53.5, H 4.2, N 3.9. IR (Nujol): $\tilde{\nu}$ = 1604 (s), 1584 (vs), 1576 (s), 1516 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.72 (d, J = 5.5 Hz, 1 H, Phpy), 7.74 (m, 1 H, Phpy), 7.56 (m, 2 H, Phpy), 7.36 (d, J = 5.4 Hz, 1 H, Phpy), 7.09 (m, 3 H, Phpy), 5.34 (s, 1 H, acac), 2.04 (s, 3 H, acac), 2.00 (s, 3 H, acac) ppm. FAB-MS (positive mode): m/z = 359 $[Pd(acac)(Phpy)]^+$.

[Pd(acac)(bzq)] (II2): Yield 0.075 g (59%). $C_{18}H_{15}NO_2Pd$ (383.7): calcd. C 56.3, H 3.9, N 3.7; found C 56.3, H 3.8, N 3.6. IR (Nujol): $\tilde{\nu}$ = 1618 (s), 1570 (vs), 1519 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.84 (d, J = 5.0 Hz, 1 H, Bzq), 8.16 (d, J = 8.1 Hz, 1 H, Bzq), 7.66 (m, 2 H, Bzq), 7.45 (m, 4 H, Bzq), 5.39 (s, 1 H, acac), 2.09 (s, 3 H, acac), 2.04 (s, 3 H, acac) ppm. FAB-MS (positive mode): m/z = 383 $[Pd(acac)(Bzq)]^+$.

[Pd(acac)(Phox)] (III2): Yield 0.078 g (60%). $C_{14}H_{15}NO_3Pd$ (351.0): calcd. C 47.8, H 4.3, N 4.0; found C 47.9, H 4.2, N 4.0. IR (Nujol): $\tilde{\nu}$ = 1634 (s), 1576 (vs), 1516 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.5 Hz, 1 H, Phox), 7.23 (m, 2 H, Phox), 7.05 (m, 1 H, Phox), 5.37 (s, 1 H, CH acac), 4.74 (t, J = 9.6 Hz, 2 H, Phox, OCH_2), 3.97 (t, J = 9.6 Hz, 2 H, Phox, NCH_2), 2.07 (s, 3 H, CH_3 acac), 1.99 (s, 3 H, CH_3 acac) ppm. FAB-MS (positive mode): m/z = 351 $[Pd(acac)(Phox)]^+$.

[Pd(bzac)(Phpy)] (I3): Yield 0.073 g (48%). $C_{21}H_{17}NO_2Pd$ (421.8): calcd. C 59.8, H 4.1, N 3.2; found C 59.7, H 4.2, N 4.0. IR (Nujol): $\tilde{\nu}$ = 1606 (s), 1590 (vs), 1560 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.89 (d, J = 5.4 Hz, 1 H, Phpy-isomer I), 8.81 (d, J = 5.4 Hz, 1 H, Phpy-isomer II), 7.98 (d, J = 7.6 Hz, 2 H, Ph-bzac isomer I), 7.81 (d, J = 7.6 Hz, 2 H, Ph-bzac isomer II), 7.77 (m, 3 H, Phpy), 7.63 (m, 3 H, Phpy), 7.42 (m, 8 H, Phpy + bzac), 7.13 (m, 6 H, Phpy + bzac), 6.06 (s, 2 H, bzac), 2.25 (s, 3 H, bzac-isomer I), 2.20 (s, 3 H, bzac-isomer II) ppm. FAB-MS (positive mode): m/z = 421 $[Pd(bzac)(Phpy)]^+$.

[Pd(bzac)(Bzq)] (II3): Yield 0.103 g (70%). $C_{23}H_{17}NO_2Pd$ (445.8): calcd. C 62.0, H 3.8, N 3.1; found C 62.1, H 3.7, N 3.1. IR (Nujol): $\tilde{\nu}$ = 1620 (s), 1590 (vs), 1562 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.95 (d, 1 H Bzq-isomer I, J = 5.2 Hz), 8.89 (d, 1 H, Bzq-isomer II, J = 5.2 Hz), 8.20 (m, 2 H, Bzq), 8.03 (d, J = 7.6 Hz, 2 H, Ph-bzac isomer I), 7.97 (d, J = 7.6 Hz, 2 H, Ph-bzac isomer II), 7.81 (m, 1 H, Bzq), 7.72 (m, 3 H, Bzq), 7.58–7.43 (m, 14 H, 8 Bzq + 6 bzac), 6.11 (s, 1 H, bzac isomer I), 6.09 (s, 1 H, bzac isomer II), 2.30 (s, 3 H, bzac isomer I), 2.23 (s, 3 H, bzac isomer II) ppm. FAB-MS (positive mode): m/z = 445 $[Pd(bzac)(Bzq)]^+$.

[Pd(bzac)(Phox)] (III3): Yield 0.084 g (55%). $C_{19}H_{17}NO_3Pd$ (413.7): calcd. C 55.2, H 4.1, N 3.4; found C 55.3, H 4.2, N 3.4. IR (Nujol): $\tilde{\nu}$ = 1631 (s), 1555 (s), 1518 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J = 7.6 Hz, 2 H, Ph-bzac isomer I), 7.87 (d, J = 8.0 Hz, 2 H, Ph-bzac isomer II), 7.70 (d, J = 7.6 Hz, 1 H, Phox-isomer I), 7.61 (d, J = 7.6 Hz, 1 H, Phox-isomer II), 7.43 (m, 6 H, bzac), 7.27 (m, 4 H, Phox), 7.08 (m, 2 H, Phox), 6.06 (s, 1 H, CH bzac-isomer I), 6.03 (s, 1 H, CH bzac-isomer II), 4.77 (m, 4 H, Phox), 4.06 (m, 4 H, Phox), 2.22 (s, 3 H, CH_3 bzac isomer I), 2.13 (s, 3 H, CH_3 bzac isomer II) ppm. FAB-MS (positive mode): m/z = 413 $[Pd(bzac)(Phox)]^+$.

[Pd(N-Phsal)(Phpy)] (I4): Yield 0.132 g (80%). $C_{24}H_{18}N_2OPd$ (456.8): calcd. C 63.1, H 4.0, N 6.1; found C 63.3, H 4.1, N 6.2. IR (Nujol): $\tilde{\nu}$ = 1606 (s), 1577 (s), 1536 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.32 (d, J = 5.6 Hz, 1 H, Phpy), 8.11 (s, 1 H, HC=N, N-Phsal), 7.81 (m, 1 H, Phpy), 7.60 (m, 3 H, 2 H N-Phsal + 1 H Phpy), 7.34 (m, 4 H, Phpy), 7.27 (m, 3 H, N-Phsal), 6.99 (d, J = 8.7 Hz, 1 H, N-Phsal), 6.89 (m, 1 H, N-Phsal), 6.55 (m, 2 H, 1 Phpy + 1 N-Phsal), 5.78 (d, J = 7.8 Hz, 1 H, N-Phsal) ppm. FAB-MS (positive mode): m/z = 456 $[Pd(N\text{-}Phsal)(Phpy)]^+$.

[Pd(N-Phsal)(Bzq)] (II4): Yield 0.124 g (78%). $C_{26}H_{18}N_2OPd$ (480.9): calcd. C 64.9, H 3.8, N 5.8; found C 65.0, H 3.9, N 5.8. IR

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(Nujol): $\tilde{\nu}$ = 1604 (s), 1574 (vs), 1556 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.41 (d, J = 5.2 Hz, 1 H, Bzq), 8.20 (d, J = 7.7 Hz, 1 H, Bzq), 8.06 (s, 1 H, –HC=N), 7.52 (m, 5 H, 3 Bzq + 2 NPhsal), 7.30 (m, 6 H, 3 Bzq + 3 NPhsal), 7.01 (d, J = 8.9 Hz, 1 H, N-Phsal), 6.91 (m, 1 H, NPhsal), 6.50 (m, 1 H, Nphsal), 5.65 (d, J = 7.9 Hz, 1 H, N-Phsal) ppm. FAB-MS (positive mode): m/z = 480 $[Pd(N\text{-}Phsal)(Bzq)]^+$.

[Pd(N-Phsal)(Phox)] (III4): Yield 0.093 g (56%). $C_{22}H_{18}N_2O_2Pd$ (448.8): calcd. C 58.9, H 4.0, N 6.2; found C 59.1, H 4.2, N 6.1. IR (Nujol): $\tilde{\nu}$ = 1628 (s), 1608 (s), 1558 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1 H, -HC=N), 7.94 (d, J = 7.7 Hz, 1 H, Phox), 7.34 (m, 7 H, 3 Phox + 4 N-Phsal), 7.16 (m, 3 H, N-Phsal), 7.05 (m, 1 H, N-Phsal), 6.58 (m, 1 H, N-Phsal), 4.25 (t, J = 9.6 Hz, 2 H, Phox, OCH_2), 2.48 (t, J = 9.6 Hz, 2 H, Phox, NCH_2) ppm. FAB-MS (positive mode): m/z = 448 $[Pd(N\text{-}Phsal)(Phox)]^+$.

[Pd(N-pClPhsal)(Phpy)] (I5): Yield 0.129 g (73%). $C_{24}H_{17}ClN_2OPd$ (491.3): calcd. C 58.7, H 3.5, N 5.7; found C 58.9, H 3.6, N 5.8. IR (Nujol): $\tilde{\nu}$ = 1606 (s), 1574 (s), 1524 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.28 (d, J = 5.8 Hz, 1 H, Phpy), 8.06 (s, 1 H, HC=N, N-pClPhsal), 7.82 (m, 1 H, Phpy), 7.63 (d, J = 7.4 Hz, 1 H, Phpy), 7.53 (d, J = 8.4 Hz, 2 H, N-pClPhsal), 7.33 (m, 4 H, Phpy), 7.27 (m, 2 H, N-pClPhsal), 6.98 (d, J = 8.7 Hz, 1 H, N-pClPhsal), 6.92 (m, 1 H, N-pClPhsal), 6.65 (m, 1 H, N-pClPhsal), 6.55 (m, 1 H, Phpy), 5.86 (d, J = 7.8 Hz, 1 H, N-pClPhsal) ppm. FAB-MS (positive mode): m/z = 490 $[Pd(N\text{-}pClPhsal)(Phpy)]^+$.

[Pd(N-pClPhsal)(Bzq)] (II5): Yield 0.121 g (71%). $C_{26}ClH_{17}N_2OPd$ (515.3): calcd. C 60.6, H 3.3, N 5.4; found C 60.7, H 3.4, N 5.4. IR (Nujol): $\tilde{\nu}$ = 1608 (s), 1570 (s), 1522 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.36 (d, J = 5.2 Hz, 1 H, Bzq), 8.19 (d, J = 7.8 Hz, 1 H, Bzq), 8.00 (s, 1 H, –HC=N), 7.59 (d, J = 8.7 Hz, 1 H, Bzq), 7.48 (m, 4 H, 2 Bzq + 2 N-pClPhsal), 7.31 (m, 4 H, 2 Bzq + 2 N-pClPhsal), 7.20 (m, 1 H, Bzq), 6.96 (m, 2 H, N-pClPhsal), 6.51 (m, 1 H, N-pClPhsal), 5.76 (d, J = 8.0 Hz, 1 H, N-pClPhsal) ppm. FAB-MS (positive mode): m/z = 515 $[Pd(N\text{-}pClPhsal)(Bzq)]^+$.

[Pd(N-pClPhsal)(Phox)] (III5): Yield 0.095 g (53%). $C_{22}H_{17}ClN_2O_2Pd$ (483.3): calcd. C 54.7, H 3.6, N 5.8; found C 54.9, H 3.7, N 5.7. IR (Nujol): $\tilde{\nu}$ = 1628 (s), 1604 (s), 1518 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.94 (m, 2 H, 1 Phox + 1, –HC=N), 7.33 (m, 5 H, 3 Phox + 2 N-pClPhsal), 7.15 (m, 4 H, N-pClPhsal), 6.55 (m, 2 H, N-pClPhsal), 4.26 (t, J = 9.6 Hz, 2 H, Phox, OCH_2), 2.52 (t, J = 9.6 Hz, 2 H, Phox, NCH_2) ppm. FAB-MS (positive mode): m/z = 482 $[Pd(N\text{-}pClPhsal)(Phox)]^+$.

[Pd(2-pcal)(Phpy)] (I6): Yield 0.086 g (67%). $C_{16}H_{12}N_2OPd$ (355.7): calcd. C 54.2, H 3.4, N 7.9; found C 54.1, H 3.6, N 7.8. IR (Nujol): $\tilde{\nu}$ = 1604 (s), 1564 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, J = 5.4 Hz, 1 H, Phpy), 8.67 (s, 1 H, 2-pcal), 7.78 (m, 1 H, Phpy), 7.60 (d, J = 8.1 Hz, 1 H, Phpy), 7.50 (m, 3 H, 2 Phpy + 1 2-pcal), 7.41 (m, 1 H, 2-pcal), 7.13 (m, 3 H, Phpy), 6.36 (m, 1 H, 2-pcal) ppm. FAB-MS (positive mode): m/z = 355 $[Pd(2\text{-}pcal)(Phpy)]^+$.

[Pd(2-pcal)(Bzq)] (II6): Yield 0.087 g (69%). $C_{18}H_{12}N_2OPd$ (379.7): calcd. C 57.1, H 3.2, N 7.4; found C 57.0, H 3.3, N 7.4. IR (Nujol): $\tilde{\nu}$ = 1618 (s), 1568 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, J = 5.2 Hz, 1 H, Bzq), 8.64 (s, 1 H, 2-pcal), 8.07 (d, J = 8.1 Hz, 1 H, Bzq), 7.50 (m, 4 H, Bzq), 7.37 (m, 2 H, Bzq), 7.29 (m, 1 H, 2-pcal), 7.09 (m, 1 H, 2-pcal), 6.38 (m, 1 H, 2-pcal) ppm. FAB-MS (positive mode): m/z = 379 $[Pd(2\text{-}pcal)(Bzq)]^+$.

[Pd(2-pcal)(Phox)] (III6): Yield 0.068 g (53%). $C_{14}H_{12}N_2O_2Pd$ (347.7): calcd. C 48.5, H 3.5, N 8.1; found C 48.6, H 3.6, N 8.1. IR (Nujol): $\tilde{\nu}$ = 1640 (s), 1620 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H, 2-pcal), 7.51 (d, J = 7.5 Hz, 1 H, Phox), 7.41 (m, 1 H, 2-pcal), 7.23 (m, 2 H, Phox), 7.10 (m, 2 H, 2-pcal + Phox), 6.40 (m, 1 H, 2-pcal), 4.78 (t, J = 9.6 Hz, 2 H, Phox, OCH_2), 4.10 (t, J = 9.6 Hz, 2 H, Phox, NCH_2) ppm. FAB-MS (positive mode): m/z = 347 $[Pd(2\text{-}pcal)(Phox)]^+$.

[Pd(oxin)(Phpy)] (I7): Yield 0.096 g (66%). $C_{20}H_{14}N_2OPd$ (404.8): calcd. C 59.4, H 3.5, N 6.9; found C 59.5, H 3.7, N 7.0. IR (Nujol): $\tilde{\nu}$ = 1603 (s), 1567 (s), 1498 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.13 (d, J = 5.6 Hz, 1 H, oxin), 8.88 (d, J = 5.2 Hz, 1 H, Phpy), 8.26 (d, J = 8.0 Hz, 1 H, oxin), 7.84 (m, 1 H, Phpy), 7.69 (d, J = 8.0 Hz, 1 H, Phpy), 7.48 (m, 4 H, Phpy), 7.22 (m, 3 H, 2 oxin + 1 Phpy), 7.07 (d, J = 7.6 Hz, 1 H, oxin), 6.92 (d, J = 8.6 Hz, 1 H, oxin) ppm. FAB-MS (positive mode): m/z = 404 $[Pd(oxin)(Phpy)]^+$.

[Pd(oxin)(Bzq)] (II7): Yield 0.102 g (72%). $C_{22}H_{14}N_2OPd$ (428.8): calcd. C 61.6, H 3.3, N 6.5; found C 61.7, H 3.4, N 6.5. IR (Nujol): $\tilde{\nu}$ = 1620 (s), 1496 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.14 (d, J = 5.5 Hz, 1 H, oxin), 8.78 (d, J = 5.0 Hz, 1 H, Bzq), 8.08 (m, 2 H, oxin + Bzq), 7.62 (d, J = 8.6 Hz, 1 H, Bzq), 7.47 (m, 5 H, 4 Bzq + 1 oxin), 7.24 (m, 2 H, oxin + Bzq), 7.04 (d, J = 7.5 Hz, 1 H, oxin), 6.84 (d, J = 8.6 Hz, 1 H, oxin) ppm. FAB-MS (positive mode): m/z = 428 $[Pd(oxin)(Bzq)]^+$.

[{Pd(μ-spy)(Phpy)}$_2$] (I8): Yield 0.200 g (75%). $C_{32}H_{24}N_4Pd_2S_2$ (741.5): calcd. C 51.8, H 3.3, N 7.6, S 8.6; found C 51.7, H 3.2, N 7.6, S 8.4. IR (Nujol): $\tilde{\nu}$ = 1604 (s), 1576 (s), 1552 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.65 (d, J = 5.7 Hz, 2 H, Phpy), 7.81 (m, 4 H, Phpy), 7.62 (m, 2 H, Phpy), 7.50 (m, 4 H, 2 Phpy + 2 spy), 7.13 (m, 4 H, 2 Phpy + 2 spy), 6.97 (m, 4 H, 2 Phpy + 2 spy), 6.75 (m, 2 H, Phpy), 6.43 (m, 2 H, spy) ppm. FAB-MS (positive mode): m/z = 741 $[\{Pd(\mu\text{-}spy)(Phpy)\}_2]^+$.

[{Pd(μ-spy)(Bzq)}$_2$] (II8): Yield 0.188 g (72%). $C_{36}H_{24}N_4Pd_2S_2$ (789.6): calcd. C 54.8, H 3.1, N 7.1, S 8.1; found C 54.9, H 3.2, N 7.1, S 8.0. IR (Nujol): $\tilde{\nu}$ = 1622 (s), 1566 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, J = 5.2 Hz, 2 H, Bzq), 7.84 (m, 4 H, Bzq), 7.49 (d, J = 7.7 Hz, 2 H, spy), 7.18 (m, 4 H, 2 Bzq + 2 spy) 7.06 (m, 6 H, 4 Bzq + 2 spy), 6.70 (m, 4 H, Bzq), 6.36 (m, 2 H, spy) ppm. FAB-MS (positive mode): m/z = 789 $[\{Pd(\mu\text{-}spy)(Bzq)\}_2]^+$.

[{Pd(μ-spy)(Phox)}$_2$] (III8): Yield 0.164 g (61%). $C_{28}H_{24}N_4O_2Pd_2S_2$ (725.5): calcd. C 46.4, H 3.3, N 7.7, S 8.8; found C 46.5, H 3.2, N 7.6, S 8.7. IR (Nujol): $\tilde{\nu}$ = 1644 (s), 1586 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, J = 6.0 Hz, 2 H, spy), 7.89 (d, J = 7.5 Hz, 2 H, Phox), 7.37 (d, J = 8.4 Hz, 2 H, spy), 7.04 (m, 4 H, 2 Phox + 2 spy), 6.86 (m, 2 H, spy), 6.68 (m, 4 H, Phox), 4.41 (m, 4 H, Phox), 4.24 (m, 2 H, Phox), 3.35 (m, 2 H, Phox) ppm. FAB-MS (positive mode): m/z = 725 $[\{Pd(\mu\text{-}spy)(Phox)\}_2]^+$.

Preparation of complexes $[Pd\{S(S)P(OEt)_2\}(C\text{^}N)]$ [C^N = (Phpy) (**I9**), (Bzq) (**II9**) or (Phox) (**III9**)].

The new complexes were obtained by treating a CH_2Cl_2 suspension (20 mL) of the different precursors **I**–**III** (0.100 g) with the corresponding amount of $[NH_4][S(S)P(OEt)_2]$ (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 and diethyl ether, and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[Pd{S$_2$P(OEt)$_2$}(Phpy)] (I9): Yield 0.127 g (79%). $C_{15}H_{18}NO_2PPdS_2$ (445.8): calcd. C 40.4, H 4.1, N 3.1, S 14.4; found C 40.5, H 4.0, N 3.0, S 14.5. IR (Nujol): $\tilde{\nu}$ = 1603 (s), 1576 (s), 1014 (vs), 956 (vs), 650 (vs), 641 (vs) cm^{-1}. ^1H NMR (300 MHz,

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$CDCl_3$): δ = 8.54 (d, J = 5.4 Hz, 1 H, Phpy), 7.86 (m, 1 H, Phpy), 7.75 (d, J = 8.1 Hz, 1 H, Phpy), 7.53 (m, 1 H, Phpy), 7.29 (m, 1 H, Phpy), 7.15 (m, 3 H, Phpy), 4.25 (m, 4 H, CH_2-O), 1.35 (t, J = 7.0 Hz, 6 H, CH_3) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 104.8 (s) ppm. FAB-MS (positive mode): m/z = 445 [Pd{$S_2P(OEt)_2$}-(Phpy)]$^+$.

[Pd{$S_2P(OEt)_2$}(Bzq)] (II9): Yield 0.131 g (84%). $C_{17}H_{18}NO_2PPdS_2$ (468.9): calcd. C 43.5, H 3.9, N 3.0, S 13.6; found C 43.6, H 4.0, N 3.0, S 13.8. IR (Nujol): $\tilde{\nu}$ = 1616 (s), 1016 (vs), 965 (vs), 656 (vs), 639 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, J = 5.1 Hz, 1 H, Bzq), 8.30 (d, J = 7.8 Hz, 1 H, Bzq), 7.77 (d, J = 8.7 Hz, 1 H, Bzq), 7.61 (m, 2 H, Bzq), 7.48 (m, 3 H, Bzq), 4.29 (m, 4 H, CH_2),1.42 (t, J = 6.9 Hz, 6 H, CH_3) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 105.2 (s) ppm. FAB-MS (positive mode): m/z = 468 [Pd{$S_2P(OEt)_2$}(Bzq)]$^+$.

[Pd{$S_2P(OEt)_2$}(Phox)] (III9): Yield 0.086 g (53%). $C_{18}H_{14}N_2O_2Pd$ (396.72): calcd. C 54.5, H 3.6, N 7.1, S 14.7; found C 54.7, H 3.7, N 7.1, S 14.8. IR (Nujol): $\tilde{\nu}$ = 1626 (s), 1020 (vs), 960 (vs), 648 (vs), 636 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (m, 2 H, Phox), 7.19 (m, 1 H, Phox), 7.07 (m, 1 H, Phox), 4.74 (t, J = 9.4 Hz, 2 H, Phox, OCH_2), 4.22 (m, 4 H, CH_2), 4.03 (t, J = 9.4 Hz, 2 H, Phox, NCH_2), 1.39 (t, J = 7.0 Hz, 6 H, CH_3) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 105.3 (s) ppm. FAB-MS (positive mode): m/z = 437 [Pd{$S_2P(OEt)_2$}(Phox)]$^+$.

Preparation of complexes [Pd(S_2CNEt_2)(C^N)] [C^N = (Phpy) (**I10**), (Bzq) (**II10**) or (Phox) (**III10**)].

In separate experiments, a CH_2Cl_2 suspension (20 mL) of the different precursors **I**–**III** (0.100 g) was added to Et_2NH (molar ratio 1:2) along with 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 and diethyl ether, and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[Pd(S_2CNEt_2)(Phpy)] (I10): Yield 0.099 g (67%). $C_{16}H_{18}N_2PdS_2$ (408.9): calcd. C 47.0, H 4.4, N 6.9, S 15.7; found C 47.1, H 4.5, N 6.8, S 15.5. IR (Nujol): $\tilde{\nu}$ = 1599 (s), 1502 (s), 987 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (d, J = 5.4 Hz, 1 H, Phpy), 7.78 (m, 2 H, Phpy), 7.54 (m, 1 H, Phpy), 7.12 (m, 4 H, Phpy), 3.86 (q, J = 7.2 Hz, 4 H, CH_2), 1.33 (m, 6 H, CH_3) ppm. FAB-MS (positive mode): m/z = 408 [Pd(S_2CNEt_2)(Phpy)]$^+$.

[Pd(S_2CNEt_2)(Bzq)] (II10): Yield 0.099 g (69%). $C_{18}H_{18}N_2PdS_2$ (432.9): calcd. C 49.9, H 4.2, N 6.5, S 14.8; found C 50.1, H 4.3, N 6.6, S 14.6. IR (Nujol): $\tilde{\nu}$ = 1614 (s), 1501 (s), 989 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (d, J = 5.1 Hz, 1 H, Bzq), 8.27 (d, 1 H, Bzq), (d, J = 8.1 Hz, 1 H), 7.77 (d, J = 8.7 Hz, 1 H, Bzq), 7.59 (m, 2 H, Bzq), 7.43 (m, 3 H, Bzq), 3.90 (q, J = 7.2 Hz, 4 H, CH_2), 1.40 (m, 6 H, CH_3) ppm. FAB-MS (positive mode): m/z = 432 [Pd(S_2CNEt_2)(Bzq)]$^+$.

[Pd(S_2CNEt_2)(Phox)] (III10): Yield 0.067 g (45%). $C_{14}H_{18}N_2OPdS_2$ (400.8): calcd. C 41.9, H 4.5, N 7.0, S 16.0; found C 42.1, H 4.6, N 7.1, S 15.9. IR (Nujol): $\tilde{\nu}$ = 1632 (s), 1522 (s), 1016 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 1 H, Phox), 7.11 (m, 3 H, Phox), 4.73 (t, J = 9.5 Hz, 2 H, Phox, OCH_2), 4.01 (t, J = 9.5 Hz, 2 H, Phox, NCH_2), 3.71 (q, J = 7.1 Hz, 4 H, CH_2), 1.27 (m, 6 H, CH_3) ppm. FAB-MS (positive mode): m/z = 400 [Pd(S_2CNEt_2)(Phox)]$^+$.

Crystal Structure Determination of [Pd(sal)(Phpy)] (I1), [Pd(bzac)-(Phpy)] (I3), [Pd(2-pcal)(Phpy)] (I6), [Pd(N-Phsal)(Bzq)] (II4), [Pd(N-pClPhsal)(Bzq)] (II5) and [Pd(N-pClPhsal)(Phox)] (III5): Data collection for **I1** and **I6** was performed at 173 K with a Siemens P4 diffractometer. The data for **I3**, **II4** and **II5** were obtained at 100 K with a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were col-

Table 3. Crystal data and structure refinement for compounds **I1**, **I3**, **I6**, **II4**, **II5** and **III5**.

?>Compound	**I1**	**I3**	**I6**	**II4**	**II5**	**III5**
Empirical formula	$C_{18}H_{13}NO_2Pd$	$C_{21}H_{17}NO_2Pd$	$C_{16}H_{12}N_2OPd$	$C_{26}H_{18}N_2OPd$	$C_{26}H_{17}ClN_2OPd$	$C_{22}H_{17}ClN_2O_2Pd$
Formula weight [g mol^{-1}]	381.69	421.76	354.68	480.82	517.27	483.23
Temperature [K]	173(2)	100(2)	173(2)	100(2)	100(2)	293(2)
Radiation, λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	trigonal	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	R-3	Cc	$P2/a$	Cc
Unit cell dimensions						
a [Å]	18.489(2)	7.6503(3)	32.1803(17)	19.6091(9)	15.5738(6)	16.7630(5)
b [Å]	8.7952(10)	19.7337(8)	32.1803(17)	6.2204(3)	6.3513(2)	20.9270(6)
c [Å]	18.502(2)	11.6607(5)	13.4614(10)	15.9310(7)	20.8049(8)	17.9880(7)
α [°]	90	90	90	90	90	90
β [°]	107.02(10)	108.53	90	97.1710(10)	93.7530(10)	112.5500(10)
γ [°]	90	90	120	90	90	90
Volume [Å^3]	2877.0(5)	1669.14(12)	12072.6(13)	1928.01(15)	2053.48(13)	5827.7(3)
Z	8	4	36	4	4	12
Calculated density [mg m^{-3}]	1.762	1.678	1. 464	1.656	1.667	1.652
Absorption coefficient [mm^{-1}]	1.296	1.126	1.149	0.984	1.056	1.113
F(000)	1520	848	5280	968	1032	2904
Theta range for collection	1.85 to 27.49°	2.06 to 28.09	3.04 to 25.00°	2.09 to 28.18°	2.62 to 28.14°	1.64 to 27.52°
Reflections collected	17930	19040	9986	10529	22431	11452
Independent reflections	6604	3842	4726	4236	4765	11451
Refinement method			full-matrix least-squares on F^2			
Data/parameters/restrains	6604/501/0	3842/226/0	4726/361/0	4236/271/2	4765/280/0	11451/757/2
Goodness-of-fit on F^2	0.843	1.044	0.890	0.852	1.095	0.978
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0316	R_1 = 0.0222	R_1 = 0.0323	R_1 = 0.0209	R_1 = 0.0208	R_1 = 0.0723
	wR_2 = 0.0732	wR_2 = 0.0541	wR_2 = 0.0620	wR_2 = 0.0511	wR_2 = 0.0543	wR_2 = 0.1572
R indices (all data)	R_1 = 0.0496	R_1 = 0.0231	R_1 = 0.0551	R_1 = 0.0214	R_1 = 0.0216	R_1 = 0.1733
	wR_2 = 0.0806	wR_2 = 0.0547	wR_2 = 0.0667	wR_2 = 0.0515	wR_2 = 0.0550	wR_2 = 0.2157

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lected based on a ω scan run. A total of 2524 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[22] and corrected for absorption with the SADABS program.[23] The data collection for complex **III5** was performed at 293 K with a Nonius Kappa-CCD single-crystal diffractometer. The crystal-detector distance was fixed at 40 mm, and a total of 124 images were collected using the oscillation method, with scan angle per frame, 2° oscillation and a 40 s exposure time per image. The data collection strategy was calculated with the program Collect.[24] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[25]

The structures were solved by direct methods[26] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-hydrogen atoms[25] (Table 3).

CCDC-686575 (for **I1**), -686576 (for **I3**), -686577 (for **I6**), -686578 (for **II4**), -686579 (for **II5**), -686580 (for **III5**) contain the supplementary crystallographic data for this paper. 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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