Synthesis and structure of tetranuclear orthometallated Pd(II) complexes derived from bis-iminophosphoranes†

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The reaction of $Pd(OAc)_2$ with bis-iminophosphoranes $Ph_3P{=}NCH_2CH_2CH_2N{=}PPh_3$ (**1a**), $[C_6H_4(C(O)N{=}PPh_3)_2\text{-}1,3]$ (**1b**) and $[C_6H_4(C(O)N{=}PPh_3)_2\text{-}1,2]$ (**1c**), gives the orthopalladated tetranuclear complexes $[\{Pd(\mu\text{-}Cl)\{C_6H_4(PPh_2{=}NCH_2\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2CH_2]_2$ (**2a**) $[\{Pd(\mu\text{-}OAc)\text{-}\{C_6H_4(PPh_2{=}NC(O)\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2C_6H_4\text{-}1',3']_2$ (**2b**) and $[\{Pd(\mu\text{-}OAc)\{C_6H_4(PPh_2{=}NC(O)\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2\text{-}C_6H_4\text{-}1',2']_2$ (**2c**). The reaction takes place in CH_2Cl_2 for **1a**, but must be performed in glacial acetic acid for **1b** and **1c**. The process implies in all cases the activation of a C–H bond on a Ph ring of the phosphonium group, with concomitant formation of *endo* complexes. This is the expected behaviour for **1a**, but for **1b** and **1c** reverses the *exo* orientation observed in other ketostabilized iminophosphoranes. The influence of the solvent in the orientation of the reaction is discussed. The dinuclear acetylacetonate complexes $[\{Pd(acac\text{-}O,O')\{C_6H_4(PPh_2{=}NCH_2\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2CH_2]$ (**3a**), $[\{Pd(acac\text{-}O,O')\{C_6H_4(PPh_2{=}NC(O)\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2C_6H_4\text{-}1',3']$ (**3b**) and $[\{Pd(acac\text{-}O,O')\{C_6H_4(PPh_2{=}NC(O)\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2C_6H_4\text{–}1',2']$ (**3c**) have been obtained from the halide-bridging tetranuclear derivatives. The X-ray crystal structure of $[\mathbf{3c}\cdot 4CHCl_3]$ is also reported.

Introduction

Bis-iminophosphoranes are species containing two formal P=N double bonds. Fig. 1 shows three structural motifs which can represent this definition. These structures can be formally derived from (i) bis-phosphines, (ii) bis-amines, or (iii) aminophosphines. Due to the presence of two N atoms, these species behave as chelating *N*,*N*-ligands towards transition metals, and show a rich coordination chemistry.[1a] In addition, bis-iminophosphoranes are quite useful synthons in a wide variety of organic reactions.[1b–d]

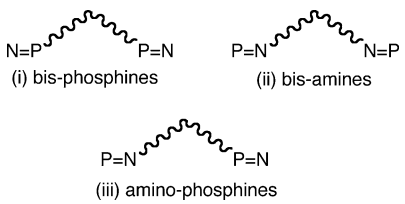

Fig. 1 Structural motifs for bis-iminophosphoranes.

The structure shown in Fig. 1(i) represents bis-iminophosphoranes derived from bis-phosphines, and comprises most of the chemistry performed in this field.[2–5] Amongst them, those built from bis(diphenylphosphino)methane $[Ph_2PCH_2PPh_2]$ are the most studied, in its neutral,[3] monoanionic (methanide)[4] or dianionic (carbenic) forms.[2,5] Complexes derived from other diphosphines are also known.[4e,f] The structure shown in Fig. 1(ii) represents those compounds obtained from bis-amines, which are relatively less-developed, although there are notable contributions in coordination chemistry[6] and in organic synthesis.[7] The compounds derived formally from aminophosphines [Fig. 1(iii)] are still scarcely-represented.[8]

Following our research in C–H bond activations on P-ylides and iminophosphoranes,[9] we have now focused our attention to bis-iminophosphoranes due to several reasons. This class of reactions on this type of substrates is scarcely represented and few examples have been found in the literature.[5g,i,j] Moreover, we have recently reported that the orthopalladation on iminophosphoranes $R_3P{=}NC(O)Aryl$ is *exo* regioselective,[9e] while that of $R_3P{=}NCH_2aryl$ can be oriented *exo*- or *endo*- as a function of the substituents and reaction temperature.[9g] Therefore, our aim was to expand the chemistry of bis-iminophosphoranes and their C–H bond activation reactions, and it was also to determine if the orientation of the palladation follows the same patterns than those found for iminophosphoranes containing a single P=N bond. We describe here the obtained results.

Results and discussion

Synthesis of the bis-iminophosphoranes

The synthesis of the bis-iminophosphoranes **1a**–**c** has been carried out using the Staudinger method[10] by reaction of the corresponding azides[11] with PPh_3 under standard experimental conditions. The IR spectra of **1a**–**c** show strong absorptions assigned to the stretch of the P=N bond (around 1300–1350 cm^{-1}) and, in the case of **1b**,**c**, additional bands due to the carbonyl group (around 1590 cm^{-1}) are also observed. The NMR spectra of **1a**–**c** show the

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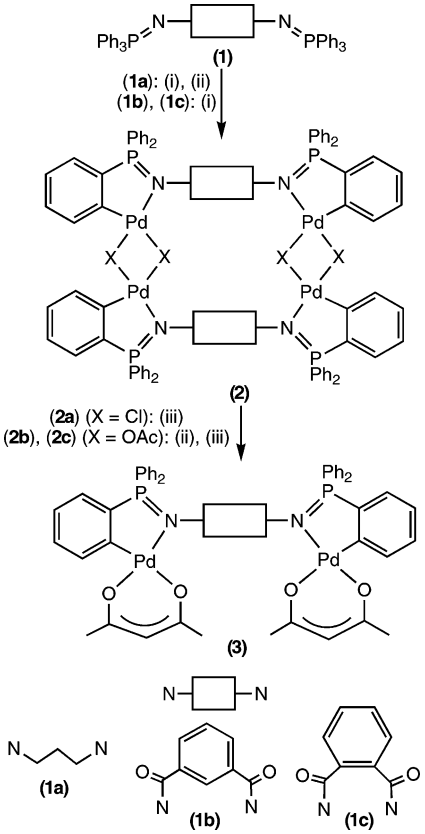
presence of a single set of signals, meaning that each compound is obtained as a single isomer. The pattern of peaks observed in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for the $(CH_2)_3$ unit (**1a**) or for the C_6H_4 ring (**1b**,**c**) suggests a high symmetry of the compounds, as corresponds to the structures shown in Scheme 1. The $^{31}P\{^{1}H\}$ NMR spectra of **1a**–**c** show a single peak on each case, centered around 11 ppm for **1a** and around 20 ppm for **1b**,**c**, being these chemical shifts in good agreement with previous results on related species.[9e–h] We have also attempted the synthesis of bis-iminophosphoranes derived from α,α′-diazidoxylene derivatives (*ortho* or *meta*) $[C_6H_4(CH_2N_3)_2$-1,2 or -1,3]. In spite of numerous reaction conditions tested, low yields of mixtures of mono and bis-substituted products were found. These mixtures could not be separated by chromatographic methods and were easily hydrolysed to the corresponding amines and phosphine oxide. Due to these reasons they were not subject of further investigation.



Scheme 1 Ligand (**1a**): (i) $Pd(OAc)_2$, CH_2Cl_2, Δ; ligands (**1b**) and (**1c**): (i) $Pd(OAc)_2$, AcOH, Δ; (ii) LiCl, MeOH, r.t.; (iii) Tl(acac), CH_2Cl_2.

Cyclopalladation reactions

Bis-iminophosphorane **1a** reacts with $Pd(OAc)_2$ (1 : 2 molar ratio) in refluxing CH_2Cl_2 to give (after elimination of the black Pd^0 formed) an orange solution which presumably contains a bridging acetate intermediate. This intermediate reacts in MeOH with an excess of LiCl to give a low yield of the tetranuclear chloride bridging derivative $[\{Pd(\mu\text{-}Cl)\{C_6H_4(PPh_2{=}NCH_2\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2CH_2]_2$ (**2a**) as represented in Scheme 1. The yield of **2a** improves slightly if the first step of the reaction is carried out in refluxing toluene.

The elemental analyses of **2a** show the incorporation of two "PdCl" units per each original ligand **1a**. Due to the neutral nature of **2a**, this implies that the ligand acts as a dianionic species. The elucidation of the bonding mode of the ligand can be easily inferred from its spectroscopic data. The IR spectrum of **2a** suggests the N-bonding of the ligand, since the absorption due to the P=N stretch appears shifted to lower wavenumbers with respect to its position in **1a** [$\Delta\nu = \nu_{complex} - \nu_{free} = -53\ cm^{-1}$]. The ^{1}H NMR spectrum of **2a** shows the symmetry of the two halves of the iminophosphorane and the presence of the palladated $Pd(C_6H_4)$ moiety. In the high field region two peaks are observed, in a 1 : 2 molar ratio, assigned to the central and terminal methylene protons, respectively. In the aromatic region, six peaks (relative intensities 2 : 1 : 4 : 2 : 4 : 1) can be easily attributed to the PPh_2 (4 : 2 : 4) and $Pd(C_6H_4)$ (2 : 1 : 1) groups. The $^{31}P\{^{1}H\}$ NMR spectrum of **2a** shows a single peak around 40 ppm. All these facts suggest that the bis-iminophosphorane acts as a bis-C,N-chelating dianionic ligand, through the iminic nitrogen and orthometallated carbon atoms, giving two *endo* palladacycles, and that it must be symmetric with respect to the central methylene carbon. The presence of a Cl^- ligand on each Pd atom should give an unsaturated dinuclear species, which completes all coordination spheres through formation of a μ-Cl bridging system and dimerization to give **2a** (Scheme 1).

Additional evidence of the presence of the chloride bridging ligands in **2a** can be obtained from its reactivity. **2a** reacts with Tl(acac) (1 : 4 molar ratio) to give the dinuclear derivative $[\{Pd(acac\text{-}O,O')\{C_6H_4(PPh_2{=}NCH_2\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2CH_2]$ (**3a**), (Scheme 1). Complex **3a** has been characterized following the same key features than those described for **2a**. Thus, the IR spectrum shows strong bands assigned to the *O*,*O*′-chelating acac ligand and the absorption due to the P=N stretch shifted to lower energies [$\Delta\nu = \nu_{complex} - \nu_{free} = -48\ cm^{-1}$]. The $^{31}P\{^{1}H\}$ NMR spectrum shows a peak around 40 ppm, as expected for an *endo* palladacycle, and the ^{1}H NMR spectrum reflects the presence of signals due to the acac ligand, the $PdC_6H_4PPh_2$ moiety and the terminal and central methylene protons.

The palladation of **1a** to give the *endo* tetranuclear complex **2a** is somewhat expected, due to the preferred metallation of the arylic Csp^2–H bonds *versus* the alkylic Csp^3–H bonds, and since only one type of phenyl ring is present. More interesting are the results obtained in the metallation of **1b** and **1c**, derived from isophthaloyl and terphthaloyl functional groups, respectively (Scheme 1). We have recently reported that the palladation of stabilized iminophosphoranes $R_3P{=}NC(O)Aryl$ occurs in a regioselective manner at the aryl ring of the benzamide unit, giving *exo* palladacycles.[9e] If **1b** is metallated with the same regioselectivity, then mononuclear derivatives with the bis-iminophosphorane acting as a NCN pincer should be expected, amongst other possibilities. In the case of **1c**, different stoichiometries can also be envisaged. The results obtained show that the orientation of the reaction is different from that expected.

The reaction of **1b** with $Pd(OAc)_2$ under the same experimental conditions than those reported for $Ph_3P{=}NC(O)Ph$ (refluxing CH_2Cl_2, 2 h)[9e] does not afford any palladated product, and unchanged **1b** is recovered at the end of the reaction time after usual workup. The same absence of palladation is obtained under different experimental conditions and/or using different Pd sources. However, the treatment of **1b** with $Pd(OAc)_2$ (1 : 2 molar

ratio) in glacial acetic acid at reflux temperature affords cleanly the tetranuclear derivative [{Pd(μ-OAc){C_6H_4(PPh_2=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,3′]$_2$ (**2b**) (Scheme 1). Complex **2b** reacts with an excess of anhydrous LiCl in MeOH to give, after metathesis of the acetate by the chloride bridging ligands, a very insoluble derivative. We were unable to characterize this solid as the corresponding chloride bridging complex due to its extreme insolubility. However, the reactivity of *in situ* prepared suspensions of this solid was the expected for the chloride bridging complex. The reaction of **2b** with an excess of LiCl in MeOH, and subsequent treatment of the suspension with Tl(acac) (1 : 4 molar ratio) gives the acetylacetonate [{Pd(acac-O,O′){C_6H_4(PPh_2=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,3′] (**3b**).

The characterization of complex **2b** shows that two metallations have been produced at the phenyl rings of the PPh_3 groups, one palladation at each phosphine of the starting compound, and that two *endo* palladacycles have been obtained. We have not observed, in the described conditions, cyclopalladation processes at the central arylic ring. Therefore, the orientation of the C–H bond activation process is, in this case, the opposite to that expected. However, we must consider that the experimental conditions of the palladation of **1b** are not the same than those reported previously for Ph_3P=NC(O)Aryl species,[9e] and also that the nature of the starting compound is different. A sensible explanation of the observed behaviour can be given taking into account these two facts. Our starting point is the high polarization of the P=N bond, which can be better considered as a P(+)–N(−) bond.[12] Due to the presence of a keto group bonded to the N atom, delocalization of the charge density through the NCO system is possible, as observed in amide functional groups. In fact, the central C_6H_4 aryl ring in **1b** has two amide substituents and, following a similar reasoning than that reported for Ph_3P=NC(O)Aryl, this ring should behave as electron rich (compared with other rings in the same molecule) due to the presence of two anionic NCO groups. Using the same argument based on charge separations, the phenyl rings bonded to the phosphonium atom should be electron poor, compared with the central ring, due to the formal positive charge located at the P atom and its deactivating nature. Now we must consider that the cyclopalladation process occurs through an electrophilic substitution on the aromatic ring, when solvents such as toluene, chloroform or even methanol are used as reaction media.[13] The importance of the solvent in the orientation of the cyclopalladation is notable, as it has been reported for imines[14] and oxazolines,[15] for which *endo* and *exo* isomers can be obtained. Other examples in which a critical role of the solvent has been reported concern the transformation between regioisomers of cyclopalladated complexes in acetic acid.[16]

All these facts are related to the different behaviour of $Pd(OAc)_2$ in solvents as $CHCl_3$ and acetic acid.[13,16,17] In chloroform $Pd(OAc)_2$ behaves as an electrophile, promoting C–H activations in electron rich aryl rings, while in acetic acid it behaves as a pseudonucleophile,[17a] and cyclopalladations in electron poor aryl rings are observed.[16,17] In our case, substrate **1b** (and, besides, **1c**) contains two types of aryl rings, namely the central ring, which should be considered as electron-rich compared with the electron-poor phosphonium phenyl rings, (see above). Therefore, an explanation of the observed orientation can be given. The orthopalladation of **1b** is performed in acetic acid, in which $Pd(OAc)_2$ behaves as a pseudonucleophile, and in this medium a C–H activation process would more likely to occur at the electron-poor ring, that is, at the phenyls of the PPh_3 groups. We believe this to be the reason for the observed orientation. A second argument can be given in favour of the obtention of *endo* isomers, and is related to the *endo* effect.[9c–f,14–16b] This effect is based on the metalloaromaticity concept,[18] and predicts a higher thermodynamic stability for cyclometallated rings containing two endocyclic conjugated double bonds (the C=C double bond and the iminic C=N bond), with respect to metallacycles without this electronic configuration. Clearly, the structure **2b**, containing two *endo* palladacycles, must show an additional stability.

The characterization of **2b** has been carried out on the basis of its analytic and spectroscopic parameters, and follows trends similar to those described for **2a** (see Experimental). The IR spectrum suggests N-bonding, since it shows the expected shift to lower energies for the band due to the P=N stretch [$\Delta\nu = \nu_{complex} - \nu_{free} = -77$ cm^{-1}], and to higher wavenumbers for that due to the carbonyl group [$\Delta\nu = \nu_{complex} - \nu_{free} = +16$ cm^{-1}] in good agreement with previous results.[9e] The $^{31}P\{^1H\}$ NMR spectrum shows clearly the incorporation of the P atom into the metallacycle, since only one signal is observed at about 52 ppm, typical region for *endo* palladacycles.[9c] The ^1H NMR spectrum of **2b** gives definitive proofs of the *endo* metallation, since signals due to the central C_6H_4 unit are clearly observed at 7.31 (H_5), 7.90 (H_4, H_6) and 10.74 (H_2) ppm. The chemical shift of the H_2 proton merits some comment, since it has undergone an important downfield shift [$\Delta\delta = \delta_{complex} - \delta_{free} = +1.41$ ppm], probably due to its location between the two carbonyl groups (Scheme 1). In fact, this shift provides structural information, since there are two components in this shift. One of them is the expected due to the high electronegativity of the oxygen atom. The other component seems to be related to the anisotropic deshielding of the C=O group for protons located on the same plane than the NC(=O) unit. The latter means that the C–H_2 bond (and the C_6H_4 core by extension) should be more or less contained on the same plane than the metallated unit [(O=C)NPC_6H_4Pd]. Besides that, four new signals assigned to the protons of the PdC_6H_4 metallated ring and peaks attibuted to the PPh_2 groups appear in the aromatic region and confirm the structure shown in Scheme 1. The fact that two sets of signals appear for the two phenyl rings of the PPh_2 moiety means that they are chemically inequivalent. An open-book structure,[15b] in which two dinuclear units [{Pd{C_6H_4(PPh_2=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,3′] are bridged by four acetate ligands accounts for these facts. The same arguments can be applied for the characterization of **3b**, with additional signals due to the acac ligand observed in the IR and ^1H NMR spectra. The signal due to H_2 in the ^1H NMR spectrum appears at 9.14 ppm, and that due to the palladated C_1 appears at 152.46 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

The reactivity of **1c** follows a similar behaviour to that described for **1b**. **1c** reacts with $Pd(OAc)_2$ (1 : 2 molar ratio) in glacial acetic acid at reflux temperature (Scheme 1) to give the tetranuclear [{Pd(μ-OAc){C_6H_4(PPh_2=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,2′]$_2$ (**2c**). Attempts to perform the orthometallation of **1c** in other solvents failed. Subsequent treatment of **2c** with excess anhydrous LiCl and Tl(acac) in MeOH gives the dinuclear acetylacetonate [{Pd(acac-*O*,*O*′){C_6H_4(PPh_2=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,2′] (**3c**). The characterization of **2c** and **3c** as *endo* derivatives has also been performed on the basis of their

analytic and spectroscopic data, and the X-ray crystal structure of **3c** has been determined.

X-Ray structure of 3c·4CHCl$_3$†

A molecular drawing of the organometallic complex is shown in Fig. 2. Table 1 collects selected bond distances and angles and parameters of data collection and structure solution and refinement are given in Table 2. The structure of **3c** shows a dinuclear complex, in which two orthometallated units [(acac)PdC$_6$H$_4$PPh$_2$NC(O)] are linked to a C$_6$H$_4$ ring in *ortho* positions through the carbonyl carbon atom. The molecule as a whole shows a notable distortion. Three main best least square planes can be defined in this molecule: (i) one plane containing the central aryl ring, defined by C25–C26–C27–C28–C29–C30; (ii) the coordination plane around Pd1, defined by Pd1–O1–O2–C6–N1; and (iii) the coordination plane around Pd2, defined by Pd2–O5–O6–C37–N2. The dihedral angles between planes (i) and (ii), and (i) and (iii) are 69.53(15)° and 64.12(14)°, respectively, while that between the two coordination planes (ii) and (iii) is 49.76(8)°. Most atoms of the organometallic fragment [(acac)PdC$_6$H$_4$PPh$_2$NC(O)] around Pd1 are located at one side of the plane (i), while the atoms of the same fragment around Pd2 are located at the other side of the plane (i). In consequence, the molecule shows pseudo-C$_2$ symmetry with respect to an imaginary axis crossing the middle points of the C25–C30 and C27–C28 bonds. This molecular arrangement is necessary in order to minimize the intramolecular interactions between fragments in ortho positions.

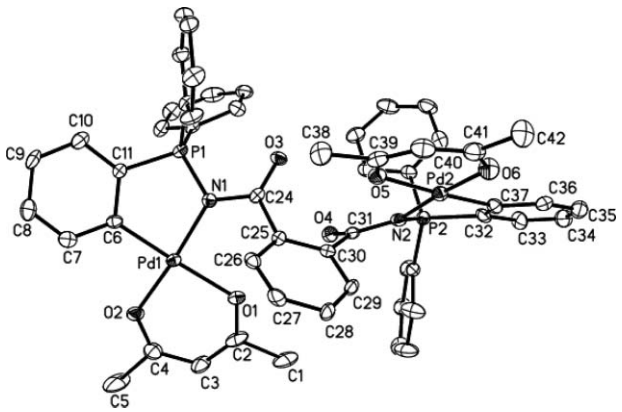


Fig. 2

Table 1 Selected bond distances [Å] and angles [°] for **3c**·4CHCl$_3$

Pd(1)–C(6)	1.970(5)	Pd(2)–C(37)	1.974(5)
Pd(1)–N(1)	2.033(4)	Pd(2)–N(2)	2.036(4)
Pd(1)–O(2)	2.005(4)	Pd(2)–O(6)	2.026(4)
Pd(1)–O(1)	2.074(4)	Pd(2)–O(5)	2.071(4)
N(1)–P(1)	1.649(4)	N(2)–P(2)	1.646(4)
C(11)–P(1)	1.777(5)	P(2)–C(32)	1.768(5)
N(1)–C(24)	1.370(6)	N(2)–C(31)	1.357(6)
C(24)–O(3)	1.221(6)	C(31)–O(4)	1.226(6)
C(24)–C(25)	1.481(7)	C(31)–C(30)	1.496(7)
O(2)–Pd(1)–O(1)	90.80(15)	O(5)–Pd(2)–O(6)	90.17(15)
O(2)–Pd(1)–C(6)	90.91(18)	O(6)–Pd(2)–C(37)	91.8(2)
C(6)–Pd(1)–N(1)	84.83(18)	C(37)–Pd(2)–N(2)	85.15(19)
N(1)–Pd(1)–O(1)	93.41(15)	N(2)–Pd(2)–O(5)	93.03(15)
C(24)–N(1)–Pd(1)	128.6(3)	C(31)–N(2)–Pd(2)	129.1(3)
P(1)–N(1)–C(24)	116.8(3)	P(2)–N(2)–C(31)	114.9(3)
Pd(1)–N(1)–P(1)	113.3(2)	Pd(2)–N(2)–P(2)	115.6(2)
N(1)–C(24)–O(3)	122.2(4)	N(2)–C(31)–O(4)	122.1(4)
O(3)–C(24)–C(25)	121.4(4)	O(4)–C(31)–C(30)	119.7(4)
N(1)–C(24)–C(25)	116.0(4)	N(2)–C(31)–C(30)	117.9(4)

Table 2 Crystallographic data for complex **3c**·4CHCl$_3$

Empirical formula	$C_{58}H_{50}Cl_{12}N_2O_6P_2Pd_2$
Formula weight	1571.14
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	15.64371(14)
b/Å	29.8167(3)
c/Å	13.64503(9)
β/°	90.1952(7)
V/Å^3	6364.60(10)
Z	4
D_{calc}/Mg m^{-3}	1.640
μ/mm^{-1}	1.169
Crystal size	0.27 × 0.17 × 0.06
Reflections collected	88744
Independent reflections	11159, R_{int} = 0.0405
Restraints/parameters	11159/0/671
R_1 [$I > 2\sigma(I)$]	0.0543
$wR2$ [$I > 2\sigma(I)$]	0.1388
R_1 [all data]	0.0615
$wR2$ [all data]	0.1432
GOF	1.022
Largest diffraction peak, hole/e Å^{-3}	1.109, −0.987
Temperature/K	100(1)
Radiation (λ)/Å	0.71073

The environment around each Pd atom can be considered as square planar, slightly distorted. Each Pd atom is surrounded by the two oxygen atoms of the acetylacetonate ligand, by the iminic nitrogen and the palladated carbon of the cyclometallated ligand. The P=N bond is endocyclic, as expected. Besides, the two organometallic fragments are very similar, as can be deduced from the comparison of respective bond distances and angles (Table 1).

The Pd–C and Pd–N bond distances found in **3c** are identical, within experimental error, to those found in related orthopalladated iminophosphoranes,[9c,d,19] and the same can be stated for the Pd–O bond distances involving the chelating acetylacetonate ligand.[20] Other internal parameters of the ligands do not deviate from published values.[21] Finally, and as it has been noted in keto-stabilized ylides,[22] the P–O intramolecular distances [2.752(4) and 2.814(4) Å] are substantially shorter than the sum of the van der Waals radii [3.32 Å],[23] while the dihedral angles P–N–C–O are −12.7(6)° and −13.5(6)°. These values suggest that intramolecular P···O contacts are also present in ketostabilized iminophosphoranes.

Conclusions

The reaction of Pd(OAc)$_2$ with bis-iminophosphoranes [Ph$_3$P=N–linker–N=PPh$_3$] (linker = aliphatic or aromatic functional group) gives *endo* palladacycles through C–H bond activation at the Ph rings of the phosphine groups in all cases. Two palladacycles are formed per each [Ph$_3$P=N–linker–N=PPh$_3$] ligand, and the dinuclear moieties rearrange giving tetranuclear complexes with acetate or chloride bridging ligands. When the linker is an aliphatic chain, CH$_2$Cl$_2$ can be used; but when the linker contains the phthaloyl functional group, acetic acid is necessary. The

palladation occurs in acetic acid with opposite orientation (*endo* complexes) with respect to that expected (*exo* derivatives by analogy with $Ph_3P{=}NC(O)aryl$, already reported). This different orientation is explained on the basis of the different behaviour of $Pd(OAc)_2$ in acetic acid (nucleophile) with respect to other solvents (an electrophile).

Experimental

Safety note

CAUTION! The organic azides are *highly hazardous* materials which can explode, and whose preparation and manipulation must be carried out with great caution. They must be stored at low temperature ($T \approx 0$ °C) and dissolved in an inert solvent.[11]

General methods

Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from nujol mulls between polyethylene sheets. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 or dmso-d_6 solutions at 25 °C (other temperatures were specified) on Bruker ARX-300, AvanceII-300, Avance-400 and Avance-500 spectrometers (δ, ppm; J, Hz); ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard while $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). The ^1H SELNO-1D and SELRO-1D NMR experiments were performed with optimized mixing times (D8/P15), depending of the irradiated signal. ESI/APCI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Other MS (FAB+) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. The bis-azides $N_3CH_2CH_2CH_2N_3$, $[C_6H_4(C(O)N{=}PPh_3)_2\text{-}1,3]$ and $[C_6H_4(C(O)N{=}PPh_3)_2\text{-}1,2]$ were prepared according to the literature.[11]

$[Ph_3P{=}NCH_2CH_2CH_2N{=}PPh_3]$ (1a)

Staudinger method:[10] To a solution of $N_3CH_2CH_2CH_2N_3$ (0.500 g, 3.96 mmol) in freshly distilled CH_2Cl_2 (20 mL), a solution of PPh_3 (2.07 g, 7.92 mmol) in CH_2Cl_2 (20 mL) was added dropwise. The addition was completed in 30 min, and during this time the evolution of N_2 was evident. The resulting solution was stirred at room temperature for 16 h, until the evolution of N_2 ceased. Then, the solvent was evaporated to dryness, giving **1a** as a white solid. The compound can be used in subsequent reactions without further purification. Yield: 1.58 g (66.9%). Anal. calc. for $C_{39}H_{36}N_2P_2$ (594.7): C, 78.77; H, 6.10; N, 4.71. Found: C, 78.05; H, 6.59; N, 4.65. IR (ν, cm^{-1}): 1310 (ν_{PN}). MS (FAB+) [m/z, (%)]: 595 (100) $[M + H]^+$. ^1H NMR ($CDCl_3$): $\delta = 1.89$ (q, 2H, $^3J_{HH} = 7.2$, CH_2), 3.13 (m, 4H, NCH_2), 7.36 (m, 12H, H_m, PPh_3), 7.45 (m, 6H, H_p, PPh_3), 7.58 (m, 12H, H_o, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 40.56 (CH_2), 44.08 (d, $^2J_{PC} = 5.1$, NCH_2), 128.34 (d, $^3J_{PC} = 11.5$, C_m, PPh_3), 131.25 (d, $^1J_{PC} = 96.4$, C_i, PPh_3), 131.25 (d, $^4J_{PC} =$ 2.4, C_p, PPh_3), 132.58 (d, $^2J_{PC} = 9.0$, C_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.18$.

$[\{Pd(\mu\text{-}Cl)\{C_6H_4(PPh_2{=}NCH_2\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2CH_2]_2$ (2a)

To a solution of **1a** (0.400 g, 0.672 mmol) in CH_2Cl_2 (20 mL), $Pd(OAc)_2$ (0.301 g, 1.344 mmol) was added, and the resulting mixture was refluxed for 1.3 h. After the reaction is completed, the cooled black suspension (presence of Pd^0) was treated with charcoal (15 min) and filtered through Celite giving an orange solution. This solution, which contains the acetate bridge intermediate, was evaporated to dryness. The orange residue was dissolved in MeOH (10 mL) and treated with an excess of anhydrous LiCl (0.100 g, 2.38 mmol) to give **2a** as a yellow solid. Yield: 0.263 g (44.7%). Anal. calc. for $C_{78}H_{68}Cl_4N_4P_4Pd_4$ (1752.9): C, 53.40; H, 3.91; N, 3.19. Found: C, 53.21; H, 3.86; N, 3.12. IR (ν, cm^{-1}): 1257 (ν_{PN}). MS (MALDI+) [m/z, (%)]: 699 (30) $[M_4/2\text{–}2Cl\text{–}Pd]^+$. ^1H NMR ($CDCl_3$): $\delta = 1.76$ (s, br, 1H, CH_2), 3.04 (dt, 2H, $^3J_{HH} = 4.8$, $^3J_{PH} =$ 13.8, NCH_2), 6.89–6.95 (m, 2H, C_6H_4), 7.18–7.23 (m, 1H, C_6H_4), 7.45 (m, 4H, H_m, PPh_2), 7.53 (m, 2H, H_p, PPh_2), 7.74 (m, 4H, H_o, PPh_2), 7.92 (d, 1H, $^3J_{HH} = 7.5$, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 39.55$.

$[\{Pd(acac)\{C_6H_4(PPh_2{=}NCH_2\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2CH_2]$ (3a)

To a solution of **2a** (0.147 g, 0.084 mmol) was added Tl(acac) (0.102 g, 0.336 mmol). The resulting suspension was stirred at room temperature for 30 min, and then filtered through Celite. The clear yellow solution was evaporated to dryness and the residue treated with cold *n*-hexane (10 mL). By subsequent stirring, **3a** was obtained as a pale yellow solid. Yield: 0.131 g (77.5%). Anal. calc. for $C_{49}H_{48}N_2O_4P_2Pd_2$ (1003.7): C, 58.63; H, 4.82; N, 2.79. Found: C, 58.64; H, 4.65; N, 3.33. IR (ν, cm^{-1}): 1584 (ν_{CO}, acac), 1514 (ν_{CO}, acac), 1262 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 903 (45) $[M\text{–acac}]^+$. ^1H NMR ($CDCl_3$): $\delta = 1.37$ (s, 3H, Me, acac), 1.61 (m, 1H, CH_2), 2.02 (s, 3H, Me, acac), 2.41 (m, 2H, NCH_2), 5.20 (s, 1H, CH, acac), 6.86 (t, 1H, $^3J_{HH} = 8.5$, C_6H_4), 6.97 (m, 1H, C_6H_4), 7.21 (m, 1H, C_6H_4), 7.41 (m, 4H, H_m, PPh_2), 7.53–7.63 (m, 6H, $4H_o + 2H_p$, PPh_2), 7.68 (d, 1H, $^3J_{HH} = 7.3$, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 39.90$.

$[C_6H_4(C(O)N{=}PPh_3)_2\text{-}1,3]$ (1b)

Compound **1b** was prepared following the Staudinger method,[10] as described for **1a**. Isophthaloyl bis-azide $[C_6H_4(C(O)N_3)_2\text{-}1,3]$ (0.844 g, 4.46 mmol) was reacted with PPh_3 (2.34 g, 8.92 mmol) in dry CH_2Cl_2 (40 mL) to give **1b** as a white solid. Yield: 3.002 g (100%). Anal. calc. for $C_{44}H_{34}N_2O_2P_2$ (684.3): C, 77.16; H, 5.00; N, 4.09. Found: C, 76.90; H, 4.92; N, 3.82. IR (ν, cm^{-1}): 1599 (ν_{CO}), 1353 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 685 (20) $[M + H]^+$. ^1H NMR ($CDCl_3$): $\delta = 7.42$ (t, 1H, $^3J_{HH} = 7.6$, H_5, C_6H_4), 7.46 (dt, 12H, $^4J_{PH} = 3.0$, $^3J_{HH} = 7.5$, H_m, PPh_3), 7.55 (m, 6H, H_p, PPh_3), 7.80 (dd, 12H, $^3J_{PH} = 12.3$, $^3J_{HH} = 7.4$, H_o, PPh_3), 8.39 (dd, 2H, $^5J_{PH} =$ 1.3, $^3J_{HH} = 7.6$, H_4, H_6, C_4H_4), 9.33 (s, 1H, H_2, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 127.06$ (C_6H_4), 128.40 (d, $^1J_{PC} = 99.4$, C_i, PPh_3), 128.60 (d, $^3J_{PC} = 12.2$, C_m, PPh_3), 130.65 (C_6H_4), 131.90 (C_6H_4), 132.06 (d, $^4J_{PC} = 2.5$, C_p, PPh_3), 133.16 (d, $^2J_{PC} = 9.9$, C_o, PPh_3), 138.11 (d, $^3J_{PC} = 20.5$, C_1, C_3, C_6H_4), 176.47 (d, $^2J_{PC} = 8.0$, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.05$.

$[\{Pd(\mu\text{-}OAc)\{C_6H_4(PPh_2{=}NC(O)\text{-}\kappa\text{-}C,N)\text{-}2\}\}_2C_6H_4\text{-}1',3']_2$ (2b)

To a solution of $Pd(OAc)_2$ (0.262 g, 1.160 mmol) in glacial acetic acid (15 mL) was added compound **1b** (0.400 g, 0.584 mmol) and

the resulting solution was refluxed for 1h. The resulting black suspension was filtered through Celite (removal of Pd^0) and the orange solution was evaporated to small volume (≈ 2 mL). By addition of Et_2O (25 mL) and subsequent stirring, **2b** precipitated as a yellow solid, which was filtered, washed with additional Et_2O (40 mL) and dried *in vacuo*. Yield: 0.313 g (55.4%). Anal. calc. for $C_{96}H_{76}N_4O_{12}P_4Pd_4$ (2026.3): C, 56.85; H, 3.78; N, 2.76. Found: C, 56.60; H, 3.79; N, 2.99. IR (ν, cm^{-1}): 1615 ($\nu_{C=O}$), 1580 ($\nu_{C=O}$), 1559 ($\nu_{C=O}$), 1276 ($\nu_{P=N}$). MS (FAB+) [*m*/*z*, (%)]: 789 (40) [M/2-Pd-2OAc]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 1.16$ (s, 3H, OAc), 2.12 (s, 3H, OAc), 6.92 (m, 2H, PdC_6H_4), 7.05 (m, 2H, PdC_6H_4), 7.21 (m, 2H, PdC_6H_4), 7.29–7.33 (m, 3H, 2H (PdC_6H_4) + H_5 (C_6H_4)), 7.41–7.48 (m, 6H, $4H_m$ + $2H_p$, PPh_2), 7.55 (m, 2H, H_p, PPh_2), 7.63 (m, 4H, H_m, PPh_2), 7.71 (m, 4H, H_o, PPh_2), 7.90 (dd, 2H, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.7$, H_4, H_6, C_6H_4), 8.26 (m, 4H, H_o, PPh_2), 10.74 (m, 1H, H_2, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.41$.

[{Pd(acac){$C_6H_4(PPh_2$=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,3′] (3b)

To a solution of **2b** (0.313 g, 0.159 mmol) in MeOH (20 mL), was added an excess of anhydrous LiCl (0.210 g, 5.0 mmol). The resulting yellow suspension was stirred for 30 min (rt) and then Tl(acac) (0.193 g, 0.636 mmol) was added. The suspension changed its colour and the resulting pale yellow suspension was stirred for 30 additional min (rt). The solvent was evaporated to dryness and the residue was extracted with CH_2Cl_2 (2 × 15 mL). The combined extracts were evaporated to dryness and the oily residue was treated with cold *n*-pentane (20 mL), giving **3b** as a yellow solid. Yield: 0.200 g (57.2%). Anal. calc. for $C_{54}H_{46}N_2O_6P_2Pd_2$ (1093.7): C, 59.27; H, 4.24; N, 2.56. Found: C, 58.97; H, 4.45; N, 2.73. IR (ν, cm^{-1}): 1615 (ν_{CO}), 1583 (ν_{CO}, acac), 1514 (ν_{CO}, acac), 1299 ($\nu_{P=N}$). MS (FAB+) [*m*/*z*, (%)]: 995 (35) [M–acac]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 1.02$ (s, 6H, Me, acac), 1.88 (m, 6H, Me, acac), 4.95 (s, 2H, CH, acac), 6.88 (m, 2H, PdC_6H_4), 7.04 (m, 2H, PdC_6H_4), 7.23–7.28 (m, 3H, 2H (PdC_6H_4) + H_5 (C_6H_4)), 7.45 (m, 8H, H_m, PPh_2), 7.55 (m, 4H, H_p, PPh_2), 7.64 (d, 2H, $^3J_{HH} = 8.0$, PdC_6H_4), 7.88 (m, 8H, H_o, PPh_2), 8.42 (dd, 2H, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.7$, H_4, H_6, C_6H_4), 9.14 (t, 1H, $^4J_{HH} = 1.4$, H_2, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 26.55$ (Me, acac), 27.29 (Me, acac), 99.65 (CH, acac), 124.56 (d, $J_{PC} = 13.9$, PdC_6H_4), 125.63 (C_5, C_6H_4), 126.44 (d, $^1J_{PC} = 13.9$, C_i, PPh_2), 128.80 (d, $^3J_{PC} = 12.6$, C_m, PPh_2), 129.16 (PdC_6H_4), 130.21 (d, $J_{PC} = 2.5$, PdC_6H_4), 130.76 (C_2, C_6H_4), 132.02 (C_4, C_6, C_6H_4), 132.40 (d, $J_{PC} = 14.2$, PdC_6H_4), 132.79 (d, $^4J_{PC} = 2.5$, C_p, PPh_2), 133.56 (d, $^2J_{PC} = 10.9$, C_o, PPh_2), 135.41 (d, $^1J_{PC} = 131.5$, C_2, PdC_6H_4), 136.51 (d, $^3J_{PC} = 11.9$, C_1, C_3, C_6H_4), 152.46 (d, $^2J_{PC} = 19.5$, C_1, PdC_6H_4), 178.94 (d, $^2J_{PC} = 5.9$, CO), 184.37 (CO, acac), 187.56 (CO, acac). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 50.98$.

[C_6H_4(C(O)N=PPh_3)$_2$-1,2 (1c)

Compound **1c** was prepared following the Staudinger method,[10] as described for **1a**. Phthaloyl bis-azide [$C_6H_4(C(O)N_3)_2$-1,2] (1.00 g, 4.62 mmol) was reacted with PPh_3 (2.42 g, 9.25 mmol) in dry CH_2Cl_2 (40 mL) to give **1c** as a white solid. Yield: 2.11 g (72.5%). Anal. calc. for $C_{44}H_{34}N_2O_2P_2$ (684.3): C, 77.16; H, 5.00; N, 4.09. Found: C, 77.30; H, 4.92; N, 3.82. IR (ν, cm^{-1}): 1580 (ν_{CO}), 1346 ($\nu_{P=N}$). MS (FAB+) [*m*/*z*, (%)]: 685 (45) [M + H]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 7.18$ (m, 12H, H_m, PPh_3) 7.32 (dt, 6H, $^5J_{PH} = 1.2$, $^3J_{HH} = 7.1$, H_p, PPh_3), 7.39 (m, 2H, H_4, H_5, C_6H_4), 7.63 (m, 2H, H_3, H_6, C_6H_4), 7.68 (m, 12H, H_o, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 127.98$ (C_3, C_6, C_6H_4), 128.12 (C_4, C_5, C_6H_4) 128.34 (d, $^3J_{PC} = 12.3$, C_m, PPh_3), 128.59 (d, $^1J_{PC} = 99.8$, C_i, PPh_3), 131.74 (d, $^4J_{PC} = 2.8$, C_p, PPh_3), 133.44 (d, $^2J_{PC} = 9.9$, C_o, PPh_3), 141.05 (d, $^3J_{PC} = 20.8$, C_1, C_2, C_6H_4), 180.00 (d, $^2J_{PC} = 8.6$, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.85$.

[{Pd(μ-OAc){$C_6H_4(PPh_2$=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,2′]$_2$ (2c)

Complex **2c** was prepared following a synthetic procedure similar to that described for **2b**. Therefore $Pd(OAc)_2$ (0.131 g, 0.583 mmol) was reacted with **1c** (0.200 g, 0.291 mmol) in glacial acetic acid (20 mL) to give **2c** as a yellow solid. Yield: 0.236 g (80.0%). Anal. calc. for $C_{96}H_{76}N_4O_{12}P_4Pd_4$ (2026.3): C, 56.85; H, 3.78; N, 2.76. Found: C, 56.99; H, 4.21; N, 2.66. IR (ν, cm^{-1}): 1614 ($\nu_{C=O}$), 1583 ($\nu_{C=O}$), 1558 ($\nu_{C=O}$), 1275 ($\nu_{P=N}$). MS (FAB+) [*m*/*z*, (%)]: 954 (30) [M/2-OAc]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (s, 3H, OAc), 2.17 (s, 3H, OAc), 6.76 (m, 2H, PdC_6H_4), 7.02–7.09 (m, 14H, $4H_o$, $4H_m$, $2H_p$ (PPh_2) + 4H (PdC_6H_4)), 7.27 (m, 2H, PdC_6H_4), 7.32 (dd, 2H, $^3J_{HH} = 6.0$, $^4J_{HH} = 3.0$, C_6H_4), 7.39 (dd, 2H, $^3J_{HH} = 5.7$, $^4J_{HH} = 3.1$, C_6H_4), 7.67 (m, 4H, H_m, PPh_2), 7.76 (m, 2H, H_p, PPh_2), 8.11 (m, 4H, H_o, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.32$ (Me, OAc), 24.28 (Me, OAc), 124.43 (d, $J_{PC} = 11.0$, PdC_6H_4), 126.31 (d, $^1J_{PC} = 74.0$, C_i, PPh_2), 126.62 (d, $^1J_{PC} = 71.1$, C_i, PPh_2), 128.40 (d, $^3J_{PC} = 10.0$, C_m, PPh_2), 128.67 (C_6H_4), 128.98 (C_6H_4), 129.18 (d, $^3J_{PC} = 10.0$, C_m, PPh_2), 130.19 (d, $^4J_{PC} = 3.0$, C_p, PPh_2), 131.95 (d, $J_{PC} = 5.0$, PdC_6H_4), 133.23 (d, $^2J_{PC} = 9.8$, C_o, PPh_2) 133.41 (m, C_p, C_o, PPh_2), 134.39 (d, $J_{PC} = 11.0$, PdC_6H_4), 136.16 (d, $^3J_{PC} = 9.0$, C_1, C_2, C_6H_4), 148.13 (d, $^2J_{PC} = 16.0$, C_1, PdC_6H_4), 177.99 (CO), 181.64 (CO, OAc), 181.96 (CO, OAc). Signals due to two C atoms of the PdC_6H_4 unit were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 53.05$.

[{Pd(acac){$C_6H_4(PPh_2$=NC(O)-κ-C,N)-2}}$_2C_6H_4$-1′,2′] (3c)

Complex **3c** was prepared following a synthetic procedure similar to that described for **3b**. Therefore **2c** (0.240 g, 0.122 mmol) was reacted with LiCl (0.210 g, 5.0 mmol) in methanol (20 mL) and with Tl(acac) (0.148 g, 0.490 mmol) to give **3c** as a yellow solid. Yield: 0.136 g (50.7%). **3c** was recrystallized from CH_2Cl_2–Et_2O, giving yellow crystals of **3c**·0.5CH_2Cl_2, which were used for analytic and spectroscopic purposes. However, they were not useful for X-ray purposes (see below). Anal. calc. for [$C_{54}H_{46}N_2O_6P_2Pd_2$]0.5$CH_2Cl_2$ (1136.2): C, 57.61; H, 4.17; N, 2.46. Found: C, 57.12; H, 4.11; N, 2.52. IR (ν, cm^{-1}): 1633 (ν_{CO}), 1588 (ν_{CO}, acac), 1512 (ν_{CO}, acac), 1300 ($\nu_{P=N}$). MS (FAB+) [*m*/*z*, (%)]: 995 (100) [M–acac]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 0.89$ (s, 6H, Me, acac), 1.89 (m, 6H, Me, acac), 4.94 (s, 2H, CH, acac), 6.89 (m, 2H, PdC_6H_4), 7.04 (m, 2H, PdC_6H_4), 7.23–7.27 (m, 4H, 2H (PdC_6H_4) + H_4, H_5 (C_6H_4)), 7.39 (m, 8H, H_m, PPh_2), 7.52 (m, 4H, H_p, PPh_2), 7.69 (d, 2H, $^3J_{HH} = 8.0$, PdC_6H_4), 7.90 (s, broad, 8H, H_o, PPh_2), 8.25 (dd, 2H, $^3J_{HH} = 5.6$, $^4J_{HH} = 3.3$, H_3, H_6, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 25.92$ (Me, acac), 27.16 (Me, acac), 99.42 (CH, acac), 124.42 (d, $^3J_{PC} = 13.7$, PdC_6H_4), 127.89 (C_4, C_5, C_6H_4), 128.66 (d, $^3J_{PC} = 12.7$, C_m, PPh_2), 129.31 (d, $^2J_{PC} = 20.4$, PdC_6H_4), 130.14 (d, $^4J_{PC} = 2.9$, PdC_6H_4), 132.25 (d, $^3J_{PC} = 14.3$, PdC_6H_4), 132.43 (d, $^4J_{PC} = 2.8$, C_p, PPh_2), 133.56 (d, $^2J_{PC} = 10.2$, C_o, PPh_2), 135.61 (d, $^1J_{PC} = 130.7$, C_2, PdC_6H_4), 139.82 (d, $^3J_{PC} = 12.4$, C_1, C_2, C_6H_4),

152.18 (d, $^2J_{PC}$ = 20.9, C_1, PdC_6H_4), 178.94 (d, $^2J_{PC}$ = 5.7, CO), 183.75 (CO, acac), 187.49 (CO, acac). Peaks of C_3 and C_6 were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 53.59.

Crystal structure determination of complex 3c·4CHCl$_3$†

Crystals of adequate quality for X-ray measurements were grown by vapour diffusion of Et_2O into a $CHCl_3$ solution of the crude product at room temperature. A single crystal was mounted at the end of a quartz fiber in a random orientation, covered with magic oil and placed under the cold stream of nitrogen. Data collection was performed at 100(1) K on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected based on three ω-scan and ϕ-scan runs. The diffraction frames were integrated using the program CrysAlis RED[24] and the integrated intensities were corrected for absorption with SADABS.[25] The structures were solved and developed by direct methods.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. The 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 structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[27] **3c** crystallizes with four molecules of solvent per dimeric organometallic unit. Two of the $CHCl_3$ sites were found to be severely disordered—so resistant to attempts to establish an acceptable atomic model, that we decided to employ PLATON SQUEEZE[28] to remove the influence of these sites form the data. *N.b.*, the values we report for stoichiometric quantities, D_c, F_{000}, *etc.*, are based on the full content of the crystal-that is, using all four molecules of $CHCl_3$. CCDC reference number 668605.

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