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Palladium iminophosphorane complexes: the precursors to the missing link in triphenylphosphane chalcogenide metallacycles†

Adolfo Fernández-Figueiras,[a] Fátima Lucio-Martínez,[a] Paula Munín-Cruz,[a] Paula Polo-Ces,[a] Francisco Reigosa,[a] Harry Adams,[b] M. Teresa Pereira *[a] and José M. Vila *[a]

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Herein we report on the synthesis, characterization and the ensuing chemistry of iminophosphorane palladacycles. Treatment of $Ph_3P{=}N\text{-}(2\text{-}OHC_6H_4)$, **1**, with sodium tetrachloropalladate gives **2** with the ligand as terdentate [*C*,*N*,*O*] allowing for only one μ-Cl ligand bonding the metal centers, resulting in a dinuclear complex. Treatment of **2** with PPh_3 gives the mononuclear complex **3**, whereas the reaction of **2** with diphosphanes $Ph_2P(CH_2)_nPPh_2$ in 1 : 2 ratio gives mixtures of **4** and **5** (n = 2) and **6** and **7** (n = 3). From them, the mononuclear complexes **4** and **6**, and the dinuclear compounds, **5** and **7**, were obtained with the parent ligand as bidentate [*C*,*N*]. The former two are of zwitterionic nature void of any counter-ion, with the phosphane ligand in the chelating mode. In a remarkable case of chemical serendipity, a solution of **2** left to stand produced crystals of complex **8**: this is the missing link in the series of triphenylphosphane chalcogenide metallacycles. The experiment is repeatable; however, direct metallation of triphenylphosphane oxide was not possible.

Introduction

Palladacycles are an amply studied branch of organometallics due, to a large extent, to their quite abundant applications: as pre-catalysts in cross-coupling reactions, such as Suzuki–Miyaura,[1–3] Mizoroki–Heck,[4,5] Negishi[6] or Sonogashira[7] and as rather powerful anticancer agents,[8,9] at times comparable to *cis*-platin;[10] likewise, some exhibit very interesting luminescence properties[11] or, alternatively, they behave as metallomesogens.[12]

A particular case of palladacycles are those that stem from the iminophosphoranes $R_3P{=}NR$. These are organic substrates which themselves exhibit a wide range of relevant applications inclusive of their use as superbases,[13] as synthetic intermediates, in particular for the Aza-Wittig reaction,[14] or as building blocks for P–N back-bone polymers.[15] The highly polarized P=N double bond, bearing a partial negative charge on the nitrogen atom, shows a strong σ-donor behavior with minor π-acceptor properties enabling them as ligands which readily undergo the cyclopalladation reaction.[16–20] The biological applications and anticancer properties of Pd(II), Pt(II) and Au(III) cyclometallated iminophosphoranes, and of the analogous coordination species, have been studied due to the non-toxic character of the ligands.[21–23] A further advantage is that the phosphorus atom in the PR_3 fragment can be used as a "spectroscopic marker" to study the *in vitro* stability and the oxidation state by $^{31}P\text{–}\{^1H\}$ NMR spectroscopy.[24] Moreover, their luminescence properties make them potentially useful as molecular probes in theragnosis,[25] and also they serve as pre-catalysts in numerous catalytic processes.[26–32]

Following our research on palladacycles more recently we have come upon new findings when employing terdentate [*C*,*N*,*S*] and tetradentate [*C*,*N*:*C*,*N*] ligands, namely the autocatalysis in the Suzuki–Miyaura reaction,[3] the coordination of the bulky potassium cation by the small crown ether rings,[33] and the chelate-to-bridging shift in diphosphane palladacycles,[34] all of which have contributed to expanding the frontiers of this ever growing field. Then, we became interested in studying related systems with terdentate [*C*,*N*,*O*] ligands albeit exchanging the C=N for the P=N double bond, in view of the interesting properties of the $R_3P{=}NR$ ligands. The immersion in the chemistry of iminophosphoranes was to seek new trends in their reactivity and/or structural features, in order to further extend the scope of this chemistry. The ensuing results are presented herein.

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[a] *Departamento de Química Inorgánica, Universidade de Santiago de Compostela, Avenida das Ciencias s/n, 15782 Santiago de Compostela, Spain*
[b] *Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK*

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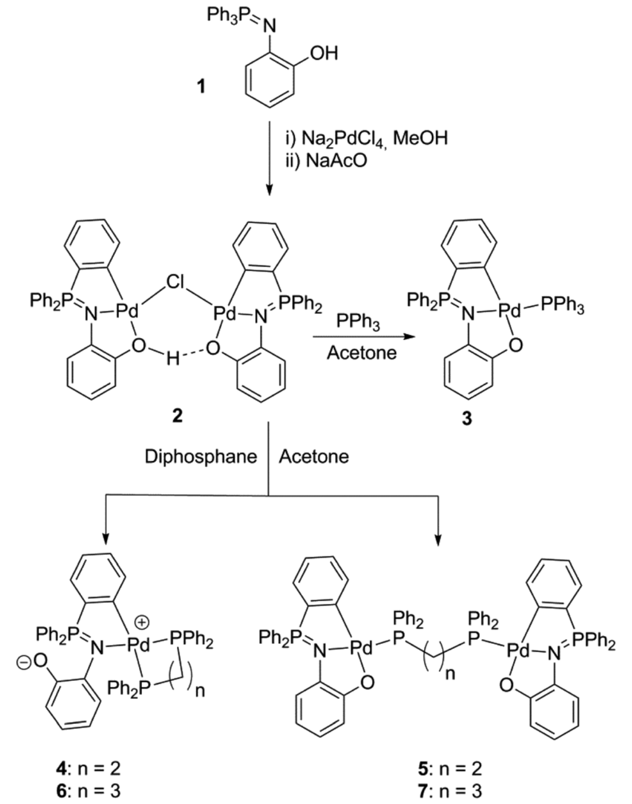
To address this study, we have used phosphanes as ancillary ligands, which readily react with the synthesized terdentate [*C*,*N*,*O*] iminophosphorane palladacycle in a bridging and chelating fashion. Herein we give an account of the novel species encountered, namely two zwitterionic mononuclear complexes with chelating diphosphane. Furthermore, we also describe a remarkable case of chemical serendipity that provided suitable crystals which gave rise to the molecular structure of the first cyclopalladated triphenylphosphane oxide, putting an end to the incomplete series of the triphenylphosphane chalcogenide metallacycles. Attempts to make the latter compound by direct palladation of the phosphane oxide were to no avail; however the preparation could be repeated by way of this newly found experiment.

Results and discussion

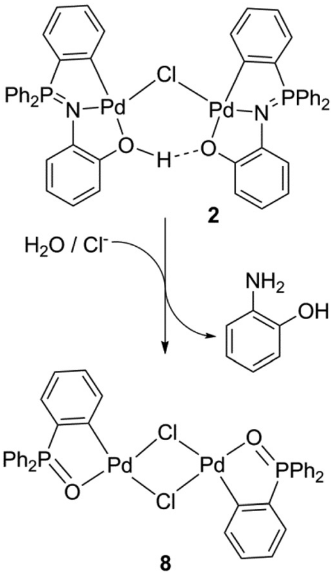
For the convenience of the reader, the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterised by elemental analysis (C, H, N), IR and ^{1}H and ^{31}P–{^{1}H} spectroscopy (see the Experimental section) and, in part, by X-ray single crystal diffraction.

Ligand **1** was readily synthesized by the Staudinger reaction[35] from triphenylphosphane and 2-hydroxyphenyl azide. As opposed to the ligands described by Urriolabeitia *et al.*,[18] the sp^2 carbon atoms available for metallation are on the phosphorus phenyl rings, giving the *endo* type species. Thus, treatment of **1** with Na_2PdCl_4 and NaAcO in refluxing methanol gave the dinuclear palladacycle **2** as an air-stable yellow solid, which was fully characterized, in contrast to the tetranuclear species described by us when using the related terdentate [*C*,*N*,*O*] with C═N double bonds.[36] In the IR spectrum of the complex, the *ν*(P═N) stretching band (see the Experimental section) appeared at lower frequency than the corresponding one in the free ligand in accordance with nitrogen coordination to the metal center. In the ^{1}H NMR spectrum, four additional multiplets appear upon metallation of one of the phosphorus phenyl rings. The signal for the phosphorus nucleus in the ^{31}P–{^{1}H} NMR spectrum was downfield shifted *ca.* 38 ppm after palladium–nitrogen coordination. Complex **2** consists of two cyclopalladated fragments bonded through a single bridging chloride ligand. This situation is relatively unusual in palladacycle chemistry where more often than not the μ-Cl ligand is accompanied by a bidentate ligand or by another bridging chloride. Yet however infrequent, a few examples have been reported in the literature. These are limited to either palladacycles or to other cyclometallated compounds of cationic[37,38] or anionic[39] nature, which need the corresponding counterion for electrical neutrality. Because palladation proceeds with deprotonation of the OH groups, and in the absence of any counterion, we tentatively suggest that the extra negative charge is compensated by H shared between the two oxygen atoms through hydrogen bonding, to produce a charge–neutral palladium compound. Further data regarding this issue are discussed below in the description of the molecular structure for **2**.

Suitable crystals of **2** were grown by slowly evaporating an acetone solution of the compound. Crystal data are given in the ESI.† The ORTEP illustration of complex **2** is shown in



Scheme 1 Reaction sequence leading to the synthesis of the iminophosphorane palladacycles.



Scheme 2 Decomposition reaction of **2** to give **8**.

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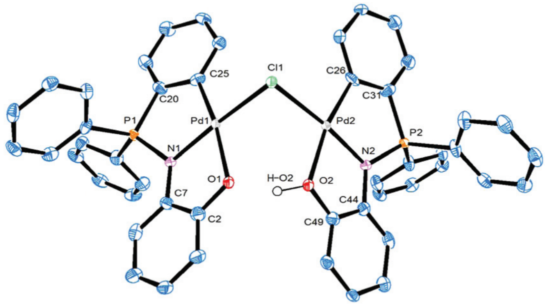

Fig. 1 Thermal ellipsoid plot for **2** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity, except H–O(2). Selected bond distances (Å) and angles (°) for **2**: Pd(1)–C(25) 1.960(3), Pd(1)–N(1) 2.010(3), Pd(1)–O(1) 2.116(2), Pd(1)–Cl(1) 2.3373(9), Pd(2)–C(26) 1.963(3), Pd(2)–N(2) 1.993(3), Pd(2)–O(2) 2.123(2), Pd(2)–Cl(1) 2.3421(9), P(1)–N(1) 1.619(3), P(2)–N(2) 1.611(3), C(25)–Pd(1)–N(1) 88.71(14), C(25)–Pd(1)–(O1) 169.85(12), N(1)–Pd(1)–O(1) 81.26(11), C(25)–Pd(1)–Cl(1) 95.12(11), N(1)–Pd(1)–Cl(1) 176.17(9), O(1)–Pd(1)–Cl(1) 94.91(7), C(26)–Pd(2)–N(2) 88.14(14), C(26)–Pd(2)–O(2) 168.60(13), N(2)–Pd(2)–O(2) 81.36(11), C(26)–Pd(2)–Cl(1) 95.81(12), N(2)–Pd(2)–Cl(1) 174.31(9), O(2)–Pd(2)–Cl(1) 94.98(7), Pd(1)–Cl(1)–Pd(2) 93.61(3).

Fig. 1. The crystals consist of discrete molecules separated by normal van der Waals distances, bearing two slightly distorted square-planar palladacycle subunits joined by a single chloride bridging ligand with a Pd–Cl–Pd bond angle of 93.61°. Each palladium atom is bonded to the ligand through a P═N nitrogen atom, an aryl carbon atom and a phenoxy oxygen atom. The bond lengths and angles at palladium are fairly the same for both metallated units. We propose a tautomeric structure where the two oxygen atoms exchange a hydrogen atom, necessary to maintain neutrality, as is depicted in Fig. 2. Due to the disorder of the center of the molecule, a low theta difference Fourier was used to show where the point of electron density was. This showed the electron density to be closer to the O(2) atom. Intramolecular hydrogen bonding is in agreement with the short O(1)–O(2) distance of 2.406 Å; the hydrogen atom has been calculated onto the O(2) atom with a distance of 0.952 Å and a H–O(1) distance of 1.499 Å; the O(1)⋯H–O(2) angle is 157.35°. This feature could account for the Pd–O bond lengths in compound **2**, Pd(1)–O(1) 2.116(2) and Pd(2)–O(2) 2.123(2), as opposed to their analogues in compounds **3**, Pd(1)–O(1) 2.0625(18), **7**, Pd(1)–O(1) 2.066(2), and **8**, Pd(1)–O(1) 2.053(3). Recently, in a rather similar case T. W. Lee *et al.* have described an iridium(III) compound where the O–H⋯O hydrogen bond contributes to the stability of the complex.[40] Therefore, the unique feature of a dinuclear single-bridged chloride palladacycle structure is made possible by the bridging O–H–O unit, whose asymmetry precludes the consideration of two totally equivalent palladacycle centers. Furthermore, DFT calculations were performed for compound **2**, which showed the presence of a strong intramolecular hydrogen bond between the O(2)–H hydrogen and the O(1) atom (see the ESI†).

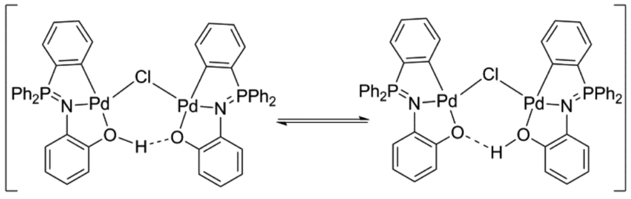

Fig. 2 Tautomeric equilibrium for **2**.

Treatment of **2** with triphenylphosphane gave the neutral mononuclear compound **3** as a yellow air-stable solid, which was fully characterized; its reactivity pattern resembles that of the related dinuclear[41] or tetranuclear[42] palladacycles.

The IR spectrum showed the shift of the ν(P═N) stretch from 1313 cm^{-1} to 1280 cm^{-1}. Two doublets in the ^{31}P–{^{1}H} NMR spectrum were assigned to the two distinct ^{31}P nuclei at δ 32.38 (PPh$_3$) and δ 37.91 (P═N) with ^{3}J(PP) 3.9 Hz.

Crystals of compound **3** were obtained by slow evaporation from an acetone solution. Crystal data are given in the ESI.† The ORTEP view of **3** is shown in Fig. 3. The compound crystalizes with an acetone solvent molecule (omitted for clarity reasons). The structure is quite similar to that of any one of the palladated subunits which comprise the structure of compound **2**, albeit with a triphenylphosphane ligand bonded to the palladium atom in place of the bridging chloride. All bond lengths and angles are within the expected values, with allowance for lengthening of the Pd(1)–N(1) bond, 2.053(2) Å, as compared to complex **2**, 1.993(3) and 2.010(3) Å, due to the stronger *trans* influence of the phosphane ligand *vs.* the bridging chloride.

The reaction of **2** with the diphosphanes Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2, 3) in 1 : 2 molar ratio in acetone at room temperature gave mixtures of compounds, **4** and **5** (n = 2) and **6** and **7** (n = 3). In both cases they could be satisfactorily separated by centrifuging the corresponding reaction mixture to give solutions containing the mononuclear complexes **4** and **6**, with chelating diphosphane, and solids comprising the dinuclear compounds, **5** and **7**, with the bridging diphosphane (Scheme 1).

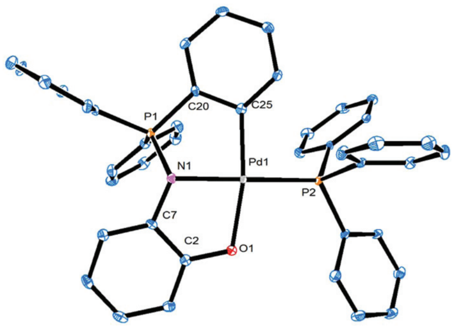

Fig. 3 Thermal ellipsoid plot for **3** shown at the 50% probability level. Hydrogen atoms and an acetone solvent molecule have been omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Pd(1)–C(25) 2.013(3), Pd(1)–N(1) 2.052(2), Pd(1)–O(1) 2.0625(18), Pd(1)–P(2) 2.2334(7), P(1)–N(1) 1.617(2), C(25)–Pd(1)–N(1) 88.02(10), C(25)–Pd(1)–O(1) 169.23(9), N(1)–Pd(1)–O(1) 81.42(8), C(25)–Pd(1)–P(2) 92.02(8), N(1)–Pd(1)–P(2) 178.22(7), O(1)–Pd(1)–P(2) 98.46(6).

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The former two, of zwitterionic nature, are innovative in the chemistry of iminophosphorane palladacycles.

The final products were air-stable solids which were fully characterized. The IR spectra showed the downfield shift of the ν(P=N) stretch in all cases appearing *ca.* 1280 cm^{-1}. The ^1H NMR spectra of **5** and **7** showed only one set of signals in accordance with the symmetrical nature of the complexes. Likewise, in the $^{31}P-\{^1H\}$ NMR spectra two singlet resonances were assigned to the two sets of equivalent phosphorus nuclei, P=N and PPh_2. Alternatively, the $^{31}P-\{^1H\}$ NMR spectra for complexes **4** and **6** showed doublets and doublets of doublet signals, as appropriate, for the three inequivalent ^{31}P nuclei (see Experimental); with (PPh_2 *trans*-C) at higher field than (PPh_2 *trans*-N) in agreement with the greater *trans* influence of the phenyl carbon atom. Fig. 4 and 5 show the ORTEP view of the molecules of **4** and **7**, respectively (see ESI†).

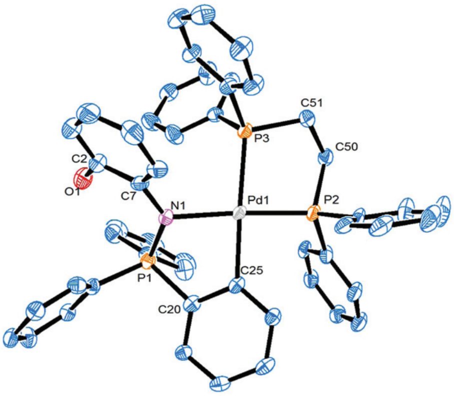

Fig. 4 Thermal ellipsoid plot for **4** shown at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **4**: Pd(1)–N(1) 2.102(2), Pd(1)–P(2) 2.2348(8), P(1)–N(1) 1.602(2), Pd(1)–P(3) 2.3548(8), C(25)–Pd(1)–N(1) 83.74(11), C(25)–Pd(1)–P(3) 176.62(8), N(1)–Pd(1)–P(3) 98.54(7), C(25)–Pd(1)–P(2) 92.89(8), N(1)–Pd(1)–P(2) 173.02(7), P(2)–Pd(1)–P(3) 84.58(3).

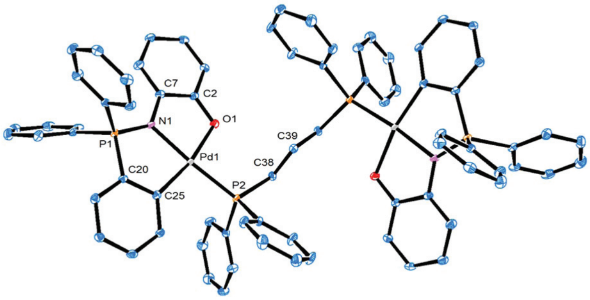

Fig. 5 Thermal ellipsoid plot for **7** shown at are drawn at the 50% probability level. Hydrogen atoms and a chloroform solvent molecule have been omitted for clarity. Selected bond distances (Å) and angles (°) for **7**: Pd(1)–C(25) 2.006(3), Pd(1)–N(1) 2.032(3), Pd(1)–O(1) 2.066(2), P(1)–N(1) 1.602(3), Pd(1)–P(2) 2.2384(8), C(25)–Pd(1)–N(1) 87.55(11), C(25)–Pd(1)–O(1) 168.60(11), N(1)–Pd(1)–O(1) 81.63(9), C(25)–Pd(1)–P(2) 98.88(9), N(1)–Pd(1)–P(2) 173.38(7), O(1)–Pd(1)–P(2) 91.85(7).

The molecular structure of **4** consists of discrete molecules with the palladium atom bonded to two chelating ligands: an iminophosphorane-[*C*,*N*] and a bis(diphenylphosphino) ethane-[*P*,*P*] in a slightly distorted square-planar conformation. The bond distances are within the expected values with differing Pd–P lengths due to the higher *trans* influence of the metallated phenyl carbon atom as opposed to the nitrogen atom. The palladium–oxygen distance of 4.612 Å precludes any interaction between them. Likewise, no interaction between the P(1) and O(2), which are 3.020 Å apart, was observed. As for complex **7** it may be envisaged as formed by two approximately square-planar palladium centers bonded through a bis (diphenylphosphino)propane ligand.

For compound **7** the X-ray diffraction analysis shows a dinuclear molecular structure whereby the two palladated units are linked by a bridging bidentate $Ph_2P(CH_2)_3PPh_2$ ligand, with the metal coordination planes [Pd,C,N,O,P] at an angle of 66.15°. The structure is crystallographically centrosymmetric with the inversion center situated at the C(39) carbon between the two phosphorus atoms. The bond lengths and angles at palladium are similar to those depicted for the structures of **3** and **4** (*vide supra*); along with the structures for **2** and **3** the palladium center is bonded to four different atoms in a slightly distorted square-planar environment; also, the Pd–O bond length is shorter than that of its counterpart in complex **2** (*vide supra*).

Recently Bhargava *et al.*[43] have reported the cyclometallation of triphenylphosphane sulfide and selenide $Ph_3P{=}X$ (X = S, Se) by treatment of the tin derivatives 2-$Me_3SnC_6H_4P(X)Ph_2$ (X = S, Se) with [$PdCl_2$(COD)] that proceeds with formation of the poorly soluble chloro-bridged dimers $[Pd_2(\mu\text{-}Cl)_2\{\kappa_2\text{-}2\text{-}C_6H_4P(X)Ph_2\}_2]$ that contain the *syn*- and *anti*-isomers; albeit no crystal structures were reported. However, the analogous chloro-bridged palladium complex with $Ph_3P{=}O$ yet remained unknown. Next we give an account of this finding that completes the missing link in the chalcogenide series of complexes $[Pd_2(\mu\text{-}Cl)_2\{\kappa_2\text{-}2\text{-}C_6H_4P(X)Ph_2\}_2]$ (X = O, S, Se). When a chloroform solution of compound **2** was left to stand in contact with air at room temperature prior to its use as the starting material for making the compounds described above we observed the formation of yellow crystals, which were filtered, conveniently dried and set aside. The corresponding X-ray crystallographic analysis proved them to be compound **8** (*vide infra*), which we should like to coin as a rather pleasant case of chemical serendipity.[44] Regrettably attempts to make compound **8** directly from triphenylphosphane oxide by standard *ortho*-palladation procedures have been unsuccessful so far. Then, our synthetic strategy consisted of several attempts at again leaving a solution of **2** to stand at room temperature exposed to air, whereupon a precipitate was formed, void of any crystals in this case, which was filtered and dried to give a yellow powder. This procedure could be repeated and for the corresponding powdery solid the spectroscopic evidence seemed to indicate that compound **8** had been formed. Thus, the $^{31}P-\{^1H\}$ NMR spectrum showed a singlet resonance at 35.7 ppm for the two equivalent ^{31}P nuclei. The IR spectrum showed a band *ca.*

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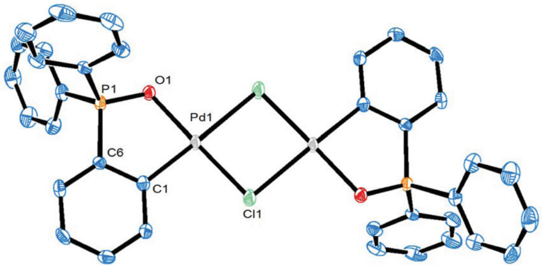

Fig. 6 Thermal ellipsoid plot for **8** shown at the 40% probability level. Hydrogen atoms and a second molecule of the compound have been omitted for clarity. Selected bond distances (Å) and angles (°) for **8**: Pd(1)–C(1) 1.960(4), Pd(1)–Cl(1) 2.3008(14), Pd(1)–O(1) 2.053(3), Pd(1)–Cl(1#) 2.4383(14), C(1)–Pd(1)–O(1) 86.79(16), C(1)–Pd(1)–Cl(1) 94.58(14), O(1)–Pd(1)–Cl(1) 178.61(9), C(1)–Pd(1)–Cl(1#) 176.40(14), O(1)–Pd(1)–Cl(1#) 92.26(9), Cl(1)–Pd(1)–Cl(1#) 86.40(5).

1162 cm^{-1} assigned to the ν(P=O) stretch, and bands at 310 and 284 cm^{-1} corresponding to the ν(Pd–Cl) stretches. Although it is not clear how **8** was formed we suggest that hydrolysis of the P=N double bond[45] produces *o*-aminophenol and the P=O bond, which binds to the metal through the oxygen atom, with the extra chloride ligand stemming as a residual impurity from the initial metal reagent (Scheme 2). Furthermore, the hydrolysis of compound **2** in solution was also attempted. Thus, an NMR tube containing a solution of **2** in wet chloroform was monitored by ^{31}P–{^{1}H} NMR. After 72 h, the major product showed a resonance at *ca.* 35 ppm assigned to the presence of compound **8.** It seems likely that triphenylphosphine oxide does not allow metallation of the aryl ring, whereas starting from **2** the palladium–carbon bond is already formed. In any case, fine tuning the process is adamant in order to give a clear picture of the preparation and this study is presently underway.

Crystal data for **8** are given in the ESI† and the ORTEP illustration is shown in Fig. 6 (together with selected bond lengths and angles). Each palladium atom, adopting a slightly distorted square-planar disposition, is bonded by a chelating $C_6H_4P(O)$ group and two bridging chloride ligands. The structure is of a centrosymmetric dinuclear palladacycle with two asymmetrically bridging chloride atoms. The phenyl carbon atom and the oxygen atom are *trans* to the di-μ-chloride unit so that these two palladated ligands are in an overall antiparallel arrangement. The asymmetry results from the differing *trans* influence of the C-phenyl and oxygen atoms. The Pd_2Cl_2 unit produces an intramolecular palladium-palladium distance of 3.456 Å which is longer than in complex **2**, 3.411 Å, in spite that in **8** the two palladium atoms are held together by two bridging ligands, and excludes the possibility of a metal–metal bond.

Experimental section

X-ray structure determination. Crystallographic data of the structures described in this work were collected on a Bruker Kappa APEX II diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a graphite monochromator by the method of the ω and φ scans at 293 K, integrated and corrected for absorption and solved and refined using routine techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined in the riding mode.

General procedures

Solvents were used without previous purification. Chemicals were of reagent grade. The phosphanes PPh_3, $PPh_2(CH_2)_2PPh_2$ (dppe) and $PPh_2(CH_2)_3PPh_2$ (dppp) were purchased from Sigma-Aldrich. Elemental analyses were carried out on a THERMO FINNIGAN, model FLASH 1112. IR spectra were recorded with a JASCO FT/IR-4600 spectrometer equipped with an ATR, model ATR-PRO ONE. The NMR spectra were recorded on Varian INOVA 400 or Bruker DPX-250 spectrometers.

Synthesis of 1

2-Hydroxyphenyl azide (300 mg, 2.22 mmol) was added to a solution of triphenylphosphane (582 mg, 2.22 mmol) in diethyl ether (20 cm^3), and the resulting mixture was stirred at room temperature for 18 hours. Compound **1** precipitated from the reaction mixture as a brown powder and was isolated by centrifugation and dried under vacuum. Yield 534 mg, 65%. $C_{24}H_{20}NOP$ (369.40): calcd: C 78.0, H 5.5, N 3.8; found: C 77.9, H 5.7, N 3.8. IR: ν(P=N): 1318 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.45 (m, 2H, H–Ar) 6.65 (m, 1H, H–Ar) 6.89 (m, 1H, H–Ar) 7.47 (m, 6H, *m*-PPh_3) 7.55 (m, 3H, *p*-PPh_3) 7.72 (m, 6H, *o*-PPh_3). ^{13}C–{^{1}H} NMR (400 MHz, acetone-d_6, δ) 150.6 (C–O) 144.4 (C–N) 139.7 (C–PC_6H_5) 132.0, 131.9 (C_o C_6H_5P) 128.7, 128.5, 128.3 (C_m, C_p C_6H_5P) 119.3, 118.5 (C_m C_6H_4N) 118.2 (C_p C_6H_4N) 115.5 (C_o C_6H_4N). ^{31}P–{^{1}H} NMR (400 MHz, $CDCl_3$, δ) 4.83 (s, P).

Synthesis of 2

A pressure tube containing Na_2PdCl_4 (150 mg, 0.51 mmol), **1** (182 mg, 0.51 mmol) and methanol (10 cm^3) was sealed under nitrogen. The resulting mixture was heated at 80 °C and after 4 hours NaAcO (42 mg, 0.51 mmol) was added to the reaction mixture and stirred at 80 °C for 1 hour. Compound **2** precipitated from the solution and was isolated by centrifugation, and then was dissolved in dichloromethane and filtered through silica to remove the black palladium formed. The solvent was removed under vacuum to give a yellow oil, which was recrystallized from dichloromethane/hexane to give the desired product as a yellow solid. Yield 167 mg, 67%. $C_{48}H_{37}ClN_2O_2P_2Pd_2$ (984.06): calcd: C 58.6, H 3.8, N 2.9; found: C 58.5, H 3.9, N 2.9. IR ν(OH): 3375 cm^{-1} ν(P=N): 1313 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6, δ) 6.31 (m, 1H, H–Ar) 6.53 (m, 2H, H–Ar) 6.75 (m, 1H, H–Ar) 7.01 (m, 2H, H–Ar) 7.17 (m, 1H, H–Ar) 7.52 (m, 1H, H–Ar) 7.65 (m, 4H, *m*-PPh_2) 7.75 (m, 2H, *p*-PPh_2) 7.97 (dd, ^4J(HP) 2.6, ^3J(HH) 7.6 Hz, 4H, *o*-PPh_2). ^{13}C–{^{1}H} NMR (400 MHz, acetone-d_6, δ) 156.9 (C–O) 149.8 (C–Pd) 144.4 (C–N) 138.7 (C–PC_6H_4) 133.2 (C_o C_6H_5P) 129.1, 127.3, 126.5 (C_m, C_p C_6H_5P) 120.0, 119.9 (C_m C_6H_4N)

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118.6 (C_p C_6H_4N) 117.8 (C_o C_6H_4N). $^{31}P-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 42.61 (s, P).

Synthesis of 3

Triphenylphosphane (22 mg, 0.08 mmol), **2** (41 mg, 0.04 mmol) and acetone (15 cm^3) were added to a flask and the resulting mixture was stirred for 18 hours; the solvent was evaporated to give a yellow oil, which was recrystallized from dichloromethane/hexane to give the desired product as a yellow solid. Yield 55.4 mg, 89%. $C_{42}H_{33}NOP_2Pd$ (736.09): calcd: C 68.5, H 4.5, N 1.9; found: C 68.3, H 4.6, N 1.8. IR: ν(P═N): 1280 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6, δ) 5.93 (m, 1H, H–Ar) 6.15 (m, 1H, H–Ar) 6.35 (m, 2H, H–Ar) 6.60 (m, 2H, H–Ar) 6.82 (m, 1H, H–Ar) 6.95 (dd, ^3J(HP) 12.2, ^3J(HH) 7.2 Hz, 1H, H–Ar) 7.44 (m, 6H, *m*-PPh_3) 7.51 (m, 3H, *p*-PPh_3) 7.66 (m, 4H, *m*-PPh_2) 7.74 (m, 2H, *p*-PPh_2) 7.79 (m, 6H, *o*-PPh_3) 7.97 (m, 4H, *o*-PPh_2). $^{13}C-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 156.6 (C–O) 147.3 (C–Pd) 135.3 ($C-PC_6H_4$) 133.2, 133.0, 132.7, 131.1 (C_o PhP) 129.0, 128.8, 128.0, 127.8 (C_m, C_p C_6H_5P) 120.8 (C_m C_6H_4N) 117.9 (C_p C_6H_4N) 117.6 (C_o C_6H_4N). $^{31}P-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 32.38 (d, ^3J(PP) 3.9 Hz, PPh_3) 37.91 (d, ^3J(PP) 3.9 Hz, P═N).

Synthesis of 4 and 5

Bis(diphenylphosphino)ethane (34 mg, 0.08 mmol) and **2** (41 mg, 0.04 mmol) were added in acetone (15 cm^3) and the resulting mixture was stirred for 18 hours. Compound **5** precipitated from the mixture as a yellow powder was isolated by centrifugation and washed with acetone (10 cm^3). Evaporation of the solvent gave a yellow oil, which was recrystallized from dichloromethane/hexane to give **4** as a yellow solid.

(**4**) Yield: 33 mg, 47%. $C_{50}H_{42}NOP_3Pd$ (872.22); calcd: C 68.9, H 4.9, N 1.6; found: C 68.7, H 5.0, N 1.5. IR: ν(P═N): 1279 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, δ) 6.07 (m, 1H, H–Ar) 6.29 (d, ^3J(HH) 7.9 Hz, H–Ar) 6.40 (m, 2H, H–Ar) 6.85 (td, ^3J(HH) 7.5 Hz, ^4J(HP)1.8 Hz, H–Ar) 6.93 (m, 2H) 7.11 (m, 1H, H–Ar) 7.25 (m, 4H, *m*-Ar) 7.38–7.65 (m, 18H, H–Ar) 7.72 (dd, ^3J(HP) 11.9 Hz, ^3J(HH) 7.4 Hz, 4H, *o*-Ar) 7.86 (dd, ^3J(HP) 12.1 Hz, ^3J(HH) 7.5 Hz, 2H, *o*-Ar) 8.13 (m, 2H, *o*-Ar). $^{13}C-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 151.8 (C–O) 145.2 (C–N) 139.2 ($C-PC_6H_4$) 134.2, 133.5, 131.8 (C_o PhP) 129.0, 128.5, 128.3 (C_m, C_p C_6H_5P) 119.7 (C_m C_6H_4N) 118.8 (C_p C_6H_4N) 115.7 (C_o C_6H_4N) 31.6 (CH_2) 28.9 (CH_2). $^{31}P-\{^1H\}$ NMR (400 MHz, CD_2Cl_2, δ) 43.45 (dd, ^2J(PP) 27.7 Hz, ^3J(PP) 15.5 Hz, PPh_2 *trans*-C) 48.44 (d, ^3J(PP) 15.5 Hz, P═N) 59.56 (d, ^2J(PP) 27.7 Hz, PPh_2 *trans*-N).

(**5**) yield: 23 mg, 41%. $C_{74}H_{60}N_2O_2P_4Pd_2$ (1346.02): calcd: C 66.0, H 4.5, N 2.1; found: C 65.8, H 4.6, N 2.2. IR: ν(P═N): 1277 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ) 6.41 (m, 4H, H–Ar) 6.53 (m, 2H, H–Ar) 6.63 (m, 2H, H–Ar) 6.73 (m, 2H, H–Ar) 6.91 (m, 4H, H–Ar) 7.35–7.61 (m, 24H, H–PPh_2) 7.73–7.89 (m, 18H, H–Ar). $^{13}C-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 155.7 (C–O) 147.2 (C–Pd) 144.9 (C–N) 138.9 ($C-PC_6H_4$) 134.0, 133.7 (C_o PhP) 128.8, 128.4, 127.9 (C_m, C_p C_6H_5P) 118.1 (C_m C_6H_4N) 117.8 (C_p C_6H_4N) 115.4 (C_o C_6H_4N) 29.1 (CH_2). $^{31}P-\{^1H\}$ NMR (400 MHz, $CDCl_3$, δ) 34.22 (s, PPh_2) 36.00 (s, P═N).

Compounds **6** and **7** were obtained following a similar procedure to that for compounds **4** and **5** using bis(diphenylphosphino)propane instead.

(**6**): Yellow solid. Yield: 33.2 mg, 45%. $C_{51}H_{44}NOP_3Pd$ (886.24); calcd: C 69.1, H 4.6, N 1.6; found: C 68.9, H 4.8, N 1.4. IR: ν(P═N): 1279 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6, δ) 6.37 (m, 1H, H–Ar) 6.61 (m, 1H, H–Ar) 6.79 (m, 2H, H–Ar) 7.04 (m, 2H, H–Ar) 7.27–7.25 (m, 26H, H–Ar) 7.66 (m, 2H, H–Ar) 7.89 (m, 4H, *o*-Ar). $^{13}C-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 153.8 (C–O) 147.3 (C–Pd) 145.3 (C–N) 139.9 ($C-PC_6H_4$) 133.3, 133.0, 132.9 (C_o PhP) 129.7, 128.3, 128.0 (C_m, C_p C_6H_5P) 121.4 (C_m C_6H_4N) 119.7 (C_p C_6H_4N) 116.8 (C_o C_6H_4N) 31.9 (CH_2) 27.6 (CH_2) 21.3 (CH_2). $^{31}P-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) −2.06 (dd, ^2J(PP) 55.3 Hz, ^3J(PP) 19.0 Hz, PPh_2 *trans*-C) 22.01 (d, ^2J(PP) 55.3 Hz, PPh_2 *trans*-N) 43.97 (d, ^3J(PP) 19.0 Hz, P═N).

(**7**): Yellow solid. Yield: 18.0 mg, 32%. $C_{75}H_{62}N_2O_2P_4Pd_2$ (1360.04); calcd: C 66.2, H 4.6, N 2.1; found: C 66.2, H 4.7, N 2.1. IR: ν(P═N): 1279 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, δ) 1.98 (m, 2H, CH_2) 2.79 (m, 4H, CH_2) 6.08 (m, 2H, H–Ar) 6.31 (m, 2H, H–Ar) 6.37 (d, ^3J(HH) 7.8 Hz, 2H, H–Ar) 6.49 (m, 2H, H–Ar) 6.60 (m, 4H, H–Ar) 6.81 (m, 4H, H–Ar) 7.16 (m, 8H, *m*-Ar) 7.30 (m, 4H, *p*-Ar) 7.48 (td, ^3J(HH) 7.7 Hz, ^4J(HP) 2.6 Hz, 8H, *m*-PPh_2) 7.58 (m, 6H, *p*-PPh_2) 7.76 (m, 8H, *o*-Ar) 7.88 (dd, ^3J(HP) 11.6 Hz, ^3J(HH) 7.7 Hz, 8H, *o*-PPh_2). $^{13}C-\{^1H\}$ NMR (400 MHz, acetone-d_6, δ) 156.7 (C–O) 147.5 (C–Pd) 145.2 (C–N) 139.4 ($C-PC_6H_4$) 123.0 (C_m C_6H_4N) 120.6 (C_p C_6H_4N) 117.5 (C_o C_6H_4N) 28.5 ($2CH_2$) 20.6 (CH_2). $^{31}P-\{^1H\}$ NMR (400 MHz, CD_2Cl_2, δ) 30.25 (s, PPh_2) 31.62 (s, P═N).

Conclusions

We have shown that for the iminophosphorane ligand derived from 2-aminophenol, palladacycles with the parent ligand as terdentate [*C*,*N*,*O*] may be prepared. The pincer-type bonding mode of the iminophosphorane promotes a dinuclear species with only one bridging chloride ligand, free of any counterion; a hydrogen atom between the two oxygen atoms ensures electrical neutrality. The ensuing complex may be reacted to give either typical mononuclear and dinuclear palladacycles, or alternatively by the use of the appropriate diphosphane, new zwitterionic metallacycles with a chelating phosphorus ligand. The most striking feature depicted herein is the serendipitous unearthing of a dinuclear chloride-bridged triphenylphosphane oxide palladacycle: the missing link in the series of triphenylphosphane chalcogenide metallacycles, which completes the series. Although direct cyclopalladation of the phosphane oxide has not yet been possible, attempts to produce the complex by the hitherto described method have so far been successful.

Conflicts of interest

There are no conflicts to declare.

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