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PAPER

A systematic study on the synthesis, reactivity and structure of ortho-palladated aryloximes, including the first cyclopalladated aryloximato and iminoaryloxime complexes†‡

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Complexes [Pd{*C*,*N*-Ar{C(Me)═NOH}-2}(μ-Cl)]$_2$ (**1**) with Ar = C_6H_4, $C_6H_3NO_2$-5 or $C_6H(OMe)_3$-4,5,6, were obtained from the appropriate oxime, $Li_2[PdCl_4]$ and NaOAc. They reacted with neutral monodentate C-, P- or N-donor ligands (L), with [PPN]Cl ([PPN] = Ph_3P═N═PPh_3), with Tl(acac) (acacH = acetylacetone), or with neutral bidentate ligands N^N (tetramethylethylenediamine (tmeda), 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bubpy)) in the presence of AgOTf or $AgClO_4$ to afford complexes of the types [Pd{*C*,*N*-Ar{C(Me)═NOH}-2}Cl(L)] (**2**), [PPN][Pd{*C*,*N*-Ar{C(Me)═NOH}-2}Cl_2] (**3**), [Pd{*C*,*N*-Ar{C(Me)═NOH}-2}(acac)] (**4**) or [Pd{*C*,*N*-Ar{C(Me)═NOH}-2}(N^N)]X (X = OTf, ClO_4) (**5**), respectively. Complexes **1** reacted with bidentate N^N ligands in the presence of a base to afford mononuclear zwitterionic oximato complexes [Pd{*C*,*N*-Ar{C(Me)═NO}-2}(N^N)] (**6**). Dehydrochlorination of complexes **2** by a base yielded dimeric oximato complexes of the type [Pd{μ-*C*,*N*,*O*-Ar{C(Me)═NO}-2}L]$_2$ (**7**). The insertion of XyNC into the Pd–C_{aryl} bond of complex **2** produced the mononuclear iminoaryloxime derivative [Pd{*C*,*N*-C(═NXy)Ar{C(Me)═NOH}-2}-Cl(CNXy)] (**8**) which, in turn, reacted with [AuCl(SMe_2)] to give [Pd{μ-*N*,*C*,*N*-C(═NXy)Ar-{C(Me)═NOH}-2}Cl]$_2$ (**9**) with loss of XyNC. Some of these complexes are, for any metal, the first containing cyclometalated aryloximato (**6**, **7**) or iminoaryloxime (**8**, **9**) ligands. Various crystal structures of complexes of the types **2**, **3**, **6**, **7**, **8** and **9** have been determined.

Introduction

Since the beginning of this century, different authors, mainly Nájera *et al.*, have been providing continuous reports on the versatile and efficient use of oxime carbopalladacyles as precatalysts in a variety of C–C coupling processes, including Mizoroki–Heck, Suzuki–Miyaura, Sonogashira, Stille, Hiyama or Ullmann-type reactions. The use of oxime palladacycles as a source of highly active palladium nanoparticles has allowed high-turnover catalyzed Heck, as well as other homo- and cross-coupling reactions. The subject has recently been reviewed.[1]

Although the syntheses of various oxime palladacycles have been reported, their reactivity has been very scarcely studied, which is surprising in view of the relevant catalytic activity of such compounds. In this paper we report the synthesis and characterization of new complexes of the types **1–9** shown in Chart 1. Various complexes of the types **1** and **2**, one anionic derivative of type **3**[2] and a few acetylacetonato[3–5] and cationic[2,6,7] complexes of types **4** and **5**, respectively, have been previously reported; some of them were characterized by X-ray crystallography,[3,7–10] but others were partly characterized.[4,11,12] Our objectives in developing this work were (1) to prepare the first family of well-characterized cyclopalladated complexes derived from oximes; (2) to prepare cyclopalladated complexes of acetophenone oxime and two of its derivatives containing substituents on the aryl group with different electronic properties (NO_2-5 and $(MeO)_3$-4,5,6), which are unprecedented; this has allowed us to study the influence of these substituents on both, the reactivity and structure of the corresponding complexes; and (3) to study deprotonation and isocyanide insertion reactions on the oxime complexes, which have allowed us to prepare the first aryloximato (**6**, **7**) and iminoaryloxime complexes (**8**, **9**) of any metal. Both include examples in which these ligands act as bridging or non-bridging.

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† Dedicated to Professors Juan Forniés, María Pilar García and Antonio Laguna on the occasion of their retirement.

‡ Electronic supplementary information (ESI) available: Additional experimental and spectroscopic data. CCDC reference numbers 837023 (**2d**), 837028 (**3**), 837027 (**3′**), 837029 (**6′b**), 837024 (**7b**·H_2O), 837025 (**8″**) and 837026 (**9**·2$CHCl_3$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11445j

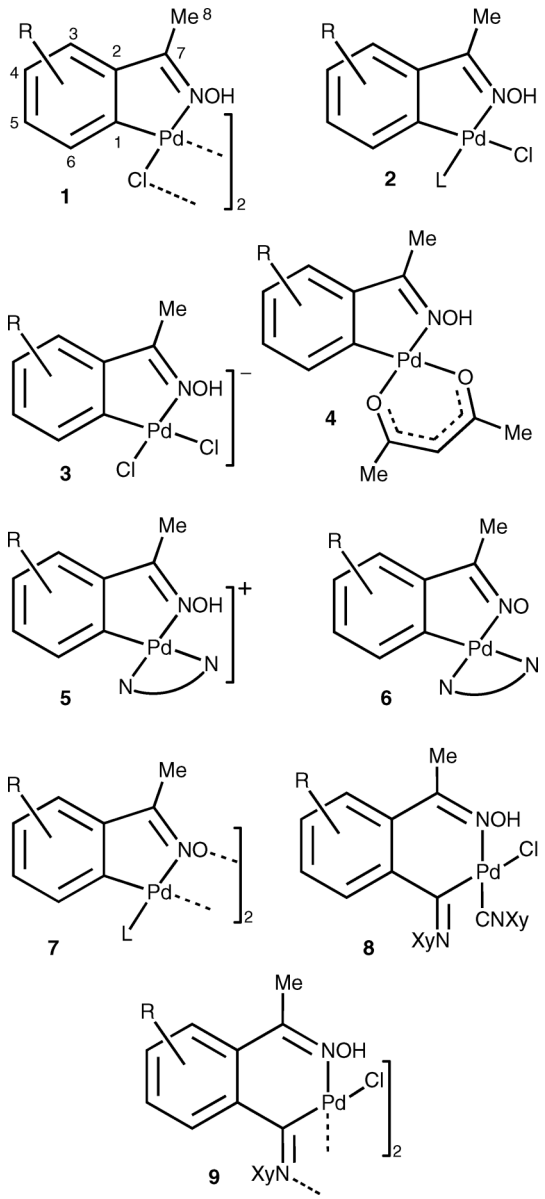


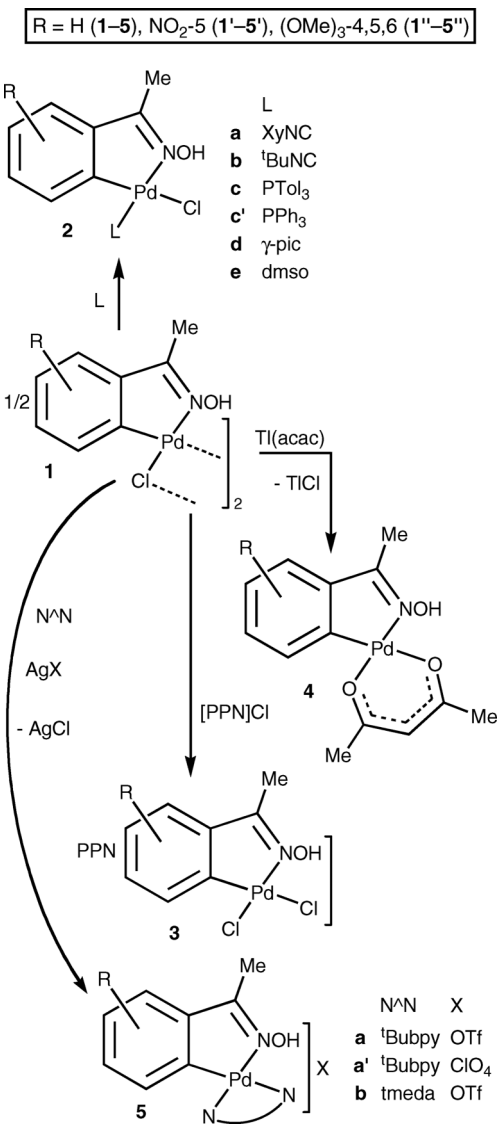
Chart 1 Types of aryloxime (**1–5**), aryloximato (**6–7**) and iminoaryloxime (**8–9**) palladium complexes included in this paper. The numbering scheme used in NMR assignments is depicted in **1**.

The ability of the Pd–C bond to insert unsaturated molecules, thought to be one of the key steps in many palladium-catalyzed reactions, prompted us, more than one decade ago, to synthesize *ortho*-functionalized arylpalladium complexes and to study their reactivity towards unsaturated species with the hope that interesting results could arise from the modified reactivity imposed by the metal on both the pre-existing *ortho*-group and that resulting from the insertion process, or from their joint reactivity favoured by their close proximity. The fruit of this idea has been the preparation of novel types of organometallic complexes and interesting organic products.[13] We report here the first insertion reaction of an isocyanide into the C–Pd bond of an orthopalladated aryloxime. We describe for the first time the use of [AuCl(SMe$_2$)] as an isocyanide scavenger. Its use allowed us to prepare, from complex **8**, the dinuclear **9**. All reported complexes could be used to prepare heterocycles.

Results and discussion

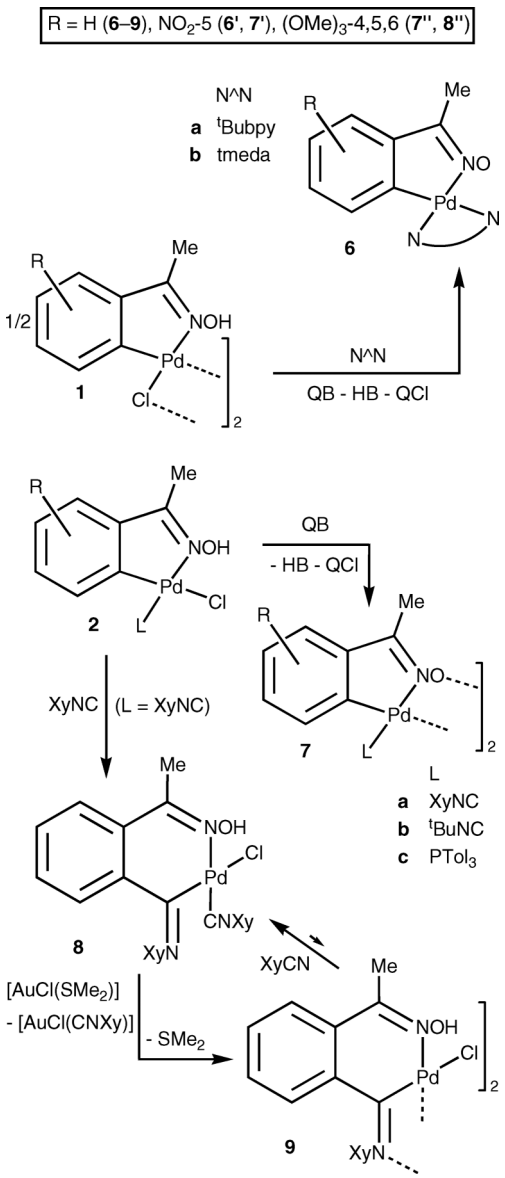
Synthesis

The dinuclear chloro-bridged oxime complexes of type **1**, (Scheme 1, Pd{*C*,*N*-Ar{C(Me)=NOH}-2}(μ-Cl)]$_2$ (Ar = C_6H_4 (**1**), $C_6H_3NO_2$-5 (**1′**), CH(OMe)$_3$-4,5,6 (**1″**)) were prepared in good yield from generated *in situ* $Li_2[PdCl_4]$, the appropriate oxime and NaOAc in MeOH, following a modification of the method first described by Onoue.[11] We used a slight defect of oxime in order to avoid the formation of by-products with N-coordinated oxime or oximato ligands. This precaution proved to be insufficient for the synthesis of **1′** which formed along with another species that we could not remove or identify. However, we isolated **1′** in the presence of a methanolic solution of concentrated aqueous HCl because we suspected that the impurity could result from a dehydrochlorination process favoured by the greater acidity of the OH proton induced by the presence of the NO_2 group.



Scheme 1

When CH_2Cl_2 suspensions of complexes of type **1** were treated with monodentate neutral C-, N- or P-donor ligands L in 1 : 2 molar ratio or in excess (L = dmso), solutions formed almost immediately from which the corresponding mononuclear derivatives of type **2** (Scheme 1, [Pd{*C*,*N*-Ar{C(Me)=NOH}-2}Cl(L)] (Ar = C_6H_4, L = XyNC (**2a**), ^{t}BuNC (**2b**), $PTol_3$ (**2c**), γ-pic (**2d**); Ar = $C_6H_3NO_2$-5, L = XyNC (**2′a**), ^{t}BuNC (**2′b**), $PTol_3$ (**2′c**), γ-pic (**2′d**); Ar = $CH(OMe)_3$-4,5,6, L = XyNC (**2″a**), ^{t}BuNC (**2″b**), PPh_3 (**2″c′**)) were isolated in good yield. The synthesis of **2a** required slow addition of the ligand because, otherwise, different amounts of **8** (see below, Scheme 2) formed as a consequence of XyNC insertion in the Pd–C_{aryl} bond. Alternatively, **2a** can be obtained from **2d**, upon replacing γ-picoline with XyNC. The C- and P-donor ligands must be *trans* to the oxime N atom because of the high C/C and C/P transphobia.[14] This has been the geometry found in similar complexes.[3,10,15] In the reported orthopalladated aryl oxime complexes containing pyridine or some of its derivatives this ligand is also *trans* to the oxime N atom.[7,9]



Scheme 2 Synthesis of complexes **6–9**. QB = NaOAc, NaH, K^{t}BuO.

Because of the scarce donor ability of the dmso ligand in complex **2e**, this was obtained in equilibrium with **1**, which required several operations before the pure product could be isolated (50% yield). This complex forms as an equimolar mixture of two isomers containing the S-coordinated ligand *trans* to C or N, respectively. Complex **2′b** and some others (**3′**, **3″**, **4″**, **5′a′**, **6a**, **6′a**, **7b**, **7c**, **7′a**, **7′b**, **8″**, Schemes 1–2) crystallized with various amounts of water, in spite of being heated in a vacuum oven. The water content deduced from their elemental analyses was confirmed in all cases by their ^{1}H NMR spectra or X-ray crystallography (**7b**·H_2O). The low isolated yield of complex **2′c** (62%) can be attributed to its partial dehydrochlorination to give **7′c** (see below), facilitated by the enhanced acidity of the OH group in the nitro-substituted oxime derivatives.

The reaction of the dinuclear complexes of type **1** with [PPN]Cl also caused bridge splitting and formation of anionic complexes [PPN][Pd{*C*,*N*-Ar{C(Me)=NOH}-2}Cl_2] (Ar = C_6H_4 (**3**), $C_6H_3NO_2$-5 (**3′**), $CH(OMe)_3$-4,5,6 (**3″**)); similarly, acetylacetonato derivatives [Pd{*C*,*N*-Ar{C(Me)=NOH}-2}(acac)] (Ar = C_6H_4 (**4**), $C_6H_3NO_2$-5 (**4′**), $CH(OMe)_3$-4,5,6 (**4″**)) were isolated in good yields from the 1 : 2 reactions of **1** with Tl(acac). Using Ag(acac) instead of Tl(acac) produced the same results.

The reaction of complexes of type **1** with neutral bidentate N^N ligands (^{t}Bubpy, tmeda), in the presence of silver salts or bases, produced different results depending on the auxiliary reagent. Thus, in the presence of AgOTf or $AgClO_4$, a suspension formed from which cationic aryloxime complexes of type **5** [Pd{*C*,*N*-Ar{C(Me)=NOH}-2}(N^N)]X (Ar = C_6H_4, X = OTf, N^N = ^{t}Bubpy (**5a**), tmeda (**5b**), Ar = $C_6H_3NO_2$-5, N^N = ^{t}Bubpy, ClO_4 (**5′a′**)) could be isolated in good yield after removing the insoluble AgCl. However, in the reaction of **1** with N^N ligands and K^{t}BuO (1 : 2 : 2, QB in Scheme 2), apart from bridge splitting and removal of the chloro ligand as above, deprotonation of the oxime function by the base occurred producing oximato complexes [Pd{*C*,*N*-Ar{C(Me)=NO}-2}(N^N)] (Ar = C_6H_4, N^N = ^{t}Bubpy (**6a**), Ar = $C_6H_3NO_2$-5, N^N = ^{t}Bubpy (**6′a**), tmeda (**6′b**)) and ^{t}BuOH, which is not surprising in view of the well known enhanced acidity of oximes upon coordination.[16] Similarly, when complexes of type **2** were treated with a base (QB = NaOAc, NaH, K^{t}BuO), oxime deprotonation and QCl precipitation took place to give aryloximato complexes [Pd{μ-*C*,*N*,*O*-Ar{C(Me)=NO}-2}L]$_2$ (Ar = C_6H_4, L = XyNC (**7a**), ^{t}BuNC (**7b**), $PTol_3$ (**7c**), Ar = $C_6H_3NO_2$-5, L = XyNC (**7′a**), ^{t}BuNC (**7′b**), $PTol_3$ (**7′c**); Ar = $CH(OMe)_3$-4,5,6, L = XyNC (**7″a**), ^{t}BuNC (**7″b**) (Scheme 2). The tetracoordination of palladium is attained by means of the oximato ligand acting as a *N*,*O*-bridging ligand.

The HRMS of **7′a**·H_2O agrees to 2.52 ppm with the calculated exact mass of the dimeric anhydrous product but its carbon content found in the elemental analysis is a bit low (47.55 *vs.* 48.07%). Since we could not assess its purity by NMR due to its insolubility, we reacted it with a solution of HCl in CH_2Cl_2 (excess) and confirmed that the NMR of the crude reaction product coincides with that of pure **2′a**. Compound **7b** or **7″b** was also prepared by reaction of the acetylacetonato complex **4** or **4″** with ^{t}BuNC in a 1 : 1 molar ratio. This reaction suggests that the oxime function can only coexist with the strongly basic acac ligand when it is chelating; otherwise, deprotonation takes place to give acacH along with an oximato complex that dimerizes to achieve the tetracoordination at palladium. As far as we are aware complexes

of the types **6** and **7** are, for any metal, the first isolated complexes containing a cyclometallated aryloximato ligand, although one such species has been claimed to be an intermediate in the efficient degradation of thiophosphate pesticides catalyzed by palladium aryloxime metallacycles.[17] Additionally, a trinuclear aryloximato palladium complex has been described,[9] but it is not a cyclometallated species.

In an attempt to obtain iminoaryloxime complexes [Pd{*C*,*N*-C(=NXy)Ar{C(Me)=NOH}-2}Cl(CNXy)] (Ar = C_6H_4 (**8**), $C_6H(OMe)_3$-4,5,6 (**8″**), Scheme 2) we reacted the corresponding complexes **1** with two equivalents of XyNC per Pd with the hope that they would produce bridge splitting and insertion in the Pd–C_{aryl} bond. However, a mixture formed that we could not resolve. It was shown by NMR to contain complexes of types **1**, **2**, and **8**, along with polyinsertion products. Complexes **8** and **8″** could be obtained, at room temperature, from the reaction of the appropriate complex **2** with excess XyNC (**8**, 1 : 1.27) or using the stoichiometric amount (**8″**). The moderate (58–69%) yields achieved can be explained because polyinsertion products start to form before the reaction is complete and thus, various operations were needed to separate the desired complex of type **8** from the accompanying impurities. The homologous reactions between **2′a** and XyNC (1 : 1) or between **2b**, **2′b** or **2″b** and ^{t}BuNC (1 : 1) did not produce the expected complexes of type **8** which could be attributed, respectively, to the electron withdrawing ability of the nitroaryl group in **2′a** and to the +I electronic effect of the ^{t}Bu group of the isocyanide, both factors disfavouring the insertion of the isocyanide which is facilitated when the aryl carbon bonded to palladium and the isocyanide carbon bear formal negative and positive charges, respectively.[18,19] Although some of these reactions do not work at all, those of **2b** and **2″b** with ^{t}BuNC (1 : 1) produced the Pd(II) complex $[Pd_2Cl_2(CN^tBu)_4]$ among other unidentified products.

Based on kinetic studies[19–21] proving that the insertion of isocyanide into σ-Pd–C bonds occurs by intramolecular migratory insertion of the σ-C donor ligand into the previously coordinated isocyanide, we refluxed complex **2a** in toluene with the hope of obtaining any of the dinuclear iminoacyl complexes resulting from insertion followed by dimerization with chloro[22] or iminoacyl bridging[23] ligands; both processes are known. However, **2a** was recovered unchanged and none of the expected complexes, namely [Pd{*C*,*N*-C(=NXy)C_6H_4{C(Me)=NOH}-2}(μ-Cl)]$_2$ or [Pd{μ-*N*,*C*,*N*-C(=NXy)C_6H_4{C(Me)=NOH}-2}Cl]$_2$ (**9**), was even detected by ^{1}H NMR. Similarly, not even trace amounts of the complex [Pd{*C*,*N*,-C(=NXy)C_6H_4{C(Me)=NOH}-2}Cl(γ-pic)] were detected after refluxing for 2 h solutions containing equimolar amounts of **2a** and γ-picoline in $CHCl_3$ or in toluene, in spite of the fact that the insertion process has been said to be assisted by donor species.[21,24]

However, complex **9** could be obtained upon abstracting the XyNC ligand present in **8** by reacting it with [AuCl(SMe_2)] (1 : 1) in $CHCl_3$ (Scheme 2). The reaction produced [AuCl(CNXy)] and the dinuclear complex **9** in which two bridging iminoacyl fragments (and not the chloro ligands) complete the tetracoordination of the palladium centers. The reaction seems to be an equilibrium since various ^{1}H NMR spectra of the reaction mixture measured in the period 0–2 h showed the invariable presence of **9** and [AuCl(CNXy)], along with small amounts of the starting compounds and an unidentified species that is likely to be the complex [Pd{*C*,*N*-C(=NXy)C_6H_4{C(Me)=NOH}-2}Cl(SMe_2)] resulting from bridge splitting in **9** by the dimethyl sulfide present in solution. This is why the isolation of pure **9** required a tedious work up (see Experimental), which explains the low isolated yield. Probably, this reaction occurs because an **8** ⇆ **9** + XyNC equilibrium exists giving a very small amount of XyNC, which, upon reaction with [AuCl(SMe_2)], would give [AuCl(CNXy)] and **9**. As far as we are aware, the abstraction of an isocyanide ligand by this means is unprecedented.

The reaction of **8″** with [AuCl(SMe_2)] failed to give **9″**, homologous of **9** with the trimethoxy substituted arene. We interpret this result assuming that the **8″** ⇆ **9″** + XyNC equilibrium can not occur because formation of the dimer **9″** would require the Xy group to be folded towards MeO-6 group and this is sterically hindered. In fact, the crystal structure of **8″** shows the iminoacyl xylyl group folded towards the XyNC ligand to avoid the above mentioned repulsion. In the case of **8** a NOESY NMR spectrum allows us to unequivocally establish that the iminoacyl xylyl group is folded towards the aryl group.

X-Ray crystal structures

The crystal structures of complexes **2d** (Fig. 1), **3** (Fig. 2), **3′** (Fig. 3), **6′b** (Fig. 4), **7b**·H_2O (Fig. 5), **8″** (Fig. 6) and **9**·2$CHCl_3$ (Fig. 7) have been determined by X-ray diffraction. As complexes **6**, **7** and **8**, **9** are, respectively, the first aryloximato and iminoaryloxime metal complexes, the crystal structures of **6′b** or **7b**·H_2O and **8″** or **9**·2$CHCl_3$ offer the first structural data of these types of complexes of any metal.

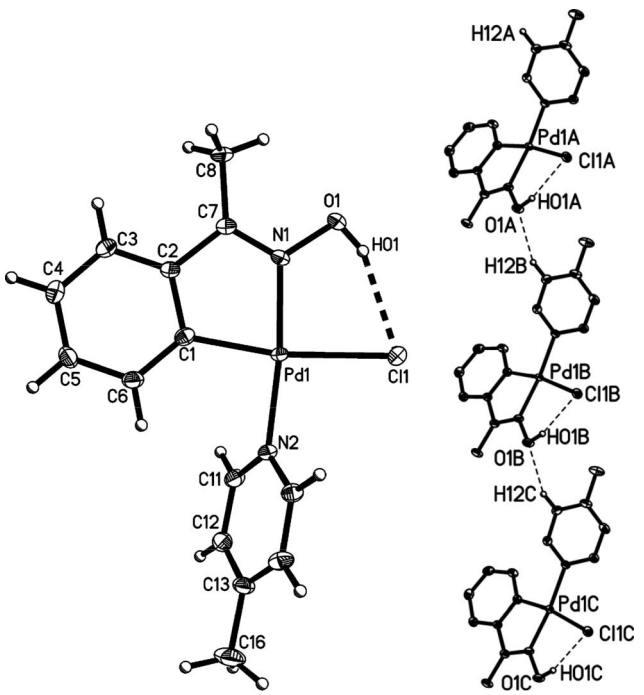


Fig. 1 Left: Thermal ellipsoid representation plot (50% probability) of complex **2d**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.9873(16), Pd(1)–N(1) 1.9945(13), Pd(1)–N(2) 2.0358(13), Pd(1)–Cl(1) 2.4367(4), N(1)–C(7) 1.290(2), N(1)–O(1) 1.3887(17), C(1)–C(2) 1.419(2), C(2)–C(7) 1.467(2); C(1)–Pd(1)–N(1) 80.00(6), C(1)–Pd(1)–N(2) 93.74(6), N(1)–Pd(1)–Cl(1) 90.29(4), N(2)–Pd(1)–Cl(1) 96.01(4). Right: Chains along the *c* axis in **2d** formed through C–H···O hydrogen bonds.

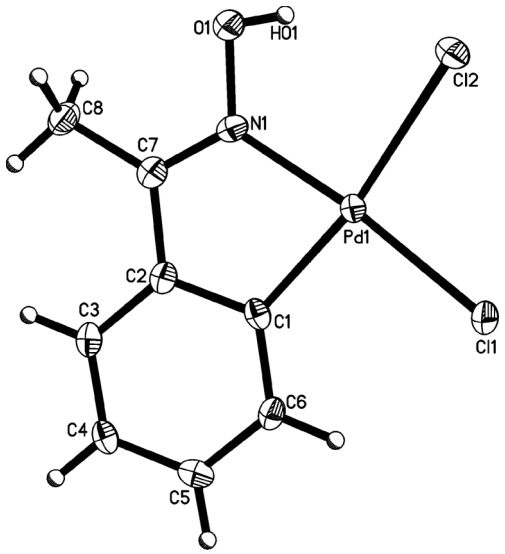


Fig. 2 Thermal ellipsoid representation plot (50% probability) of the anion of complex **3**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.977(3), Pd(1)–N(1) 1.989(2), Pd(1)–Cl(1) 2.2775(7), Pd(1)–Cl(2) 2.4364(7); C(1)–Pd(1)–N(1) 80.37(11), C(1)–Pd(1)–Cl(1) 93.57(9), N(1)–Pd(1)–Cl(2) 90.53(7), Cl(1)–Pd(1)–Cl(2) 95.48(3).

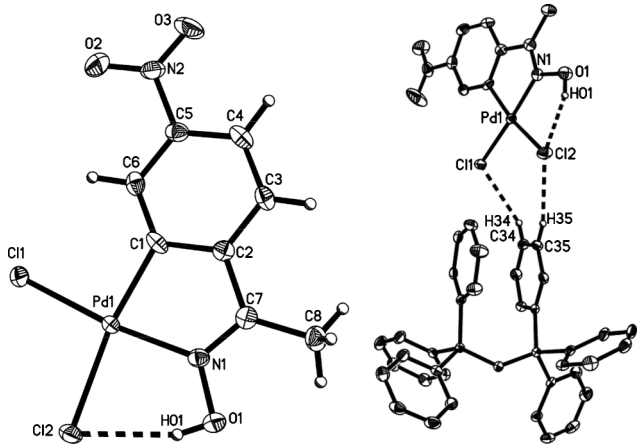


Fig. 3 Left: Thermal ellipsoid representation plot (50% probability) of the anion of complex **3′**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.981(2), Pd(1)–N(1) 2.001(2), Pd(1)–Cl(1) 2.2958(7), Pd(1)–Cl(2) 2.4371(7), N(1)–O(1) 1.378(3), C(1)–C(2) 1.426(4), C(2)–C(7) 1.469(4), N(1)–C(7) 1.299(3); C(1)–Pd(1)–N(1) 80.54(10), C(1)–Pd(1)–Cl(1) 92.97(8), N(1)–Pd(1)–Cl(2) 89.03(6), Cl(1)–Pd(1)–Cl(2) 97.58(2). Right: C–H···Cl hydrogen bond interactions in **3′** giving discrete cation–anion entities.

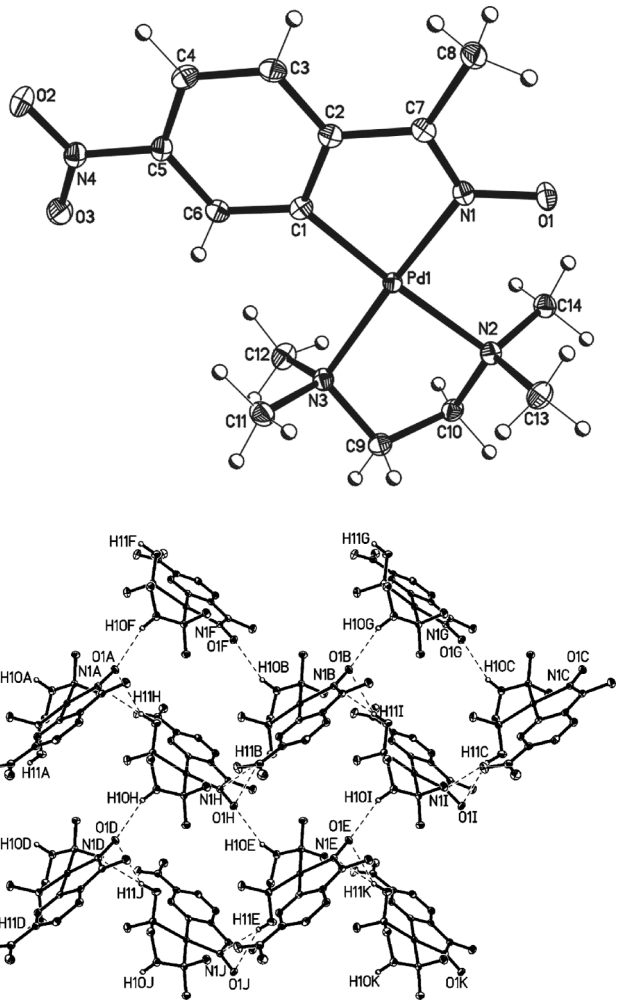


Fig. 4 Up: Thermal ellipsoid representation plot (50% probability) of complex **6′b**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.0078(18), Pd(1)–N(1) 2.0199(16), Pd(1)–N(2) 2.1800(16), Pd(1)–N(3) 2.1349(16), N(1)–O(1) 1.301(2), C(1)–C(2) 1.421(3), C(2)–C(7) 1.449(3), N(1)–C(7) 1.320(2); C(1)–Pd(1)–N(1) 80.74(7), C(1)–Pd(1)–N(3) 99.79(7), N(3)–Pd(1)–N(2) 82.76(6), N(1)–Pd(1)–N(2) 97.06(6). Down: Layers parallel to the *ab* plane in **6′b** formed through C–H···O and C–H···N hydrogen bonds.

The bond distances found in the oxime derivatives **2** and **3** are similar to their homologous in ten crystal structures of aryloxime palladium complexes previously reported.[3,7,8,25] The structures of the oxime (**2d**, **3**, **3′**) and oximato (**6′b**, **7b**·H_2O) complexes display many commonalities but, while the oxime derivatives show N(1)–O(1) bond distances (1.378(3)–1.391(3) Å) indicative of a N–O single bond, in the neutral oximato complex **6′b** an appreciable shortening of this distance is observed (1.301(2) Å). This, along with the lengthening of N(1)–C(7) (1.320(2) *vs.* 1.290(2)–1.299(3) Å) and the shortening of C(2)–C(7) (1.449(3) *vs.* 1.466(4)–1.469(4) Å) suggests some electron delocalization over the C(2)–C(7)–N(1)–O(1) moiety. This is not observed in the dinuclear oximato complex **7b**·H_2O in which the *N*,*O*–bridging role of the oximato ligand justifies the lengthening of the N(1)–O(1) bond distances to values intermediate between those in oxime and non-bridging oximato ligands (1.3512(18) and 1.3558(17) Å).

The Pd–Cl bond distances *trans* to carbon in **3** and **3′** (2.4364(7) and 2.4371(7) Å, respectively) are longer than those *trans* to nitrogen (2.2775(7) and 2.2958(7) Å, respectively), as expected for the greater *trans* influence of carbon with respect to nitrogen. The same reason justifies the longer Pd–N(2) (2.1800(16) Å) with respect to Pd–N(3) (2.1349(16) Å) in **6b**. The five-membered ring in complex **7b**·H_2O is folded around the O(1)···O(2) axis in such a way that the two planar subunits form a torsion angle of 59.3°. The Pd–N bond distances in **7b**·H_2O are rather long (2.0296(14), 2.0334(13) Å) caused by the great *trans* influence of the isocyanide

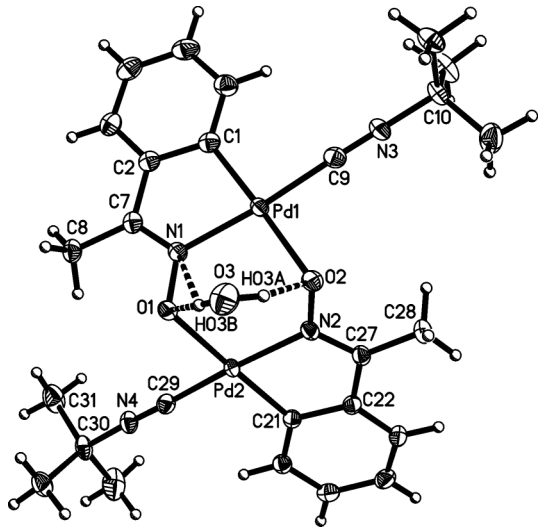


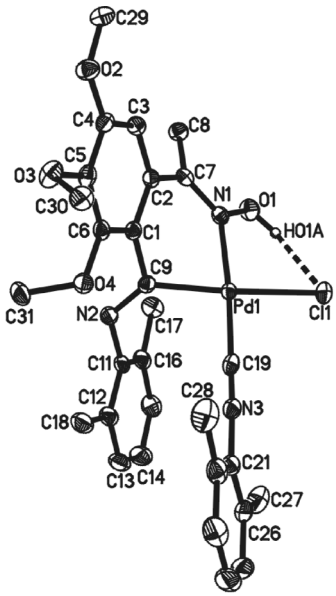
Fig. 5 Thermal ellipsoid representation plot (50% probability) of complex **7b**·H_2O. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.9909(18), Pd(2)–C(21) 1.9867(16), Pd(1)–N(1) 2.0296(14), Pd(2)–N(2) 2.0334(13), Pd(1)–O(2) 2.1191(12), Pd(2)–O(1) 2.1395(12), Pd(1)–C(9) 1.9510(18), Pd(2)–C(29) 1.9501(17), N(1)–O(1) 1.3512(18), N(2)–O(2) 1.3558(17), N(1)–C(7) 1.303(2), N(2)–C(27) 1.297(2), C(2)–C(7) 1.467(2), C(22)–C(27) 1.465(2), C(1)–C(2) 1.420(2), C(21)–C(22) 1.419(2); C(1)–Pd(1)–N(1) 80.63(7), C(21)–Pd(2)–N(2) 80.67(6), C(9)–Pd(1)–C(1) 94.35(7), C(29)–Pd(2)–C(21) 93.26(7), N(1)–Pd(1)–O(2) 97.32(5), N(2)–Pd(2)–O(1) 96.35(5), C(9)–Pd(1)–O(2) 87.69(6), C(29)–Pd(2)–O(1) 89.87(6), C(7)–N(1)–Pd(1) 117.56(11), C(27)–N(2)–Pd(2) 117.50(11), O(1)–N(1)–Pd(1) 123.44(10), O(2)–N(2)–Pd(2) 124.30(10), N(1)–O(1)–Pd(2) 108.03(9), N(2)–O(2)–Pd(1) 110.41(9), C(2)–C(1)–Pd(1) 112.68(12), C(22)–C(21)–Pd(2) 112.48(12), C(1)–C(2)–C(7) 115.88(15), C(21)–C(22)–C(27) 116.21(14), N(1)–C(7)–C(2) 113.23(15), N(2)–C(27)–C(22) 113.10(14).

ligand. In the dimer **9**·2$CHCl_3$ the Pd(1)–Pd(2) distance 3.201 Å is slightly shorter than twice the van der Waals radius of palladium (3.26 Å).

The oxime chloro complexes (**2d**, **3′**, **8″** and **9**·2$CHCl_3$) show intramolecular O–H···Cl hydrogen bonds. Additionally, classical O–H···O (**7b**·H_2O) or non-classical intra C–H···Cl (in **3′** giving discrete entities cation–anion (Fig. 3, right)) or intermolecular C–H···O (**2d**, chains along *c* axis (Fig. 1, right), **6′b**, **7b**·H_2O) or C–H···N (**6′b**) hydrogen bonds are also present, which in the case of **8″** cause the molecules to pack in a zig–zag chain along the *c* axis. In the oxime chloro complexes **6′b** the nonclassical intermolecular C–H···O and C–H···N hydrogen bond links the molecules into layers parallel to the *ab* plane (Fig. 4, below).[26]

Although complexes **8** and **9** could be described as carbenes, the crystal structures of **8″** and **9** do not support such an assignment. The C(aryl)–C(sp^2) bond distances (1.480(3) Å in **8″**, 1.480(5) and 1.482(5) Å in **9**) are close to the standard C(aryl)–C(sp^2) overall value (1.488 Å)[27] and the C=N bond distances are even shorter than the standard C(sp^2)=N(3) value (1.316 Å;[27] 1.260(3) Å in **8″**, 1.279(4), 1.287(4) Å in **9**), which confirms they are iminobenzoyl derivatives.

All complexes were characterized by NMR (when soluble) and IR spectroscopies (see discussion in the ESI‡ and data in the Experimental section).



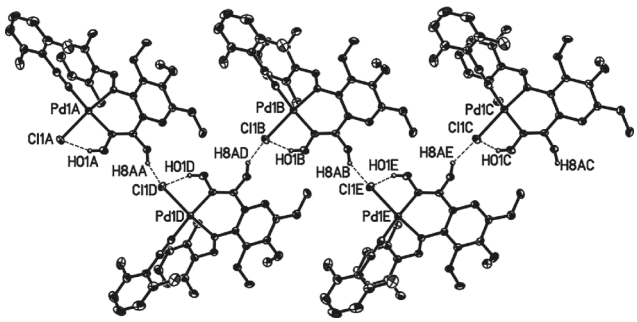


Fig. 6 Up: Thermal ellipsoid representation plot (50% probability) of complex **8″**. Selected bond lengths (Å) and angles (°): Pd(1)–C(9) 1.989(2), Pd(1)–C(19) 1.941(2), Pd(1)–N(1) 2.0689(19), Pd(1)–Cl(1) 2.4406(6), N(1)–C(7) 1.279(3), C(2)–C(7) 1.483(3), C(1)–C(2) 1.403(3), C(1)–C(9) 1.480(3), N(1)–O(1) 1.390(2), N(2)–C(9) 1.260(3); C(19)–Pd(1)–C(9) 90.50(9), C(9)–Pd(1)–N(1) 84.74(8), C(19)–Pd(1)–Cl(1) 96.55(7), N(1)–Pd(1)–Cl(1) 88.30(5), C(7)–N(1)–O(1) 114.52(19), C(7)–N(1)–Pd(1) 128.82(15), O(1)–N(1)–Pd(1) 115.72(14), N(1)–C(7)–C(2) 117.2(2), C(1)–C(9)–Pd(1) 110.65(15), C(9)–N(2)–C(11) 122.2(2). Down: Packing diagram of **8″** showing a zig–zag chain along the *c* axis.

Experimental

We describe below the syntheses of only one complex of each type, and leave for the ESI‡ the detailed syntheses of all the remaining complexes. Although complexes **1**,[11] **2b**[12] and **4**[4] were previously reported, we also include them in the ESI‡ because their characterization was incomplete.

General

When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. The solvents were distilled before use. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were obtained with a Carlo Erba 1106 microanalyzer. The molar conductivities were measured with a CRISON micro CM 2200

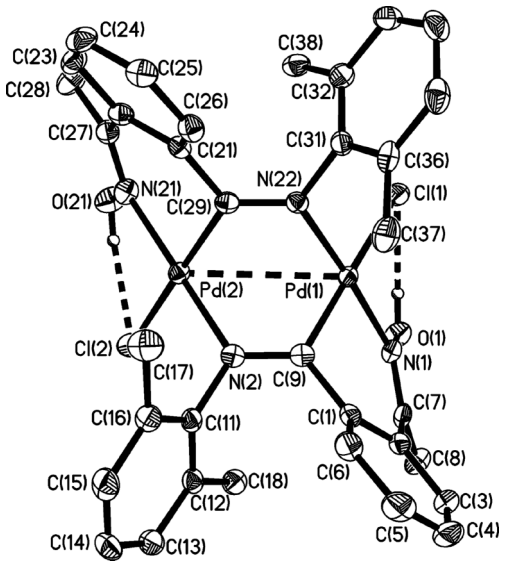


Fig. 7 Thermal ellipsoid representation plot (50% probability) of complex **9**·2$CHCl_3$ (solvent omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)–Pd(2) 3.2068(4), Pd(1)–C(9) 1.942(3), Pd(2)–C(29) 1.941(3), Pd(1)–N(1) 2.042(3), Pd(2)–N(21) 2.028(3), Pd(1)–Cl(1) 2.4318(9), Pd(2)–Cl(2) 2.4205(9), Pd(1)–N(22) 2.058(3), Pd(2)–N(2) 2.048(3), N(1)–C(7) 1.293(4), N(21)–C(27) 1.285(5), C(2)–C(7) 1.472(5), C(22)–C(27) 1.485(5), C(1)–C(2) 1.404(5), C(21)–C(22) 1.408(5), N(2)–C(11) 1.454(4), N(22)–C(31) 1.449(4); N(1)–O(1) 1.395(4), N(21)–O(21) 1.393(4), N(2)–C(9) 1.279(4), N(22)–C(29) 1.287(4); C(9)–Pd(1)–N(1) 85.52(13), C(9)–Pd(1)–N(22) 89.96(12), N(1)–Pd(1)–Cl(1) 88.16(8), N(22)–Pd(1)–Cl(1) 96.34(8), N(1)–Pd(1)–Pd(2) 118.22(8), C(9)–Pd(1)–Pd(2) 62.87(10), N(22)–Pd(1)–Pd(2) 59.32(8), Cl(1)–Pd(1)–Pd(2) 115.38(2), C(29)–Pd(2)–N(21), 86.31(13), C(29)–Pd(2)–N(2) 90.58(12), N(21)–Pd(2)–Cl(2) 90.01(9), N(2)–Pd(2)–Cl(2) 93.53(8), C(29)–Pd(2)–Pd(1) 63.38(10), N(21)–Pd(2)–Pd(1) 121.93(8), N(2)–Pd(2)–Pd(1) 59.42(8), Cl(2)–Pd(2)–Pd(1) 112.95(3), C(7)–N(1)–Pd(1) 128.9(2), C(27)–N(21)–Pd(2) 130.0(2), C(9)–N(2)–Pd(2) 119.0(2), C(29)–N(22)–Pd(1) 119.1(2), N(1)–C(7)–C(2) 118.4(3), N(21)–C(27)–C(22) 119.1(3).

conductimeter on *ca.* 5×10^{-4} M solutions in acetone. The IR spectra were recorded on a Perkin-Elmer 16 F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. The NMR spectra were recorded in Varian 200, 300 or 400 NMR spectrometers. The NMR assignments were performed, in some cases, with the help of APT, HMQC and HMBC experiments. The atom numbering used in the NMR assignments is shown in Chart 1. The oximes ArC(Me)=NOH [Ar = Ph, $C_6H_4NO_2$-4, $C_6H_2(OMe)_3$-3,4,5)] were prepared from the appropriate ketone ArC(=O)Me, NH_2OH·HCl and NaOAc·$3H_2O$ following a previously reported method.[28] [AuCl(SMe_2)][29] was prepared from Na[$AuCl_4$] and SMe_2.

Synthesis of [Pd{*C*,*N*-C_6H_3}{C(Me)=NOH}-2,NO_2-5}(μ-Cl)]$_2$ (1′). A suspension of $PdCl_2$ (720 mg, 4.06 mmol) and LiCl (414 mg, 9.76 mmol) in MeOH (8 mL) was refluxed until it dissolved and then it was allowed to cool at room temperature. To this solution was added another containing C_6H_4{C(Me)=NOH}NO_2-4 (658 mg, 3.76 mmol) and NaOAc (334 mg, 4.06 mmol) in MeOH (10 mL). The reaction mixture was concentrated under vacuum (5 mL), refluxed for 7 h, cooled at room temperature, filtered through a short pad of Celite, and treated with a saturated aqueous solution of HCl (0.5 mL) in MeOH (3 mL). After stirring the suspension for 15 min, H_2O (50 mL) was added. The resulting orange suspension was centrifuged, the solid was washed with diluted HCl (20 mL, 0.3 M), centrifuged again and decanted. The solid was stirred with a mixture of acetone and Et_2O (1 : 20, 3 × 21 mL), filtered and dried with a nitrogen stream to give pale orange **1′**. Yield: 1180 mg, 98%. Mp > 250 °C. ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 2.30 (s, 3 H, Me^8), 7.38 (d, H^3, $^3J_{HH}$ = 8 Hz), 7.82 (d, H^6, $^3J_{HH}$ = 8 Hz), 7.98 (s, H^4), 10.58 (s, 1 H, OH). (400 MHz, dmso-d_6, 20 °C, two isomers in 3.5(M):1(m) molar ratio): δ 2.34 (br s, 3 H, Me^{8M}), 2.38 (br s, 3 H, Me^{8m}), 7.52 (d, 1H, Ar^M, $^3J_{HH}$ = 7 Hz), 7.61 (br s, 1H, Ar^m), 7.93 (d, 1H, Ar^M, $^3J_{HH}$ = 7 Hz), 8.03 (br s, 1H, Ar^m), 8.28 (s, 1H, Ar^M), 8.72 (br s, 1H, Ar^m), 10.38 (br s, 1 H, OH^m), 10.91 (s, 1 H, OH^M). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 25 °C): δ 12.5 (Me^8), 122.2 (CH^4), 127.29 (CH$^{3\text{ or }6}$), 127.33 (CH$^{3\text{ or }6}$), 147.8 (C^5), 150.6 (C^2), 152.7 (C^1), 168.2 (C^7). IR (cm^{-1}): ν(OH) 3444, ν_{asym}(NO_2) 1525. Anal. Calcd for $C_8H_7ClN_2O_3Pd$: C, 29.93; H, 2.20; N, 8.73. Found: C, 29.69; H, 1.99; N, 8.47.

Synthesis of [Pd{*C*,*N*-C_6H_4}{C(Me)=NOH}-2}Cl(γ-pic)] (2d). To a suspension of **1** (539 mg, 0.98 mmol) in CH_2Cl_2 (5 mL) was added γ-pic (190 μL, 1.95 mmol). A solution immediately formed which was stirred at room temperature for 1.5 h and filtered through a short pad of Celite. The solution was concentrated under vacuum to 1 mL and Et_2O (15 mL) was added. The resulting suspension was stirred for 15 min, filtered, and the solid collected was washed with Et_2O (3 × 2 mL) and dried by suction to give **2d** as a pale yellow solid. Yield: 649 mg, 90%. Mp: 169 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.28 (s, 3 H, Me^8), 2.47 (s, 3 H, Me, γ-pic), 6.27 (dd, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.92 (td, H$^{4\text{ or }5}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.07 (td, H$^{4\text{ or }5}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.12 (dd, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.28 (apparent d, *meta*-CH, pic, $^3J_{HH}$ = 6 Hz), 7.28 (apparent d, *orto*-CH, pic, $^3J_{HH}$ = 6 Hz), 10.10 (s, 1 H, OH). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ 11.0 (Me^8), 21.2 (Me, γ-pic), 124.8 (CH, Ar), 125.1 (CH, Ar), 126.5 (*meta*-CH, pic), 128.9 (CH$^{4\text{ or }5}$), 131.1 (CH$^{3\text{ or }6}$), 143.6 (C^2), 150.6 (*para*-C, pic), 152.3 (*ortho*-CH, pic), 153.1 (C^1), 165.4 (C^7). IR (cm^{-1}): ν(OH) 3147, ν(C=N) 2195. Anal. Calcd for $C_{14}H_{15}ClN_2OPd$: C, 45.55; H, 4.10; N, 7.59. Found: C, 45.33; H, 4.00; N, 7.59. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of Et_2O into a solution of **2d** in CH_2Cl_2.

Synthesis of [PPN][Pd{*C*,*N*-C_6H_4}{C(Me)=NOH}-2}Cl_2] (3). To a suspension of **1** (65 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) was added [PPN]Cl (141 mg, 0.24 mmol). The resulting solution was stirred for 2 h, filtered through a short pad of Celite, concentrated under vacuum to 0.5–1 mL, and Et_2O (15 mL) was added. A suspension formed which was filtered and the solid collected was washed with Et_2O (3 × 2 mL) and dried by suction to give pale tan **3**. Yield: 167 mg, 83%. Mp: 177 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.14 (s, 3 H, Me), 6.87–6.95 (m, 3 H, H$^{3-5}$), 7.42–7.50 (m, 24 H, *ortho*- + *meta*-CH, [PPN]), 7.67 (td, 6 H, *para*-CH, [PPN], $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.87 (d, 1 H, H^6 Ar, $^3J_{HH}$ = 7 Hz), 10.88 (s, 1 H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 10.7 (Me^8), 123.1 (CH^4), 123.6 (CH$^{3\text{ or }5}$), 126.8 (X part of an AA'X system, N = 109.2 Hz, *ipso*-C, [PPN]), 127.5 (CH$^{3\text{ or }5}$), 129.5–129.6 (m, *meta*-CH, [PPN]), 131.9–132.0 (m, *ortho*-CH, [PPN]), 133.8 (*para*-CH, [PPN]), 134.7 (CH^6), 143.4 (C^2), 152.0 (C^1), 162.1 (C^7). ^{31}P{^{1}H} NMR (81. MHz, $CDCl_3$, 25 °C): δ 21.64. IR (cm^{-1}): ν(OH) not

observed. Λ_M (Ω^{-1} cm^2 mol^{-1}): 105 (5.32×10^{-4} M). Anal. Calcd for $C_{44}H_{38}Cl_2N_2OP_2Pd$: C, 62.17; H, 4.51; N, 3.30. Found: C, 61.96; H, 4.55; N, 3.34. Crystals of **3** suitable for an X-ray diffraction study grew by the liquid diffusion method using CH_2Cl_2 and Et_2O.

Synthesis of [Pd{*C*,*N*-C$_6$H{C(Me)=NOH}-2,(OMe)$_3$-4,5,6}](acac)] (4′). To a suspension of **1″** (82 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was added Tl(acac) (68 mg, 0.22 mmol). After 3 h of stirring CH_2Cl_2 (20 mL) was added and the suspension was filtered through a short pad of Celite. The solution was concentrated under vacuum to 1 mL. Upon the addition of Et_2O a suspension formed which was filtered and the solid collected was washed with Et_2O (2 × 1 mL). The pale cream powder was dried, first by suction, and then in an oven at 70 °C overnight to give **4″**·0.1H_2O: Yield: 65 mg, 68%. Mp: 152 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.58 (br s, 0.2 H, H_2O), 2.03 (s, 3 H, Me, acac), 2.13 (s, 3 H, Me, acac), 2.25 (s, 3 H, Me^8), 3.80 (s, 3 H, OMe), 3.85 (s, 3 H, OMe), 3.93 (s, 3 H, OMe), 5.44 (s, 1 H, CH, acac), 6.60 (s, 1 H, CH, Ar), 9.20 (s, 1 H, OH). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ 11.3 (Me^8), 27.2 (Me, acac), 27.6 (Me, acac), 56.5 (OMe), 61.0 (OMe), 62.0 (OMe), 101.0 (CH, acac), 106.3 (CH^3), 133 (C^1), 138.3 (C^2), 144.1 (C$^{4\text{ or }5\text{ or }6}$), 151.0 (C$^{4\text{ or }5\text{ or }6}$), 159.1 (C$^{4\text{ or }5\text{ or }6}$), 165.3 (C^7), 185.5 (CO), 188.9 (CO). IR (cm^{-1}): ν(OH) 3321. Anal. Calcd for $C_{16}H_{21.2}NO_{6.1}Pd$: C, 44.53; H, 4.95; N, 3.23. Found: C, 44.29; H, 5.34; N, 3.36.

Synthesis of [Pd{*C*,*N*-C$_6$H$_4${C(Me)=NOH}-2}(^{t}Bubpy)]OTf (5a). To a suspension of **1** (100 mg, 0.18 mmol) in acetone (5 mL) were added ^{t}Bubpy (98 mg, 0.37 mmol) and AgOTf (95 mg, 0.37 mmol). A suspension immediately formed which was stirred in the dark for 25 min, and filtered through a short pad of Celite. The solution was concentrated under vacuum to 2 mL, Et_2O (10 mL) was added and the suspension was filtered. The solid collected was washed with Et_2O (3 × 2 mL) and dried by suction to give **5a** as a yellow powder: Yield: 95 mg, 82%. Mp: 216 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.44 (s, 18 H, Me, ^{t}Bu), 2.44 (s, 3 H, Me^8), 7.13 (t, 1 H, H^4, Ar, $^3J_{HH}$ = 7 Hz), 7.18 (td, 1 H, H^5, Ar, $^3J_{HH}$ = 7 Hz,$^4J_{HH}$ = 2 Hz), 7.22 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz,$^4J_{HH}$ = 2 Hz), 7.24 (d, 1 H, H^6, $^3J_{HH}$ = 7 Hz), 7.66 (d, 1 H, H$^{12\text{ or }12'}$, ^{t}Bubpy, $^4J_{HH}$ = 2 Hz), 7.67 (d, 1 H, H$^{12\text{ or }12'}$, $^4J_{HH}$ = 2 Hz), 8.07 (s, 1 H, H$^{10\text{ or }10'}$), 8.08 (s, 1 H, H$^{10\text{ or }10'}$), 9.15 (br s, 2 H, H$^{13+13'}$), 10.60 (br s, 1 H, OH). (400 MHz, $CDCl_3$, –60 °C): δ 1.38 (s, 9 H, Me, ^{t}Bu), 1.46 (s, 9 H, Me, ^{t}Bu), 2.37 (s, 3 H, Me^8), 7.19 (br m, 2 H, CH, Ar), 7.27 (br m, 2 H, CH, Ar), 7.59 (d, 1 H, H$^{12\text{ or }12'}$, $^3J_{HH}$ = 5 Hz), 7.67 (d, 1 H, H$^{12\text{ or }12'}$, $^3J_{HH}$ = 5 Hz), 7.88 (s, 1 H, H$^{10\text{ or }10'}$), 7.99 (s, 1 H, H$^{10\text{ or }10'}$), 9.16 (br m, 1 H, H$^{13\text{ or }13'}$), 9.23 (d, 1 H, H$^{13\text{ or }13'}$, $^3J_{HH}$ = 5 Hz), 10.44 (br s, 1 H, OH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 12.5 (Me^8), 30.2 (Me, ^{t}Bu), 35.6 (*C*Me$_3$), 118.9 (br, CH$^{10+10'}$), 120.4 (q, TfO, $^1J_{CF}$ = 320 Hz), 124.2 (CH$^{12+12'}$), 125.4 (CH^4), 126.4 (CH$^{3\text{ or }5}$), 129.8 (CH$^{3\text{ or }5}$), 131.9 (CH^6), 142.4 (C^2), 151.7 (br, CH$^{13+13'}$), 156.3 (C^1), 164.8 (C$^{11+11'}$), 179.1 (C^7), C^9 and C$^{9'}$ not observed. ^{19}F{^{1}H} NMR: (282 MHz, $CDCl_3$, 25 °C): δ –78.6 (OTf). IR (cm^{-1}): ν(OH) not observed. Λ_M (Ω^{-1} cm^2 mol^{-1}): 121 (5.04×10^{-4} M). Anal. Calcd for $C_{27}H_{32}F_3N_3O_4PdS$: C, 49.28; H, 4.90; N, 6.39; S, 4.87. Found: C, 48.93; H, 5.18; N, 6.33; S, 4.46.

Synthesis of [Pd{*C*,*N*-C$_6$H$_3${C(Me)=NO}-2,NO$_2$-5}(tmeda)] (6′b). To a suspension of **1′** (87 mg, 0.14 mmol) in CH_2Cl_2 (15 mL) were successively added, under nitrogen, tmeda (42 μL, 0.280 mmol) and KO^{t}Bu (32 mg, 0.29 mmol), with a 5 min interval. The resulting suspension was stirred for 2 h, and filtered through a short pad of Celite. The solution was concentrated under vacuum to 1 mL and Et_2O (20 mL) was added. The suspension was filtered and the solid collected was washed with Et_2O (3 × 2 mL) and dried, first by suction and then in a vacuum oven at 75 °C for 5 h to give **6′b** as an orange solid. Yield: 103 mg, 95%. Mp: 202 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.13 (s, 3 H, Me^8), 2.67 (br m, 2 H, CH_2, tmeda), 2.78 (br m, 2 H, CH_2, tmeda), 2.88 (s, 6 H, Me, tmeda), 2.93 (s, 6 H, Me, tmeda), 6.98 (d, 1 H, H^3, $^3J_{HH}$ = 8 Hz), 7.93 (d, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.94 (s, 1 H, H^6). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 10.8 (Me^8), 47.9 (Me, tmeda), 50.3 (Me, tmeda), 58.7 (CH_2, tmeda), 63.3 (CH_2, tmeda), 119.4 (CH^3), 121.6 (CH^4), 124.2 (CH^6), 140.5 (C^5), 154.9 (C^7), 155.8 (C^1), 157.1 (C^2). Anal. Calcd for $C_{14}H_{22}N_4O_3Pd$: C, 41.96; H, 5.53; N, 13.98. Found: C, 41.76; H, 5.80; N, 13.75. Crystals of **6′b** suitable for an X-ray diffraction study were grown by the liquid diffusion method using CH_2Cl_2 and n-pentane.

Synthesis of [Pd{μ-*C*,*N*,*O*-C$_6$H$_4${C(Me)=NO}-2}(CN^{t}Bu)]$_2$ (7b). To a suspension of KO^{t}Bu (44 mg, 0.39 mmol) in CH_2Cl_2 (5 mL) was added **2b** (141 mg, 0.39 mmol). After 90 min of stirring the suspension was filtered through a short pad of Celite and the solution was concentrated under vacuum to 1 mL. Upon the addition of Et_2O (10 mL) a suspension formed which was filtered and the pale tan solid collected was washed with Et_2O (2 × 5 mL) and dried by suction to give **7b**. Yield: 92 mg, 73%. Mp: 161 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.61 (s, 9 H, Me, ^{t}Bu), 2.23 (s, 3 H, Me^8), 6.77 (td, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.02 (td, H^4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.06 (dd, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.13 (d, H^6, $^3J_{HH}$ = 7 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 10.6 (Me^8), 30.1 (Me, ^{t}Bu), 57.6 (t, *C*Me$_3$, $^1J_{CN}$ = 5 Hz), 123.4 (CH^3), 124.3 (CH^4), 125.3 (CH^5), 135.2 (t, C≡N, $^1J_{CN}$ = 18 Hz), 136.6 (CH^6), 146.9 (C^2), 154.5 (C^1), 163.7 (C^7). IR (cm^{-1}): *ν*(C≡N) 2200. Anal. Calcd for $C_{26}H_{32}N_4O_2Pd_2$: C, 48.39; H, 5.00; N, 8.68. Found: C, 48.18; H, 5.13; N, 8.63. Crystals of **7b**·H_2O suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH_2Cl_2 and Et_2O.

Synthesis of [Pd{*C*,*N*-C(=NXy)C$_6$H{C(Me)=NOH}-2-(OMe)$_3$-4,5,6}Cl(CNXy)] (8″). To a solution of **2″a** (210 mg, 0.422 mmol) in CH_2Cl_2 (5 mL) was slowly added a solution of XyNC (55.5 mg, 0.423 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred for 5 h. The reaction mixture was concentrated under vacuum to dryness and the residue was stirred with Et_2O (25 mL). The suspension was filtered, the solid collected was washed with Et_2O (3 × 1.5 mL), dried by suction, recrystallized from CH_2Cl_2 and Et_2O and dried in a vacuum oven at 70 °C for 10 h to give **8″**·0.3H_2O as a pale yellow solid: Yield: 155 mg, 58%. Mp: 195 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.56 (s, 0.6 H, H $_2$O), 2.03 (s, 3 H, Me, Xy^{im}), 2.16 (s, 6 H, Me, Xy^{Pd}), 2.35 (s, 3 H, Me, Xy^{im}), 2.50 (s, 3 H, Me^8), 3.95 (s, 3 H, OMe), 3.98 (s, 3 H, OMe), 3.99 (s, 3 H, OMe), 6.61 (d, 1 H, *meta*-CH, Xy^{im}, $^3J_{HH}$ = 7 Hz), 6.82 (s, H^3), 6.88 (t, 1 H, *para*-CH, Xy^{im}, $^3J_{HH}$ = 8 Hz), 7.06 (d, 2 H, *meta*-CH, Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.16 (d, *meta*-CH, Xy^{im}, $^3J_{HH}$ = 8 Hz), 7.22 (t, *para*-CH, Xy^{im}, $^3J_{HH}$ = 8 Hz), 10.66 (s, 1 H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 14.8 (Me^8), 18.2 (Me, Xy^{im}), 18.5 (Me, Xy^{Pd}), 18.7 (Me, Xy^{im}), 56.4 (OMe), 61.0 (OMe), 61.6 (OMe), 107.2 (CH^3), 122.7 (C^1), 123.5 (*para*-CH, Xy^{im}), 125.7 (br, *ipso*-C, Xy^{Pd}),

Table 1 Crystal data and structure refinement of complexes **2d**, **3**, **3'**, and **6'b**

Complex	**2d**	**3**	**3'**	**6'b**
Formula	$C_{14}H_{15}ClN_2OPd$	$C_{44}H_{38}Cl_2N_2OP_2$ Pd	$C_{44}H_{37}Cl_2N_3O_3P_2Pd$	$C_{14}H_{22}N_4O_3Pd$
Fw	369.13	850.00	895.01	400.76
T/K	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P -1	P 2(1)	P 2(1)	P 2(1)/n
a/Å	9.1285(4)	10.4042(4)	10.5577(7)	8.4822(8)
b/Å	9.2016(4)	13.5259(6)	13.2121(9)	11.5612(11)
c/Å	10.0426(4)	13.7681(6)	14.6686(11)	15.6484(15)
α (°)	90.108(2)	90	90	90
β (°)	108.795(2)	101.603(2)	105.436(2)	90.517(2)
γ (°)	114.271(2)	90	90	90
Volume/Å^3	719.11(6)	1897.94(14)	1972.3(2)	1534.5(3)
Z	2	2	2	4
ρ_c/Mg m^{-3}	1.705	1.487	1.507	1.735
μ/mm^{-1}	1.468	0.752	0.732	1.228
F(000)	368	868	912	816
Crystal size/mm	0.21 × 0.20 × 0.20	0.23 × 0.07 × 0.04	0.24 × 0.17 × 0.05	0.20 × 0.12 × 0.07
θ range (°)	2.46 to 28.03	2.00 to 28.27	2.00 to 28.65	2.19 to 28.72
No. rflns coll.	8249	22172	31495	18671
No. indep. rflns/R_{int}	3211/0.0133	8427/0.0319	9375/0.0280	3762/0.0234
Transmission	0.7577/0.7001	0.9705/0.8522	0.9643/0.7603	0.9190/0.8100
Restraints/params	0/179	1/474	2/501	0/204
Goodness–of–fit on F^2	1.076	1.041	1.103	1.110
R_1 ($I > 2\sigma(I)$)	0.0172	0.0318	0.0305	0.0232
wR_2 (all reflns)	0.0448	0.0681	0.0690	0.0526
Largest diff. peak/hole/e Å^{-3}	0.398/–0.637	0.715/–0.315	0.765/–0.670	0.513/–0.0463

126.6 (*ortho*-C, Xy^{im}), 126.7 (*ortho*-C, Xy^{im}), 127.1 (*meta*-CH, Xy^{im}), 127.8 (*meta*-CH, Xy^{Pd}), 128.2 (C^2), 128.8 (*meta*-CH, Xy^{im}), 129.7 (*para*-CH, Xy^{Pd}), 135.3 (*ortho*-C, Xy^{Pd}), 141.3 (C°N), 145.4 (C$^{4\text{ or }5\text{ or }6}$), 148.6 (C$^{4\text{ or }5\text{ or }6}$), 150.7 (*ipso*-C, Xy^{im}), 153.2 (C$^{4\text{ or }5\text{ or }6}$), 156.1 (C^7), 172.4 (*C*═NXy). IR (cm^{-1}): ν(OH) not observed; 2191 ν(C≡N). Anal. Calcd for $C_{29}H_{32.6}ClN_3O_{4.3}Pd$: C, 54.95; H, 5.18; N, 6.63. Found: C, 54.85; H, 5.08; N, 6.63. Crystals of **8″** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using $CHCl_3$ and Et_2O.

Synthesis of [Pd{μ-*C*,*N*,*N*'-C(═NXy)C$_6$H$_4$}{C(Me)═NOH}-2}(Cl)]$_2$ (9). To a solution of **8** (107 mg, 0.20 mmol) in $CHCl_3$ (4 mL), was added [AuCl(SMe$_2$)] (58.5 mg, 0.20 mmol). After 1.5 h of stirring, the slightly darkened solution was filtered through a short pad of anhydrous $MgSO_4$. The yellow solution was concentrated to dryness, the residue was stirred with a Et_2O/n-hexane mixture (1 : 1, 20 mL), and the resulting suspension was filtered. The solid collected was treated in CH_2Cl_2 (5 mL) with [AuCl(SMe$_2$)] (58.5 mg, 0.20 mmol) for 30 min and the reaction mixture was filtered through a short pad of anhydrous $MgSO_4$ and concentrated under vacuum to 1 mL. Upon the addition of Et_2O (10 mL) and n-hexane (2 mL) a suspension formed which was filtered. The solution was concentrated to dryness and the residue was stirred with n-hexane. The suspension was filtered and the solid collected was dried by suction to give pale yellow **9**. Yield: 30 mg, 37%. Mp: 246 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.73 (s, 3 H, Me^{Xy}), 2.52 (s, 6 H, Me^8 + Me^{Xy}), 6.56 (dd, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.68 (m, 1 H, *meta*-CH, Xy), 6.84–6.88 (m, 2 H, *meta*- + *para*-CH, Xy), 7.07 (td, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.31 (td, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.52 (dd, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 11.30 (s, 1 H, OH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.8 (Me^8), 19.2 (Me, Xy), 20.4 (Me, Xy), 123.1 (CH^6), 126.4 (*para*-CH, Xy), 127.9 (*meta*-CH, Xy), 128.5 (CH^3), 128.9 (*meta*-CH, Xy), 129.3 (CH^4), 129.5 (*ortho*-C, Xy), 130.0 (CH^5), 130.8 (*ortho*-C, Xy), 132.2 (C^2), 133.0 (C^1), 146.6 (*ipso*-C, Xy), 156.9 (C^7), 207.0 (*C*═NXy). IR (cm^{-1}): ν(OH) not observed. Anal. Calcd for $C_{17}H_{17}ClN_2OPd$: C, 50.15; H, 4.21; N, 6.88. Found: C, 49.78; H, 4.24; N, 6.89. Crystals of **9**·2$CHCl_3$ suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of the complex in $CHCl_3$.

X-Ray structure determinations of complexes 2d, 3, 3′, 6′b, 7b·H$_2$O, 8″ and 9·2CHCl$_3$. For clarity, solvent contents are omitted here, but are defined in Tables 1 and 2. Fig. 1–7 show the ellipsoid representation. All complexes were measured on a Bruker Smart APEX machine. Data were collected using monochromated Mo-Kα radiation. The structures were solved by direct methods. All were refined anisotropically on F^2. Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. The OH were refined freely and also with DFIX in complex **3′**, **7b**·H_2O and **9**·2$CHCl_3$, the ordered methyl groups were refined using rigid groups, and the others were refined using a riding model.

Special features and exceptions

For complex **3**: the Flack parameter[22] is –0.026(15); **3′**: the Flack parameter is 0.000(14); **8″**: one methyl is disordered over two positions, *ca.* 57 : 43% ; **9**·2$CHCl_3$: the structure contains two solvent residues: one dichloromethane is disordered over two positions, *ca.* (83 : 17%) and an ill-defined region of residual electron density was identified also as disordered dichloromethane, but the refinement was far from satisfactory. Only the hydrogen of the main part of one dichloromethane was included in the refinement.

Table 2 Crystal data and structure refinement of complexes **7b**·H_2O, **8″** and **9**·2$CHCl_3$

Complex	**7b**·H_2O	**8″**	**9**·2$CHCl_3$
Formula	$C_{26}H_{34}N_4O_3Pd_2$	$C_{29}H_{32}ClN_3O_4Pd$	$C_{36}H_{36}Cl_8N_4O_2Pd_2$
Fw	663.37	628.43	1053.09
T/K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C\,2/c$	$P\,2(1)/n$	$P\,2(1)/n$
a/Å	27.9117(12)	13.1876(11)	16.9138(6)
b/Å	11.4690(5)	8.0675(14)	11.0175(4)
c/Å	18.9722(8)	12.4618(9)	22.5029(9)
α (°)	90	90	90
β (°)	116.729(2)	105.989(2)	90.541(2)
γ (°)	90	90	90
Volume/Å^3	5424.4(4)	2854.4(4)	4193.2(3)
Z	8	4	4
ρ_c/Mg m^{-3}	1.625	1.462	1.668
μ/mm^{-1}	1.359	0.782	1.405
F(000)	2672	1288	2096
Crystal size/mm	0.31 × 0.22 × 0.12	0.25 × 0.12 × 0.09	0.19 × 0.11 × 0.05
θ range (°)	1.95 to 28.16	1.61 to 28.66	1.81 to 28.26
No. rflns coll.	30421	18582	47665
No. indep. rflns/R_{int}	6181/0.0182	6757/0.0241	9799/0.0475
Transmission	0.8539/0.7527	0.9330/0.8188	0.9331/0.8385
Restraints/parameters	3/332	1/354	144/527
Goodness–of–fit on F^2	1.039	1.099	1.109
R_1 ($I > 2\sigma(I)$)	0.0198	0.0356	0.0466
wR_2 (all reflns)	0.051	0.0886	0.0935
Largest diff. peak/hole/e Å^{-3}	0.729/–0.449	1.171/–0.337	0.831/–0.772

Conclusion

The work reports the synthesis, reactivity and structure of the first family of well-characterized cyclopalladated complexes derived from oximes. This group of complexes includes cyclopalladated acetophenone oxime and two of its derivatives containing substituents on the aryl group with different electronic properties (NO_2-5 and $(MeO)_3$-4,5,6), which are unprecedented. Deprotonation reactions of the oxime and isocyanide insertion, have allowed us to prepare the first aryloximato and iminoaryloxime complexes of any metal. [AuCl(SMe_2)] has been successfully used for the first time as an isocyanide ligand scavenger.

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