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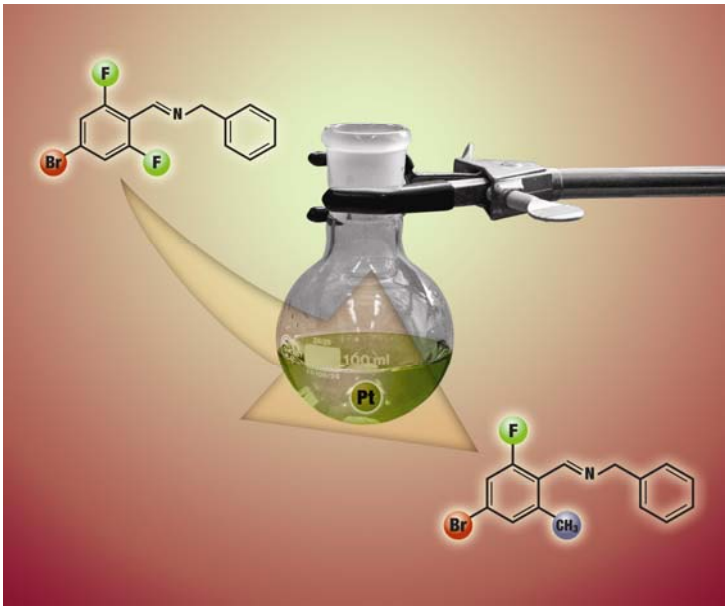


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# Regioselective functionalization of iminophosphoranes through Pd-mediated C–H bond activation: C–C and C–X bond formation†‡

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The orthopalladation of iminophosphoranes [$R_3P$=N–$C_{10}H_7$-1] ($R_3$ = $Ph_3$ **1**, *p*-$Tol_3$ **2**, $PhMe_2$ **3**, $Ph_2Me$ **4**, N–$C_{10}H_7$-1 = 1-naphthyl) has been studied. It occurs regioselectively at the aryl ring bonded to the P atom in **1** and **2**, giving *endo*-[Pd(μ-Cl)($C_6H_4$-($PPh_2$=N-1-$C_{10}H_7$)-2)-κ-C,N]$_2$ (**5**) or *endo*-[Pd(μ-Cl)-($C_6H_3$-(P(*p*-Tol)$_2$=N–$C_{10}H_7$-1)-2-Me-5)-κ-C,N]$_2$ (**6**), while in **3** the 1-naphthyl group is metallated instead, giving *exo*-[Pd(μ-Cl)($C_{10}H_6$-(N=$PPhMe_2$)-8)-κ-C,N]$_2$ (**7**). In the case of **4**, orthopalladation at room temperature affords the kinetic *exo* isomer [Pd(μ-Cl)($C_{10}H_6$-(N=$PPh_2$Me)-8)-κ-C,N]$_2$ (**11exo**), while a mixture of **11exo** and the thermodynamic *endo* isomer [Pd(μ-Cl)($C_6H_4$-(PPhMe=N–$C_{10}H_7$-1)-2)-κ-C,N]$_2$ (**11endo**) is obtained in refluxing toluene. The heating in toluene of the acetate bridge dimer [Pd(μ-OAc)($C_{10}H_6$-(N=$PPh_2$Me)-8)-κ-C,N]$_2$ (**13exo**) promotes the facile transformation of the *exo* isomer into the *endo* isomer [Pd(μ-OAc)($C_6H_4$-(PPhMe=N–$C_{10}H_7$-1)-2)-κ-C,N]$_2$ (**13endo**), confirming that the *exo* isomers are formed under kinetic control. Reactions of the orthometallated complexes have led to functionalized molecules. The stoichiometric reactions of the orthometallated complexes [Pd(μ-Cl)($C_{10}H_6$-(N=$PPhMe_2$)-8)-κ-C,N]$_2$ (**7**), [Pd(μ-Cl)($C_6H_4$-($PPh_2$=NPh)-2)]$_2$ (**17**) and [Pd(μ-Cl)($C_6H_3$-(C(O)N=$PPh_3$)-2-OMe-4)]$_2$ (**18**) with $I_2$ or with CO results in the synthesis of the *ortho*-halogenated compounds [$PhMe_2$P=N–$C_{10}H_6$–I-8] (**19**), [I–$C_6H_4$-($PPh_2$=NPh)-2] (**21**) and [$Ph_3$P=NC(O)$C_6H_3$–I-2-OMe-5] (**23**) or the heterocycles [$C_{10}H_6$-(N=$PPhMe_2$)-1-(C(O))-8]Cl (**20**), [$C_6H_5$-(N=$PPh_2$-$C_6H_4$–C(O)-2]$ClO_4$ (**22**) and [$C_6H_3$-(C(O)-1,2-N–$PPh_3$)-OMe-4]Cl (**24**).

## Introduction

The transformation of the C–H bond, ubiquitous in organic entities, in other types of C–X bonds (X = C, O, N, S, P and so on) is a versatile strategy to build new structures or to introduce new functional groups.[1] This methodology is very convenient since it avoids the use of pre-functionalized substrates, decreases the number of reaction steps, and reduces waste disposals. However, this useful and apparently easy reaction has two main drawbacks. The first one is the inherent inertia of the robust and slightly polar C–H bond,[2] since the cleavage of most types of C–H bonds involve energies of dissociation of around or higher than 100 kcal $mol^{-1}$.[3] The second one is the ubiquity of the C–H bond since, in the absence of a given source of discrimination, many C–H bonds in the same molecule can be simultaneously functionalized, resulting in the formation of isomers. For instance, an aryl ring can be functionalized in *ortho*, *meta* or *para* with respect to a given position. Therefore, there is not an efficient synthetic pathway for a particular isomer.

The use of transition metals (TM) provides a brilliant solution to the lack of reactivity, since TM are able to activate and finally cleave the C–H bond replacing it for a more reactive C–M bond.[2] This new bond is, in most cases, highly reactive towards a large variety of substrates. In addition, several strategies have been developed to achieve selective C–H bond activations. Among them, one of the most successful is based on the introduction of ancillary groups, bonded to the target substrate, containing donor atoms able to bond to the metal.[4] This group is usually called a "directing group" (DG). After the DG bonds to the metal, only the C–H bonds in the vicinity of the metal will be activated. The metallic systems that result from the bonding of a donor atom and subsequent intramolecular C–H bond activation, with concomitant C–M bond formation, are called cyclometallated (Fig. 1).[5]

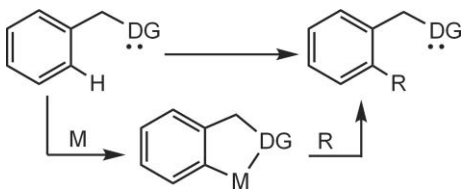


**Fig. 1** General strategy CH bond activation-functionalization.

Cyclometallated compounds derived from Pd, or palladacycles,[6] are by far the most widely used in synthesis, although cyclometallated complexes of other metals, mainly Ru, Rh and Cu, have also interesting applications.[7] During the last few years the use of palladacycles as synthetic tools has increased dramatically, as evidenced by the number of papers appearing in the literature.[8]

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† Based on the presentation given at Dalton Discussion No. 12, 13–15th September 2010, Durham University, UK.

‡ Electronic supplementary information (ESI) available: Experimental details for the synthesis of compounds **2–4**, **8–10**, **12exo**, **14** and **15**, and complete crystallographic tables of **13exo**. CCDC reference number 766306. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003241g

Orthopalladation provides an easy incorporation of functional groups on target molecules. The introduction of methyl,[9] acetate,[10] methoxy,[10] arylsulfonyl,[11] ethoxycarbonyl,[12] halogen,[13] amide,[14] amine,[15] alkynyl,[16] alkenyl,[17] acyl[18] or aryl[19] functional groups, as well as cyclization processes[20] and mechanistic studies[21] have been reported. We have used this strategy very recently for the successful functionalization of α-amino acids.[22]

Our aim here is to use the sequence orthopalladation-functionalization for modification of iminophosphoranes (Fig. 2), species of stoichiometry $R_3P{=}NR'$ (R = alkyl, aryl; R′ = alkyl, aryl, cyano, keto, *etc.*) which are versatile and valuable precursors in organic synthesis.[23,24] Therefore to provide new synthetic methods, alternative to the already established methods of Staudinger,[25] Kirsanov[26] or Pomerantz,[27] is highly desirable. The proposed method seems feasible since orthopalladation of iminophosphoranes through C–H bond activation is a well known process.[28,29] We have also shown that in these species it is possible to direct the activation to a particular C–H bond in the cases where two palladations are available.[29b,d,f,h,i] When the substrates are carbonyl-stabilized iminophosphoranes (Fig. 3a) the palladation is selectively directed to this ring, giving *exo* compounds. In contrast, non-stabilized benzyl iminophosphoranes (Fig. 3b) undergo palladation either at the benzyl ring or at the aromatic rings bonded to the phosphine group, depending on the phosphine substituents and the reaction conditions. This fact is advantageous, since it allows the functionalization of the same substrate at two different positions only by changing the reaction conditions.

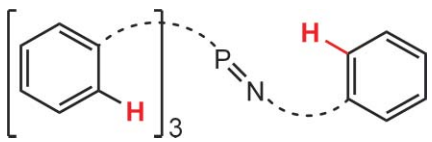



**Fig. 2** Functionalizable positions on iminophosphoranes.

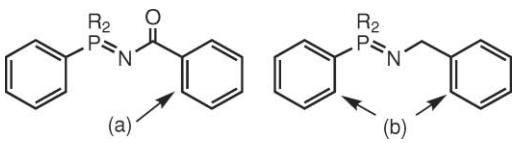



**Fig. 3** Different orientations in orthopalladated iminophosphoranes.

Driven by this hypothesis, we have attempted the functionalization of three types of iminophosphoranes, shown in Fig. 4: stabilized systems containing the benzamide ring (**A**), semi-stabilized systems containing the N-phenyl ring (**B**) and semi-stabilized systems containing the N-1-naphthyl group (**C**). While orthopalladated complexes of **A** and **B** have been reported,[28j,29b,i] those derived from **C** are unknown. We have found that species **A** can be functionalized regioselectively at the *ortho* position of the benzamide ring, and that species **B** are functionalized only at the phenyl ring bonded to the P atom. In the case of **C** we have found that the orthopalladation can be directed, regioselectively, to either the N-naphthyl ring or the P-aryl ring (kinetic *vs.* thermodynamic control), as a function of the reaction conditions and the nature of the phosphine substituents. From the kinetic isomer, functionalization at the 1-naphthyl ring has been easily achieved. Therefore, at least three different modified species have been obtained, providing selective reaction paths to high-added value modified materials that are not easily prepared by conventional methods.

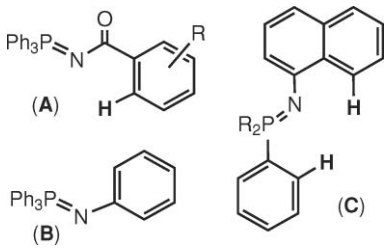


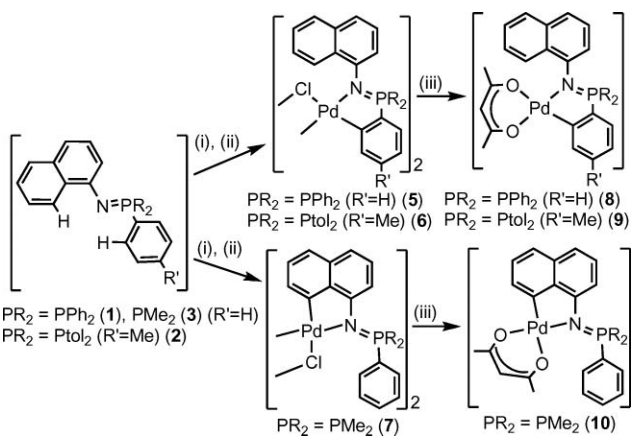

**Fig. 4** Iminophosphoranes of interest.

## Results and discussion

### Study of orthopalladation of naphthyl-iminophosphoranes

The iminophosphorane $Ph_3P{=}N\text{-}1\text{-}C_{10}H_7$ (**1**) has been prepared following reported methods.[30a] The substrates **2–4**, also containing the 1-naphthyl group, have been prepared following the same experimental procedure, by reaction of 1-naphthyl azide[30b] with the corresponding phosphines. The IR spectra of **1–4** show intense absorptions in the 1335–1350 $cm^{-1}$ region, assigned to the $\nu_{P=N}$ stretch. These values are similar to those found in related species.[28i,29a] The $^{31}P\{^1H\}$ NMR spectra of **1–4** show a single peak on each case, with chemical shifts around 4–8 ppm, similar to previous values found for related systems.[28i,29a]

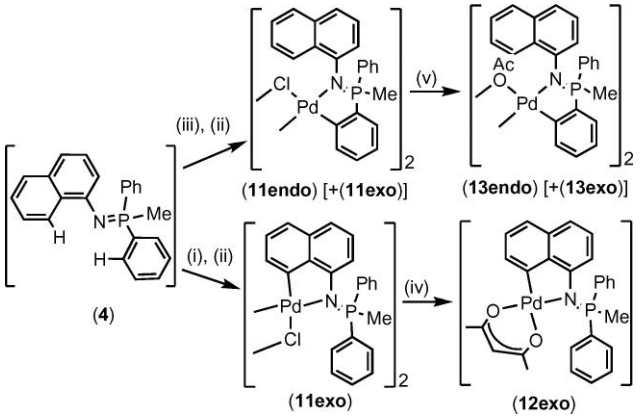
The reactivity of **1–4** towards Pd has been carried out using the usual palladating systems, and the best results were obtained with $Pd(OAc)_2$ (OAc = acetate). Thus, the reaction of $Pd(OAc)_2$ with **1** (1 : 1 molar ratio) in $CH_2Cl_2$ at 25 °C, and further treatment of the plausible acetate intermediate (see below) with LiCl in MeOH gives the orthopalladated $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}(PPh_2{=}N\text{–}C_{10}H_7\text{-}1)\text{-}2)\text{-}\kappa\text{-}C,N]_2$ (**5**) (Scheme 1). Other conditions were tested, from refluxing $CH_2Cl_2$ to refluxing toluene, but **5** was obtained in all studied cases. The incorporation of the Pd atom takes place regioselectively at the *ortho* position of one phenyl ring bonded to the P atom, giving *endo* derivatives.[29] **5** is insoluble in common organic solvents, and a full characterization has been carried out on the more soluble acac complex **8** (acac = acetylacetonate), obtained by reaction of **5** with Tlacac (1 : 2 molar ratio) (Scheme 1).




**Scheme 1** (i) $Pd(OAc)_2$, $CH_2Cl_2$; (ii) LiCl, MeOH; (iii) Tl(acac), $CH_2Cl_2$.

The *endo* palladation is evident from the observation in the $^1$H NMR spectrum of **8** of seven signals due to the naphthyl ring. The permanence of the peak at 9.10 ppm, assigned to the proton at 8-position of the naphthyl ring, is especially relevant since this position should be the most prone to undergo activation and further metalation. Moreover, four well separated signals in the $^1$H NMR spectrum of **8** can be assigned to the presence of a $PdC_6H_4$ ring. The formation of the *endo* palladacycle is also inferred from the deshielding of the $^{31}$P resonance, which moves from 3.50 ppm in **1** to 47.80 ppm in **8**. This large downfield shift has been observed in related *endo* systems.[29] In the case of **5**, two signals were observed in the $^{31}P\{^1H\}$ NMR spectrum, in the same region, due to the presence of the *cis* and *trans* isomers.

Since the variation of the reaction conditions and/or the palladating reagent did not change the orientation of the palladation, we modified the phosphine. We had found previously that the palladation of $Ph_3P{=}NCH_2Ph$ occurs at the $PPh_3$ fragment, and that more basic phosphines promoted changes in selectivity.[29d] Thus, iminophosphoranes **2**–**4**, derived from P(*p*-tol)$_3$, $PPhMe_2$ and $PPh_2Me$, respectively, were reacted with $Pd(OAc)_2$ (Schemes 1 and 2). We indeed found the expected change of reactivity.




**Scheme 2** (i) $Pd(OAc)_2$, $CH_2Cl_2$; (ii) LiCl, MeOH; (iii) $Pd(OAc)_2$, tol, Δ; (iv) Tl(acac), $CH_2Cl_2$; (v) AgOAc, $CH_2Cl_2$.

The reaction of [(*p*-tol)$_3$P=N-1-$C_{10}H_7$] (**2**) with $Pd(OAc)_2$ under the same reaction conditions as those employed in the palladation of **1** ($CH_2Cl_2$, 25 °C) afforded the *endo* complex [Pd(μ-Cl)($C_6H_3$-(P(*p*-tol)$_2$=N–$C_{10}H_7$-1)-2-Me-5)-κ-C,N]$_2$ (**6**). Other reaction conditions (reflux, $CH_2Cl_2$ or toluene) also afforded **6** with only small changes in the reaction yield. In clear contrast with these results, the treatment of [$PhMe_2P{=}N{-}C_{10}H_7$-1] (**3**) with $Pd(OAc)_2$ (1 : 1 molar ratio) in $CH_2Cl_2$ at r.t., and further reaction with LiCl in MeOH, yields the *exo* complex [Pd(μ-Cl)($C_{10}H_6$-(N=$PPhMe_2$)-8)-κ-C,N]$_2$ (**7**). A moderate or strong increase of the temperature (refluxing $CH_2Cl_2$, $CHCl_3$ or toluene) does not promote a different palladation pathway, since **7** is obtained under all the studied conditions. It is noteworthy that **7** is obtained as a single isomer, since only one peak is observed in the $^{31}P\{^1H\}$ NMR spectrum. The *trans* configuration is probably adopted to minimize the interaction between the two phosphine groups.

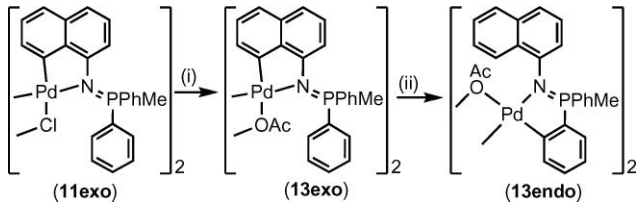
The change of orientation in the orthopalladation seems to shed light on its mechanism. The starting substrates **1** and **2**, and in general the iminophosphoranes, can be represented in two canonical forms,[29] one neutral with a formal double bond P=N and another one zwitterionic in which the N atom supports a formal negative charge while the P atom supports a formal positive charge P(+)–N(−). In complexes **5** and **6** the palladation reaction occurs at the aryl rings bonded to the phosphonium P atom, which are the most electron-deficient rings of the molecule compared with the naphthyl rings. This observation is incompatible with an electrophilic substitution on an aromatic ring ($S_EAr$), where palladation is favoured at the most electron-rich aryl group, and strongly suggests a concerted metalation–deprotonation (CMD) mechanism.[31] In iminophosphorane **3**, two phenyl groups have been replaced by two methyl groups, decreasing notably the formal positive charge at the P atom. In **3**, the Ph ring bonded to the P atom is less electron-deficient than in previous cases, but the comparison should also be done with the competing naphthyl group. This decrease, according to the experimental data, seems to be large enough to promote the change in the orientation of the palladation, which is directed to the naphthyl ring in **7**.

The change from the regioselective *endo* palladation in $Aryl_3P{=}N{-}Np$ systems (**1** or **2**; Np = naphthyl) to the regioselective *exo* palladation in $Me_2PhP{=}N{-}Np$ (**3**) in mild reaction conditions suggests that the modulation of the electronic properties of the iminophosphorane by phosphine modification is relevant. Therefore, intermediate behaviour should be expected for a phosphine with intermediate electronic and steric properties with respect to those known for $PAryl_3$ and $PPhMe_2$.

Indeed, the reaction of [$MePh_2P{=}N{-}C_{10}H_7$-1] (**4**) with $Pd(OAc)_2$ (1 : 1 molar ratio) in $CH_2Cl_2$ at 25 °C and further treatment of the acetate intermediate with excess LiCl in MeOH gives the *exo* complex [Pd(μ-Cl)($C_{10}H_6$-(N=$PPh_2Me$)-8)-κ-C,N]$_2$ (**11exo**). Complex **11exo** reacts with Tlacac (1 : 2 molar ratio) to give [Pd(acac-*O*,*O*′)($C_{10}H_6$-(N=$PPh_2Me$)-8)-κ-C,N] (**12exo**). This metallation has been attempted at different temperatures. Interestingly, we have found that an increase of the temperature promotes the formation of the *endo* complex [Pd(μ-Cl)($C_6H_4$-(PPhMe=N–$C_{10}H_7$-1)-2)-κ-C,N]$_2$ (**11endo**). Therefore, when **4** was reacted with $Pd(OAc)_2$ in refluxing $CH_2Cl_2$, followed by the usual workup, we obtained a mixture of **11exo**/**11endo** in molar ratio 1/0.2. Further increase of the temperature (toluene 80 °C) gives a **11exo**/**11endo** molar ratio of 0.5/1 and when the reaction is performed in refluxing toluene the **11exo**/**11endo** molar ratio is 0.4/1. The reaction of **4** with $Pd(OAc)_2$ in toluene at 25 °C gives **11exo** as the only reaction product, showing that the reaction temperature, and not the nature of the solvent, is the critical parameter in the final distribution of the products. Complex **11endo** could no be isolated in pure form, and could not be fully characterized.

The results mentioned above suggest that **11exo** is the kinetic isomer of the reaction and that **11endo** is the thermodynamic isomer. However, it could also be possible that the formation of **11exo** from **4** and $Pd(OAc)_2$ was irreversible and that the isomer *exo* does not transform in the isomer *endo*. Aiming to clarify this point we have attempted the transformation of **11exo** into **11endo** by heating **11exo** in toluene and monitoring the reaction by $^{31}$P NMR. However, we did not observe any transformation under these reaction conditions. Our group reported that this type of transformation occurs only under the assistance of acetate ligands.[29d] We prepared then the acetate bridge **13exo** (Scheme 3) by reaction of **11exo** with AgOAc (1 : 2 molar ratio). Subsequent heating of **13exo** in toluene-$d_8$ promotes the slow disappearance of




**Scheme 3** (i) Ag(OAc), $CH_2Cl_2$, rt; (ii) Toluene, 80 °C.

the peak at 35.13 ppm (due to **13exo**) and the appearance of new signals at 48.50 ppm, assigned to the acetate dimer **13endo** (see Scheme 3). The molar ratio after heating at 40 °C for 30 min (**13exo**/**13endo** = 1/0.1) is very similar to that found for the mixture **11exo**/**11endo** obtained in refluxing $CH_2Cl_2$. Further heating at 80 °C and at reflux temperature produced mixtures of composition 0.5/1 and 0.4/1, respectively, reproducing the ratios **11exo**/**11endo** obtained from isolated products. In a separate experiment, **13exo** was heated at 80 °C since the beginning of the reaction. The observed **13exo**/**13endo** molar ratios were 1/0.2 (after 10 min) 1/0.8 (after 1 h) and 0.4/1 (after 2 h). It seems clear that the metallation of **13exo** is reversible and that **13exo** and **13endo** are the kinetic and thermodynamic isomers, respectively, of the orthopalladation of **4** with $Pd(OAc)_2$. It is remarkable that the transformation of the isomers occurs in toluene, an aprotic and apolar solvent. While similar isomerizations reported the use of acidic medium as acetic acid,[32] very few have been reported in aprotic media.[33] The transformation of **13exo** into **13endo** in non protic solvents seems to suggest an intramolecular transfer of the proton, assisted by the basic acetate ligand, although the participation of the solvent in the proton transfer (mainly in the case of toluene) could not be discarded.[34]

The X-ray determination of the molecular structure of complex **13exo** confirms the structure proposed here. Crystals of **13exo** adequate for X-ray diffraction were obtained by slow diffusion of vapour of $Et_2O$ into a $CH_2Cl_2$ solution of the crude complex at 5 °C. A drawing of the molecular structure of **13exo** is shown in Fig. 5 and selected bond distances (Å) and angles (deg) are summarized in Table 1. The most relevant crystallographic parameters are collected in Table S1 (ESI). Complex **13exo** shows the typical open-book structure, very usual in complexes with acetate bridges. The relative arrangement of the two cyclopalladated units is *trans*, probably in order to minimize intramolecular interactions. Even with this conformation the steric hindrance between the two bulky

**Table 1** Selected bond distances (Å) and angles (°) for **13exo**

| | | | |
|---|---|---|---|
| Pd1–C1O1 | 1.954(3) | Pd2–C2O1 | 1.956(3) |
| Pd1–O2 | 2.0524(19) | Pd2–O3 | 2.0466(18) |
| Pd1–O4 | 2.153(2) | Pd2–O1 | 2.1658(18) |
| Pd1–N1 | 2.086(2) | Pd2–N2 | 2.079(2) |
| P1–N1 | 1.621(2) | P2–N2 | 1.622(2) |
| N1–C109 | 1.419(3) | N2–C209 | 1.421(3) |
| O3–C124 | 1.270(3) | O1–C224 | 1.242(3) |
| O4–C124 | 1.247(3) | O2–C224 | 1.265(3) |
| C101–Pd1–O2 | 90.48(11) | C201–Pd2–O3 | 91.40(10) |
| C101–Pd1–N1 | 81.81(10) | C201–Pd2–N2 | 81.91(10) |
| O2–Pd1–O4 | 84.19(8) | O3–Pd2–O1 | 82.91(7) |
| N1–Pd1–O4 | 102.74(8) | N2–Pd2–O1 | 102.75(8) |
| C101–Pd1–Pd2 | 119.09(8) | C201–Pd2–Pd1 | 119.32(7) |
| O2–Pd1–Pd2 | 80.44(5) | O3–Pd2–Pd1 | 80.32(5) |
| N1–Pd1–Pd2 | 105.73(6) | N2–Pd2–Pd1 | 106.39(6) |

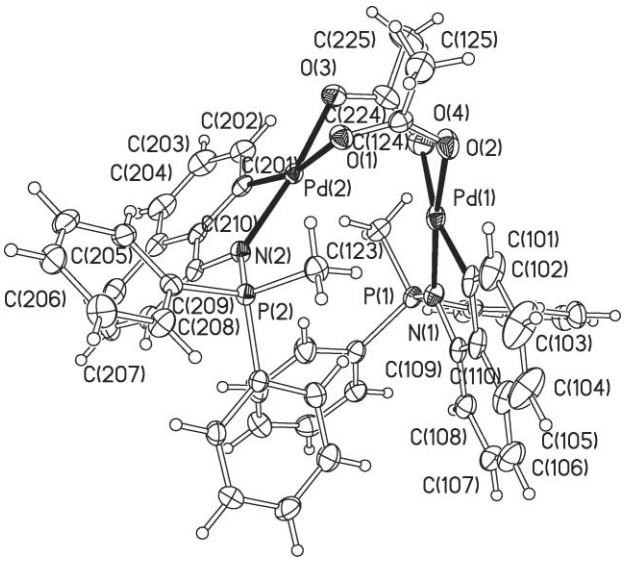
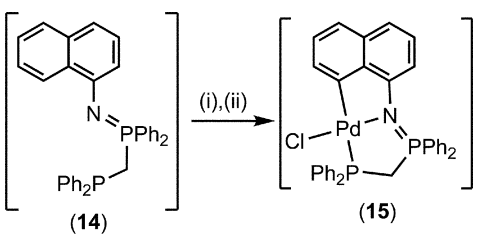



**Fig. 5** Molecular structure of **13exo** with ellipsoids drawn at the 50% probability level.

phosphine groups is high, as can be deduced by the fact that the two molecular planes are not eclipsed, but slightly staggered.

Each Pd atom is located on a slightly distorted square-planar environment, surrounded by the iminic nitrogen, the two oxygens of the acetate groups and the carbon atom at the peri positions of the naphthalene ring, confirming the *exo* palladation. The Pd(1)–N(1) and Pd(1)–N(2) bond distances [2.086(2) and 2.079(2) Å, respectively] are larger than those found in related acetate bridged complexes,[35] which are in the range 2.006(2)–2.037(2) Å. The Pd–C bond distances [Pd(1)–C(101) 1.954(3) Å and Pd(2)–C(201) = 1.956(3) Å] fall in the usual range of distances found for this type of complex,[35] as well as the Pd–O bond distances. Other internal parameters are as expected and do not merit further comment.

Aiming to expand the scope of functionalizable substrates, we have also tested the orthopalladation of iminophosphorane **14**, which contains an additional phosphine group and is expected to behave as a tridentate ligand. Compound **14** has been obtained by reaction of $Ph_2PCH_2PPh_2$ with 1-naphthylazide (1 : 1 molar ratio). The reaction was performed maintaining an excess of phosphine, by adding dropwise the azide to a solution of the bis-phosphine; otherwise, the bis-iminophosphorane $H_2C(PPh_2{=}N\text{-}1\text{-}C_{10}H_7)_2$ was obtained. As expected, **14** reacts with $Pd(OAc)_2$ (1 : 1 molar ratio) in refluxing $CH_2Cl_2$, followed by treatment with LiCl in MeOH, to give **15** as depicted in Scheme 4.



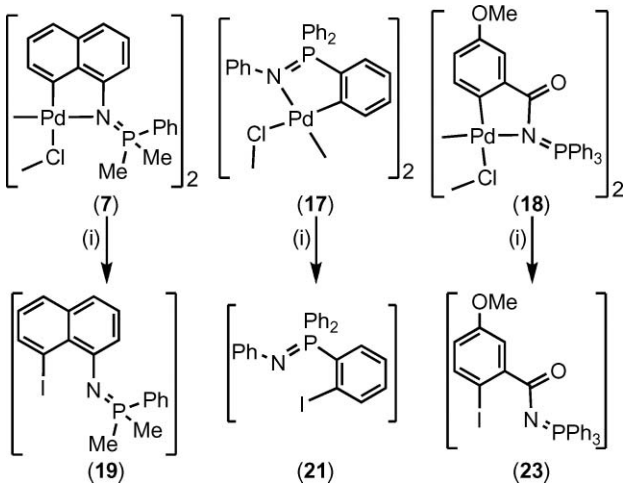

**Scheme 4** (i) $Pd(OAc)_2$, $CH_2Cl_2$; (ii) LiCl, MeOH.

The characterization of the $\kappa^3$-C,N,P bonding mode of the iminophosphorane in **15** is unambiguous. Moreover, the structure of **15** is relevant, since it contains a naphthyl group and a

phosphine fragment arranged in *trans*. This type of disposition is usually very unstable due to the antisymbiotic effect.[36] This effect, referred to the pair of groups aryl/phosphine, has been renamed as transphobia.[37] Probably the release of energy during the formation of two chelating rings is responsible for the stabilization. In summary, we have demonstrated the possibility to palladate several iminophosphoranes at selected positions. In most cases the palladation is selective regardless of the reaction conditions, while in others it is also possible to direct it as a function of the temperature. The next step will be the functionalization of iminophosphoranes by using these new orthopalladated complexes as synthetic tools.

### Stoichiometric functionalization of iminophosphoranes

The formation of new C–I and C–C bonds in iminophosphoranes has been achieved by the reaction of the corresponding orthopalladated complexes with stoichiometric amounts of $I_2$ or CO, respectively. Reactions on selected compounds (of types **C**, **B** and **A** in Fig. 4) are depicted in Schemes 5 ($I_2$) and 6 (CO). **3** belongs to **C**-type compounds and has been functionalized through orthopalladated **7**. $Ph_3P{=}NPh$ and **16** belong to the **B**- and **A**-type compounds, respectively, and react through **17** and **18**. It has been demonstrated that almost all the different functional groups—the naphthyl in **3**, the phosphine in $Ph_3P{=}NPh$ and the benzamide ring in **16**—have been successfully modified.




**Scheme 5** (i) $I_2$, phen, $CH_2Cl_2$, r.t.

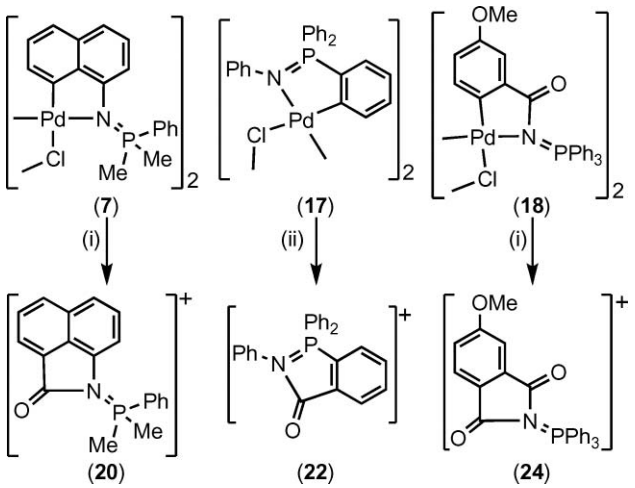
The treatment of **7**, **17** or **18** with elemental iodine (1 : 2 molar ratio) in $CH_2Cl_2$ for 15 h at room temperature gives a black suspension, from which a solid characterized as $PdI_2$ was separated. Subsequent workup of the respective solutions following reported procedures[22,38] gives the corresponding iodinated derivatives **19**, **21** or **23** (Scheme 5). The proposed reaction mechanism is very similar to that reported previously,[22,38] *via* the oxidative addition of the $I_2$ to the cyclopalladated complex, followed by the formation of the C–I bond by reductive elimination. A symmetrization process is responsible for the formation of the insoluble $PdI_2$ (eliminated from the reaction medium) and one intermediate (not isolated) of plausible stoichiometry $PdCl_2L_2$ (L = modified N-bonded iminophosphorane). This intermediate was reacted with phenantroline giving $PdCl_2$(phen) and releasing the free iminophosphorane.

Therefore, we have been able to synthesize three different types of modified iminophosphoranes, using orthopalladated complexes, by regioselective introduction of an iodine atom at specific positions. Compound **19** contains the 8-I-$C_{10}H_6$-1-N skeleton, which could be used in the preparation of other useful derivatives, for instance 8-iodo-1-aminonaphthalene. Although the synthesis reported here involves a four step process (azide, iminophosphorane, orthopalladation, iodination) from the 1-aminonaphthalene to the final product, it can be considered an alternative to traditional methods.[39] Not only do our obtained yields range from moderate to high, but also in most reported synthesis the starting material is an halogenated and/or aminated derivative or a doubly aminated substrate. Besides, compound **21** is also very interesting, since it contains the fragment *o*-$IC_6H_4PPh_2$, and it is a precursor for (2-iodophenyl)-diphenylphosphine, a very versatile reagent.[40a] Two main methods have been reported for the synthesis of this phosphine. The method of Tunney and Stille[40b] involves the use of $Ph_2PSiMe_3$ under Pd-catalysis but gives low yields (20%), while the method of Schlosser[40c] uses the borane-adduct $Ph_3P{\cdot}BH_3$ as starting material and strong deprotonating reagents (BuLi and KO$^t$Bu). The method reported here is the simplest of all methods currently available. However, for iodinated benzamide **30**, this method is not competitive with standard procedures from lithiated complexes. More work to determine the tolerance towards different functional groups present on the benzamide ring has to be done in order to assess the competitivity of this method for similar iodinated benzamides.

A different approximation to the functionalization of orthopalladated substrates is the carbonylation process. The treatment of palladacycles with CO is an excellent method for the formation of new C–C bonds, resulting in the synthesis of carbo- or heterocycles.[6,41] We have used this methodology recently to synthesize isoindolones from phenylglycine.[22] Therefore, if we react the orthopalladated derivatives from iminophosphoranes **A**, **B** and **C** we can expect the incorporation of the CO molecule at a naphthyl ring, at a P-phenyl ring and at a benzamide ring, respectively. A solution of the chloride bridge dimers **7** and **18**, or a freshly prepared solution of the solvate obtained by reaction of **17** with $AgClO_4$ (1 : 2 molar ratio) in THF, were stirred under a CO atmosphere for 15 h (Scheme 6). During this time the starting organometallic complexes decomposed to black $Pd^0$. The corresponding heterocycles **20**, **22** and **24** (Scheme 6) can be isolated after elimination of the $Pd^0$ and removal of the solvent.

The new heterocycles are interesting since they contain fragments that are potentially biologically active. For instance, heterocycle **20** can be considered as a N-phosphonium derivative of the benzo[*cd*]indol-2(1*H*)-one.[42] These types of derivative have been tested as enzyme inhibitors or hypotensive agents.[42] On the other hand, compounds **22** and **24** can also be considered as P-derivatives of the isoindolone skeleton: in the case of **22** the $PPh_2$ group replaces the $CH_2$ unit, while **24** is a N-phosphonium substituted isoindoldione. The isoindolone skeleton is also present on a wide variety of molecules with high biological activity. All these organic structures can be built up very easily from iminophosphoranes, under controlled conditions and in a few reaction steps (4). The tolerance of these reactions towards the presence of different functional groups on the aryl rings to




**Scheme 6** (i) CO, -Pd(0); (ii) $AgClO_4$, CO, -Pd(0).

be functionalized is currently under study in our laboratories. This will determine the prospect of applicability of the synthetic methods described here.

## Conclusions

The orthopalladation of naphthyl-substituted semistabilized iminophosphoranes can be oriented regioselectively towards the naphthyl ring or towards the phosphine aryl rings, as a function of the substituents at the P atom and the reaction temperature, giving *exo* or *endo* complexes, respectively. The *exo* compound is the kinetic isomer while the *endo* is the thermodynamic isomer. The functionalization of different iminophosphoranes, as $PhMe_2P{=}N$-1-Np (Np = naphthyl), $Ph_3P{=}N{-}Ph$ and $Ph_3P{=}NC(O)C_6H_3R$, has been achieved through their orthopalladated complexes. The *exo* derivative of $PhMe_2P{=}N$-1-Np allows for the introduction of an iodine atom or a CO group at the 8 position of the naphthyl fragment, giving derivatives of 8-iodo-naphthaleneamine or of benzo[*cd*]indolone, while the orthopalladation of $Ph_3P{=}N{-}Ph$ results in the synthesis of derivatives like $Ph_2PC_6H_4$-2-I or phosphaisoindolones. The stabilized iminophosphorane $Ph_3P{=}NC(O)C_6H_3R$ undergoes stoichiometric introduction of iodine or CO gives iodobenzamido-iminophosphoranes or N-substituted phthalimides with a phosphonium group.

## Experimental section

### Safety note

*Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See *J. Chem. Educ.* 1973, **50**, A335–A337.

### General methods

Solvents were dried and distilled using standard procedures before use. Elemental analyses (CHNS) were carried out on a Perkin-Elmer 2400-B microanalyser. IR spectra (4000–380 $cm^{-1}$) were recorded on Perkin-Elmer Spectrum One or Spectrum 100 spectrophotometers. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded in $CDCl_3$, $CD_2Cl_2$ and DMSO-$d_6$ solutions at 25 °C on Bruker AV300, AV400 or AV500 spectrometers ($\delta$ in ppm, $J$ in Hz) at $^1H$ operating frequency of 300.13, 400.13 or 500.13 MHz respectively. $^1H$ and $^{13}C$ spectra were referenced using the solvent signal as internal standard, while $^{31}P$ spectra were externally referenced to $H_3PO_4$ (85%). ESI (ESI+) mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. The mass spectra (MALDI+) were recorded from $CHCl_3$ solutions on a MALDI-TOF Microflex (Bruker) spectrometer (DCTB as matrix). $Ph_3P{=}NPh$ is commercial (Aldrich) and was used as supplied. Compounds $Ph_3P{=}N$-1-$C_{10}H_7$ (**1**),[30a] $Ph_3P{=}NC(O)C_6H_4$-3-OMe (**16**)[27,29i] and complexes $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}(PPh_2{=}NPh)\text{-}2)\text{-}\kappa\text{-}C,N]_2$ (**17**)[28i,j] and $[Pd(\mu\text{-}Cl)(C_6H_3\text{-}(C(O)N{=}PPh_3)\text{-}2\text{-}OMe\text{-}4)\text{-}\kappa\text{-}C,N]_2$ (**18**)[29b,i] were preparared by reported methods.

### $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}(PPh_2{=}N{-}C_{10}H_7\text{-}1)\text{-}2)\text{-}\kappa\text{-}C,N]_2$ (5)

To a solution of **1** (0.40 g, 1.00 mmol) in $CH_2Cl_2$ (20 mL), $Pd(OAc)_2$ (0.223 g, 1.00 mmol) was added. The resulting orange solution was stirred at 25 °C for 4 h. After the reaction time, partial decomposition was evident since black palladium was observed. This suspension was filtered through a Celite pad, and the resulting orange solution was evaporated to dryness. The orange residue was dissolved in methanol (20 mL) and anhydrous LiCl (0.168 g, 4.0 mmol) was added. The subsequent stirring (2 h at 25 °C) results in the precipitation of **5** as an orange solid, which was filtered, washed with MeOH (5 mL) and $Et_2O$ (25 mL) and dried *in vacuo*. Obtained: 0.36 g (67% yield). Anal. Calc. for $[C_{56}H_{42}Cl_2N_2P_2Pd_2]$ (1088.6): C, 61.78; H, 3.89; N, 2.57. Found: C, 61.50; H, 3.52; N, 2.28. IR: 1274 ($\nu_{P=N}$) $cm^{-1}$. MS (MALDI+): 509 (40%) $[M/2\text{–}Cl]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 44.52, 45.53$. $^1H$ NMR ($CDCl_3$): $\delta =$ 6.72–8.28 (m, 20 H, $C_{10}H_7{+}H_3{+}H_4{+}H_5$, $C_6H_4$, *cis* + *trans*), 8.98, 9.44 (2d, $2H_6$, $C_6H_4$, *cis* + *trans*, $^3J_{HH} = 7.5$).

### $[Pd(\mu\text{-}Cl)(C_6H_3\text{-}(P(p\text{-}tol)_2{=}N{-}C_{10}H_7\text{-}1)\text{-}2\text{-}Me\text{-}5)\text{-}\kappa\text{-}C,N]_2$ (6)

Complex **6** was obtained following a synthetic method similar to that described for **5**. Therefore, $Pd(OAc)_2$ (0.126 g, 0.56 mmol) reacted with **2** (0.250 g, 0.56 mmol) in dry $CH_2Cl_2$ (20 mL) and with anhydrous LiCl (0.095 g, 2.24 mmol) in MeOH (20 mL) to give **6** as a yellow solid. Obtained: 0.208 g (64% yield). Anal. Calc. for $[C_{62}H_{54}Cl_2N_2P_2Pd_2]$ (1172.78 g $mol^{-1}$): C, 63.49; H, 4.64; N, 2.39. Found: C, 62.95; H, 4.30; N, 2.19. IR: 1269 ($\nu_{P=N}$) $cm^{-1}$. MS (MALDI+): 544 (45%) $[M/2\text{-}Cl]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 42.78, 44.71. $^1H$ NMR ($CDCl_3$): $\delta = 2.04, 2.05, 2.14, 2.18, 2.31,$ 2.35 (6 s, Me, *cis* and *trans*), 6.28–8.21 (m, 28 H, $C_{10}H_7 + H_3 + H_4$, $C_6H_3$, *cis* and *trans*), 9.06, 9.88 (d, 2H, $H_6$, $C_6H_3$, *cis* and *trans*, $^3J_{HH} = 7.5$).

### $[Pd(\mu\text{-}Cl)(C_{10}H_6\text{-}(N{=}PPhMe_2)\text{-}8)\text{-}\kappa\text{-}C,N]_2$ (7)

Complex **7** was obtained following a synthetic method similar to that described for **5**. Therefore, $Pd(OAc)_2$ (0.241 g, 1.07 mmol) reacted with **3** (0.300 g, 1.07 mmol) in dry $CH_2Cl_2$ (30 mL) and with anhydrous LiCl (0.180 g, 4.2 mmol) in MeOH (20 mL) to give **7** as a yellow solid. Obtained: 0.20 g (45% yield). Anal. Calc. for $[C_{36}H_{34}Cl_2N_2P_2Pd]$ (840.36): C, 51.45; H, 4.08; N, 3.33. Found:

C, 50.93; H, 3.80; N, 2.91. IR: 1288 ($\nu_{P=N}$) $cm^{-1}$. MS (FAB +): 385 (40%) $[M/2–Cl]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 33.81$. $^1H$ NMR ($CDCl_3$): $\delta = 2.24$ (d, 6H, Me, $PMe_2$, $^2J_{HP} = 12.8$), 5.95 (d, 1H, $H_7$, $C_{10}H_6$, $^3J_{HH} = 7.5$), 6.80 (t, 1H, $H_6$, $C_{10}H_6$, $^3J_{HH} = 7.8$), 6.92–6.94 (m, 2H, $H_4 + H_3$, $C_{10}H_6$), 7.01 (d, 1H, $H_5$, $C_{10}H_6$, $^3J_{HH} = 7.0$), 7.24 (d, 1H, $H_2$, $C_{10}H_6$, $^3J_{HH} = 7.9$), 7.44–7.53 (m, 3H, $H_m + H_p$, PPh), 7.77 (m, 2H, $H_o$, PPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.52$ (d, Me, $PMe_2$, $^1J_{PC} = 70.7$), 111.10 (d, $C_7$, $C_{10}H_6$, $^3J_{PC} = 7.6$), 118.45, 122.61, 124.78, 125.03, 128.61 (s, $C_2$, $C_3$, $C_4$, $C_5$, $C_6$, $C_{10}H_6$), 129.46 (d, $C_m$, PPh, $^3J_{PC} = 12.0$), 130.67 (d, $C_o$, PPh, $^2J_{PC} = 10.1$), 132.78 (s, $C_p$, PPh), 141.94 (d, $C_8$, $C_{10}H_6$, $^2J_{PC} = 4.1$), 144.33 (d, $C_1$, $C_{10}H_6$, $^3J_{PC} = 1.9$). Peaks assigned to the $C_4$ and $C_8$ carbons of the $C_{10}H_7$ ring, and $C_i$ carbon of the Ph ring were not observed.

### [Pd(μ-Cl)($C_{10}H_6$-(N=$PPh_2$Me)-8)-κ-C,N]$_2$ (11exo)

Complex **11exo** was obtained following a synthetic method similar to that described for **5**. Therefore, $Pd(OAc)_2$ (0.131 g, 0.58 mmol) reacted with **4** (0.200 g, 0.58 mmol) in dry $CH_2Cl_2$ (30 mL) at 25 °C and with anhydrous LiCl (0.100 g, 2.36 mmol) in MeOH (20 mL) to give **11exo** as a yellow solid. Obtained: 0.110 g (40% yield). Anal. Calc. for [$C_{46}H_{38}Cl_2N_2P_2Pd_2$] (964.57): C, 57.28; H, 3.97; N, 2.90. Found: C, 56.53; H, 3.41; N, 2.69. IR: 1288 ($\nu_{P=N}$) $cm^{-1}$. MS (FAB +): 446 (40%) $[M/2–Cl]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.62$. $^1H$ NMR ($CDCl_3$): $\delta = 2.70$ (d, 3H, Me, PMe), 5.72 (d, 1H, $H_7$, $C_{10}H_6$, $^3J_{HH} = 7.4$), 6.64 (t, 1H, $H_6$, $C_{10}H_6$, $^3J_{HH} = 7.7$), 6.74 (d, 1H, $C_{10}H_6$, $^3J_{HH} = 7.1$), 6.78–6.83 (m, 2H, $H_5 + H_3$, $C_{10}H_6$), 6.92 (m, 1H, $C_{10}H_6$), 7.48–7.59 (m, 6H, $H_m$+ $H_p$, $PPh_2$), 7.75 (m, 4H, $H_o$, $PPh_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.90$ (d, Me, PMe, $^1J_{PC} = 77.4$), 110.73 (d, $C_7$, $C_{10}H_6$, $^3J_{PC} = 7.7$), 117.41 (s, $C_5$, $C_{10}H_6$), 121.37 (s, $C_{10}H_6$), 123.92 (s, $C_3$, $C_{10}H_6$), 124.02 (s, $C_6$, $C_{10}H_6$), 126.90 (d, $C_i$, $PPh_2$, $^1J_{PC} = 93.6$), 127.91 (s, $C_{10}H_6$), 128.49 (d, $C_m$, $PPh_2$, $^3J_{PC} = 12.4$), 131.61 (d, $C_o$, $PPh_2$, $^2J_{PC} = 9.9$), 132.15 (s, $C_p$, $PPh_2$), 133.48 (s, $C_{4a}$, $C_{10}H_6$), 141.12 (d, $C_{8a}$, $C_{10}H_6$, $^3J_{PC} = 16.6$), 141.83 (s, $C_1$, $C_{10}H_6$), 152.39 (d, $C_8$, $C_{10}H_6$, $^2J_{PC} = 2.6$).

### [Pd(μ-Cl)($C_{10}H_6$-(N=$PPh_2$Me)-8)-κ-C,N]$_2$ (11exo) and [Pd(μ-Cl)($C_6H_4$-(PPhMe=N–$C_{10}H_7$-1)-2)-κ-C,N]$_2$ (11endo)

To a solution of **4** (0.35 g, 1.02 mmol) in toluene (20 mL), $Pd(OAc)_2$ (0.230 g, 1.02 mmol) was added. The resulting brown solution was refluxed for 2 h. Decomposition of the Pd salt was evident since black Pd was observed. The suspension was filtered through a Celite pad, the resulting orange solution was evaporated to dryness and the residue was dissolved in methanol (20 mL). The addition of anhydrous LiCl (0.174 g, 4.1 mmol) resulted in the precipitation of an orange solid, which was filtered, washed with MeOH (10 mL) and $Et_2O$ (25 mL) and dried *in vacuo*. Obtained: 0.21 g (42% yield). This solid was characterized as the mixture **11endo/11exo** (1/0.4) by integration of the corresponding resonances in the $^{31}P\{^1H\}$ NMR spectrum: a sharp peak at 31.6 ppm matches with that found for **11exo**, while a very broad resonance centered at 47.95 ppm is assigned to the different isomers of **11endo** since it falls in the same region as that found in **5** and **6**. IR: 1290 ($\nu_{P=N}$) $cm^{-1}$. MS (FAB +): 446 (30%) $[M/2–Cl]^+$.

### [Pd(μ-OAc)($C_{10}H_6$-(N=$PPh_2$Me)-8)-κ-C,N] (13exo)

To a suspension of **11exo** (0.227 g, 0.24 mmol)) in 20 mL of $CH_2Cl_2$, AgOAc (0.086 g, 0.52 mmol) was added, and the mixture was stirred under exclusion of light for 30 min. After the reaction time, the suspension obtained was filtered through a Celite pad, and the resulting solution was evaporated to dryness. The orange residue was stirred with $Et_2O$ (25 mL), giving **13exo** as a yellow solid. Obtained: 0.170 g (71% yield). Anal. Calc. for [$C_{50}H_{44}N_2O_4P_2Pd_2$] (1011.68): C, 59.36; H, 4.38; N, 2.77. Found: C, 58.95; H, 4.19; N, 2.56. IR: 1581 ($\nu_{CO}$, acac), 1548 ($\nu_{CO}$, acac), 1256 ($\nu_{P=N}$) $cm^{-1}$. MS (MALDI +): 447 (60%) $[M/2–OAc]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 35.09$. $^1H$ NMR ($CDCl_3$): $\delta = 1.87$ (s, 3H, Me, OAc), 2.20 (d, 3H, Me, PMe, $^2J_{HP} = 12.9$), 5.93 (d, 1H, $H_7$, $C_{10}H_6$, $^3J_{HH} = 7.4$), 6.72 (t, 1H, $H_6$, $C_{10}H_6$, $^3J_{HH} = 7.0$), 6.80 (d, 1H, $C_{10}H_6$, $^3J_{HH} = 7.0$), 6.88 (d, 1H, $H_5$, $C_{10}H_6$, $^3J_{HH} = 7.6$), 6.99 (t, 1H, $C_{10}H_6$, $^3J_{HH} = 6.7$), 7.18–7.21 (m, 1H, $C_{10}H_6$), 7.44–7.70 (m, 10H, $H_m + H_p + H_o$, $PPh_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.13$ (d, Me, PMe, $^1J_{PC} = 79.5$), 24.87 (s, Me, OAc), 112.32 (s broad, $C_7$, $C_{10}H_7$), 117.62 (s broad, $C_5$, $C_{10}H_7$), 122.33 (s broad, $C_{10}H_7$), 124.28 (s broad, $C_{10}H_7$), 124.82 (s broad, $C_6$, $C_{10}H_7$), 127.19 (s broad, $C_{10}H_7$), 128.87 (s broad, $C_m$, $PPh_2$), 131.87 (s broad, $C_p$, $PPh_2$), 132.47 (s broad, $C_o$, $PPh_2$), 141.84 (s broad, $C_1$, $C_{10}H_7$), 153.78 (s broad, $C_8$, $C_{10}H_7$). The peaks assigned to the $C_i$, ($PPh_2$), $C_{4a}$, $C_{8a}$ ($C_{10}H_6$) and CO (OAc) carbon atoms were not observed.

### [Pd(μ-OAc)($C_{10}H_6$-(N=$PPh_2$Me)-8)-κ-C,N]$_2$ (13exo) and [Pd(μ-OAc)($C_6H_4$-(PPhMe=N–$C_{10}H_7$-1)-2)-κ-C,N]$_2$ (13endo)

The mixture **13exo/13endo** was prepared following the same synthetic method as that reported for **13exo**. Therefore, **11exo/11endo** (0.18 g, 0.19 mmol) reacted with $AgClO_4$ (0.069 g, 0.41 mmol) in $CH_2Cl_2$ (20 mL) to give **13exo/13endo** as a deep orange solid. Obtained: 0.11 g (58% yield). This solid was characterized as the mixture **13endo/13exo** (1/0.4) by integration of the corresponding resonances in the $^{31}P\{^1H\}$ NMR spectrum: a broad peak at 35.1 ppm is assigned to **13exo**, while a very broad signal about 48–49 ppm is assigned to the different isomers of **13endo**. IR: 1579 ($\nu_{CO}$,acac), 1545 ($\nu_{CO}$, acac), 1265 ($\nu_{P=N}$) $cm^{-1}$. MS (MALDI +): 447 (55%) $[M/2–OAc]^+$.

### [$PhMe_2P$=N–$C_{10}H_6$–I-8] (19)

To a solution of **7** (0.237 g, 0.28 mmol) in 20 mL of $CH_2Cl_2$, $I_2$ (0.143 g, 0.56 mmol) was added. The black suspension was stirred for 15 h at 25 °C, then the precipitated $PdI_2$ was eliminated by filtration through a Celite pad. The resulting red solution was evaporated to half volume, and 1,10-phenanthroline (0.055 g, 0.28 mmol) was added. The immediate precipitation of $PdCl_2$(phen) was evident. This suspension was stirred at 25 °C for 4 h, then the solid $PdCl_2$(phen) was eliminated by filtration, and the solution was evaporated to a small volume (about 1–2 mL). By addition of a mixture of $Et_2O$–n-hexane (20 mL 1 : 3) and stirring, **19** was obtained as an orange solid, which was filtered, washed with n-hexane and dried *in vacuo*. Obtained: 0.143 g (63% yield). Anal. Calc. for [$C_{18}H_{17}INP$] (405.2): C, 53.35; H, 4.23; N, 3.46. Found: C, 52.85; H, 4.21; N, 3.32. IR: 1335 ($\nu_{P=N}$) $cm^{-1}$. MS (MALDI +): 405 (40%) $[M]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 9.85$. $^1H$ NMR ($CDCl_3$): $\delta = 1.45$ (d, 3H, Me, $PMe_2$, $^2J_{HP} = 13.2$), 1.90 (d, 3H, Me, $PMe_2$, $^2J_{HP} = 12.6$), 5.56 (d, 1H, $H_2$, $C_{10}H_6$, $^3J_{HH} = 6.5$), 6.71–6.77 (m, 2H, $H_3$, $C_{10}H_6$ + $H_o$, PPh), 7.06 (td, $H_m$, PPh, $^3J_{HH} = 8.0$, $^4J_{HP} = 3.2$), 7.31 (td, $H_p$, PPh, $^3J_{HH} = 7.5$, $^5J_{HP} = 1.2$), 7.54–7.62 (m, 2H, $H_4 + H_6$, $C_{10}H_6$), 7.73 (d, 1H, $H_7$, $C_{10}H_6$, $^3J_{HH} = 8.0$), 7.98

(ddd, 1H, $H_5$, $C_{10}H_6$, $^3J_{HH} = 7.5$, $^6J_{HP} = 2.4$, $^4J_{HH} = 1.3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 12.44$ (s, Me, $PMe_2$, $^1J_{PC} = 81.2$), 20.22 (s, Me, $PMe_2$, $^1J_{PC} = 59.0$), 124.25 (d, $C_7$, $C_{10}H_6$, $^5J_{PC} = 2.6$), 124.86 (s, $C_3$, $C_{10}H_6$), 126.45 (d, $C_4$, $C_{10}H_6$, $^5J_{PC} = 2.7$), 128.60 (s, $C_6$, $C_{10}H_6$), 128.03 (d, $C_m$, PPh, $^3J_{PC} = 11.6$), 128.50 (d, $C_5$, $C_{10}H_6$, $^5J_{PC} = 6.4$), 129.84 (d, $C_o$, PPh, $^2J_{PC} = 8.4$), 129.97 (d, $C_i$, PPh,$^1J_{PC} = 94.4$), 131.25 (overlapped $C_2$, $C_{10}H_6$ + $C_p$, PPh), 133.14 (s, $C_8$, $C_{10}H_6$), 135.25, 142.84 (2 s, $C_{4a}$ + $C_{8a}$, $C_{10}H_6$),145.40 (d, $C_1$, $C_{10}H_6$, $^2J_{PC} = 5.0$).

### [$C_{10}H_6$-(N=PPhMe$_2$)-1-(C(O))-8]Cl (20)

A solution of **7** (0.216 g, 0.26 mmol) in 20 mL of $CH_2Cl_2$ was stirred under a CO atmosphere (1 atm) for 15 h. After a few minutes, a clear decomposition is evident. However, stirring was maintained during 15 h. After the reaction time the black Pd was eliminated by filtration, and the orange solution was evaporated to dryness. By $Et_2O$ addition (20 mL) and stirring, **20** was obtained as an orange solid. Obtained: 0.120 g (68% yield). Anal. Calc. for [$C_{19}H_{17}NOP$]Cl (341.8): C, 66.77; H, 5.01; N, 4.10. Found: C, 66.90; H, 4.70; N, 3.81. IR: 1605 ($\nu_{C=O}$). MS (MALDI +): 280 (100%) [M–CO+2H]$^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 44.19$. $^1H$ NMR ($CDCl_3$): $\delta = 1.67$, 1.84 (broad, $PMe_2$), 7.00 (d, 1H, $H_2$, $C_{10}H_6$, $^3J_{HH} = 6.0$), 7.46–7.63 (m, 5H, 3H, $C_{10}H_6$ + $H_m$, PPh), 7.75–7.78 (m, 3H, $H_p$ + $H_o$, PPh), 8.07–8.11 (m, 2H, $C_{10}H_6$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 17.25, 18.29 (2 s, $PMe_2$), 106.57 (s, $C_2$, $C_{10}H_6$), 119.72 (s, $C_{10}H_6$), 123.87 (s, $C_{10}H_6$), 128.34 (overlapped $C_m$, PPh + 1 CH, $C_{10}H_6$), 128.72 (d, $C_o$, PPh, $^2J_{PC} = 10.6$), 129.04 (s, $C_1$, $C_{10}H_6$), 129.59 (d, $C_p$, $PPh_2$, $^4J_{PC} = 7.2$), 130.79 (s, $C_{10}H_6$), 131.98 (s, $C_{10}H_6$), 137.09 (s, $C_8$, $C_{10}H_6$), 169.69 (s, CO).

### [I–$C_6H_4$-($PPh_2$=NPh)-2] (21)

Compound **21** was prepared following the same experimental method as that described for **19**. Therefore, **17** (0.305 g, 0.31 mmol) reacted with $I_2$ (0.156 g, 0.61 mmol) and 1,10-phenanthroline (0.061 g, 0.31 mmol) in $CH_2Cl_2$ (20 mL) to give **21** as an orange solid. Obtained: 0.158 g (54% yield). Compound **21** was recrystallized from $CH_2Cl_2$–$Et_2O$ (1 : 3). Anal. Calc. for [$C_{24}H_{19}INP$] (479.3): C, 60.14; H, 4.00; N, 2.92. Found: C, 59.75; H, 3.81; N, 2.73. IR: 1324 ($\nu_{P=N}$) cm$^{-1}$. MS (MALDI+): 480 (30%) [M]$^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.50$. $^1H$ NMR ($CDCl_3$): $\delta =$ 6.26 (dd, 1H, $H_3$, $C_6H_4$, $^3J_{HH} = 6.8$, $^4J_{HH} = 4.0$), 6.46 (d, 1H, $H_o$, NPh, $^3J_{HH} = 8.1$), 6.76 (t, 1H, $H_p$, NPh, $^3J_{HH} = 7.4$), 6.94 (t, 1H, $H_m$, NPh, $^3J_{HH} = 7.8$), 7.15 (t, 1H, $H_4$, $C_6H_4$, $^3J_{HH} = 7.1$), 7.29–7.36 (m, 2H, $H_5$ + $H_6$, $C_6H_4$), 7.46 (m, 1H, $H_p$, $PPh_2$), 7.54 (m, 2H, $H_m$, $PPh_2$), 7.63 (m, 2H, $H_m$, $PPh_2$), 7.70 (m, 2H, $H_o$, $PPh_2$), 7.82 (m, 2H, $H_o$, $PPh_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 120.99$ ($C_o$, NPh), 121.09 ($C_p$, NPh), 128.62 ($C_p$, $PPh_2$), 129.46 ($C_m$, NPh), 129.68 ($C_m$, PPh), 130.21 ($C_m$, PPh), 132.97 ($C_3$, $C_6H_4$), 133.07 ($C_4$, $C_6H_4$), 133.28 (overlapped, $C_5$ + $C_6$, $C_6H_4$), 133.71 ($C_o$, PPh), 133.92 ($C_o$, PPh).

### [$C_6H_5$-(N=$PPh_2$-$C_6H_4$–C(O)-2]$ClO_4$ (22)

To a suspension of **17** (0.159 g, 0.16 mmol) in 20 mL of dry THF $AgClO_4$ (0.073 g, 0.35 mmol) was added, and the resulting mixture was stirred under exclusion of light for 30 min. After this time the insoluble AgCl was filtered, and the freshly prepared solution was stirred under a CO atmosphere (1 atm) for 15 h at 25 °C. During this time the decomposition was evident, since black Pd was formed. After the reaction time the Pd(0) was filtered off and the obtained orange solution was evaporated to dryness. The residue was dissolved in the minimal amount of $CHCl_3$ (about 1–2 mL) and treated with $Et_2O$ (25 mL). Further stirring gave **22** as an orange solid. Obtained: 0.100 g (64% yield). Anal. Calc. for [$C_{25}H_{19}NOP$]$ClO_4$ (479.85): C, 62.58; H, 3.99; N, 2.92. Found: C, 62.59; H, 3.85; N, 2.78. IR: 1593 ($\nu_{C=O}$). MS (MALDI+): 380 (10%) [M–$ClO_4$]$^+$. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta = 44.97$. $^1H$ NMR ($CD_2Cl_2$): $\delta = 6.70$ (t, $H_p$, NPh, $^3J_{HH} = 7.3$), 6.77–6.99 (m, 7H, $H_m$ + $H_o$, NPh + 3H, $C_6H_4$), 7.21 (d, 1H, $H_3$, $C_6H_4$, $^3J_{HH} = 7.6$), 7.40–7.45 (m, 4H, $H_m$, $PPh_2$), 7.51–7.54 (m, 2H, $H_p$, $PPh_2$), 7.70–7.75 (m, 4H, $H_o$, $PPh_2$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta = 121.44$ (s, $C_p$, NPh), 124.1 (d, $C_4$, $C_6H_4$, $^3J_{PC} = 13.5$), 126.42 (d, $C_o$, NPh, $^3J_{PC} = 11.1$), 127.66 (s, $C_m$, NPh), 128.05 (d, $C_3$, $C_6H_4$, $^2J_{PC} = 21.8$), 128.98 (d, $C_m$, $PPh_2$, $^3J_{PC} = 11.9$), 129.97 (d, $C_5$, $C_6H_4$, $^4J_{PC} = 2.8$), 133.00 (d, $C_p$, $PPh_3$, $^4J_{PC} = 2.4$), 133.29 (d, $C_o$, $PPh_2$, $^2J_{PC} = 10.1$), 135.28 (d, $C_3$, $C_6H_4$, $^3J_{PC} = 13.9$). Peaks due to quaternary C atoms were not observed.

### [$Ph_3P$=N–C(O)-$C_6H_3$–I-2-OMe-5] (23)

Compound **23** was prepared following the same experimental method as that described for **19**. Therefore, **18** (0.160 g, 0.14 mmol) reacted with $I_2$ (0.074 g, 0.29 mmol) and 1,10-phenanthroline (0.028 g, 0.14 mmol) in $CH_2Cl_2$ (20 mL) to give **23** as an orange solid. Obtained: 0.121 g (39% yield). Compound **23** was recrystallized from $CH_2Cl_2$–$Et_2O$ (1 : 3). Anal. Calc. for [$C_{26}H_{21}INO_2P$] (537.33): C, 58.12; H, 3.94; N, 2.61. Found: C, 57.77; H, 3.64; N, 2.39. IR: 1586 ($\nu_{C=O}$), 1349 ($\nu_{P=N}$) cm$^{-1}$. MS (MALDI+): 537 (20%) [M]$^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.11$. $^1H$ NMR ($CDCl_3$): $\delta = 3.71$ (s, 3H, OMe), 6.73 (dd, 1H, $H_3$, $C_6H_3$, $^3J_{HH} = 8.7$, $^4J_{HH} = 3.0$), 7.18 (d, 1H, $H_4$, $C_6H_3$, $^3J_{HH} = 8.5$), 7.34 (d, 1H, $H_6$, $C_6H_3$, $^4J_{HH} = 3.0$), 7.41 (m, 6H, $H_m$, $PPh_3$), 7.50 (m, 3H, $H_p$, $PPh_3$), 7.77 (m, 6H, $H_o$, $PPh_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 55.68$ (s, OMe), 115.44 (s, $C_6H_3$), 116.25 (s, $C_6H_3$), 123.65 (s, $C_2$, $C_6H_3$), 127.73 (d, $C_i$, $PPh_3$,$^1J_{PC} = 99.3$), 128.75 (d, $C_m$, $PPh_3$, $^3J_{PC} = 12.4$), 131.04 (s, $C_6H_3$), 132.40 (d, $C_p$, $PPh_3$, $^4J_{PC} = 2.8$), 133.28 (d, $C_o$, $PPh_3$, $^2J_{PC} = 10.1$), 140.31 (d, $C_1$, $C_6H_3$, $^3J_{PC} = 20.1$), 157.84 (s, $C_5$, $C_6H_3$), 176.43 (d, CO, $^2J_{PC} = 8.2$).

### [$C_6H_3$-((C(O))$_2$-1,2-N–$PPh_3$)-OMe-4]Cl (24)

Compound **24** was obtained following the same experimental procedure as that reported for **20**. Therefore, a solution of **18** (0.220 g, 0.20 mmol) in 20 mL of $CH_2Cl_2$ was stirred under CO atmosphere (1 atm) for 15 h at 25 °C, giving **24** as a yellow solid. Obtained: 0.125 g (66% yield). Anal. Calc. for [$C_{27}H_{22}NO_3P$]Cl (473.9): C, 68.43; H, 4.47; N, 2.96. Found: C, 68.60; H, 4.28; N, 2.80. IR: 1630, 1641 ($\nu_{C=O}$). MS (MALDI +): 438 (48%) [M]$^+$. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta = 29.34$. $^1H$ NMR ($CDCl_3$): $\delta = 3.94$ (s, OMe), 7.20 (d, 1H, $H_5$, $C_6H_3$, $^3J_{HH} = 7.6$), 7.33 (d, 1H, $H_3$, $C_6H_3$, $^4J_{HH} = 1.2$), 7.48 (m, 6H, $H_m$, $PPh_3$), 7.54 (m, 3H, $H_p$, $PPh_3$), 7.68 (m, 6H, $H_o$, $PPh_3$), 7.77 (d, $H_6$, $C_6H_3$, $^3J_{HH} = 8.0$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta = 56.24$ (s, OMe), 108.07 (s, $C_3$, $C_6H_3$), 120.36 (s, $C_5$, $C_6H_3$), 124.58, 135.29 (2 s, $C_1$, $C_2$, $C_6H_3$), 125.32 (s, $C_6$, $C_6H_3$), 128.64 (d, $C_m$, $PPh_3$, $^3J_{PC} = 12.0$), 132.08–132.27 ($C_p$, $C_o$, $PPh_3$), 164.89 (s, $C_3$, $C_6H_3$), 167.78, 167.87 (s, CO).

### X-Ray crystallography

Crystals of adequate quality for X-ray measurements were grown by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of the crude product at −15 °C. A single crystal of **13exo·2OEt₂** was mounted at the end of a quartz fiber in a random orientation, covered with magic oil and placed under a cold stream of nitrogen. Data collection was performed at low temperature (150 K) on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). An hemisphere of data was collected based on three ω-scan or φ-scan runs. The diffraction frames were integrated using the program CrysAlis RED[43] and the integrated intensities were corrected for absorption with SADABS.[44] The structure was solved and developed by Patterson and Fourier methods.[45] All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed at idealized positions and treated as riding atoms. Each H atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structure was refined to $F_o^2$, and all reflections were used in the least-squares calculations.[46]

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