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Synthesis and characterization of Pd^{II} complexes containing cyclic bis-ylides

Larry R. Falvello, Marina E. Margalejo, Rafael Navarro*, Esteban P. Urriolabeitia

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, E-50009 Zaragoza, Spain

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Dedicated in honor of Professor R. Usón

Abstract

The reaction of Ph₂PCH₂PPh₂ (dppm) with ClCH₂C(O)CH₂Cl (1:1 molar ratio) in refluxing CHCl₃ gives the new ylidephosphonium salt **1**, through quaternization of the two P atoms of the dppm and spontaneous loss of HCl. Compound **1** reacts with NEt₃ in CHCl₃ or CH₂Cl₂ solution (1:1 molar ratio) giving a mixture of the bis-ylide compound **2a** and the ylide-methanide **2b** (molar ratio **2a**:2**b** = 1:2). This mixture (prepared in situ) reacts with PdCl₂(NCMe)₂ to give the corresponding dichloride(bis-ylide) complex **3a** (coordination through the two ylidic carbons) and the dichloride(ylide-methanide) complex **3b** (coordination through the ylide carbon and the methanide carbon), in a molar ratio **3a**:3**b** = 1:2. The reaction of the mixture **3a**:3**b** with AgClO₄ (1:2 molar ratio, NCMe or Me₂CO) in the presence of neutral ligands L gives the corresponding mixtures of the dicatoinci complexes [Pd(L)₂(C,C-bis-ylide)](ClO₄)₂ (**4a**, L = NCMe; **5a**, L = pyridine) and [Pd(L)₂(C,C-ylide-methanide)](ClO₄)₂ (**4b**, L = NCMe; **5b**, L = pyridine) (molar ratio **4a**:4**b** = 1:2; molar ratio **5a**:5**b** = 3:1). On the other hand, the reaction of Ph₂PCH₂PPh₂ (dppm) with ClCH₂C(=CH₂)CH₂Cl (1:1 molar ratio) in refluxing ClCH₂CH₂Cl gives the bis-phosphonium salt **6**. This salt reacts with Li^tBu and PdCl₂(NCMe)₂ (1:2.2:1 molar ratio) in THF affording the ylide-methanide complex **7**. The crystal structures of complexes **3b**·3dmso and **7**·CHCl₃ have been determined by X-ray diffraction.

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1. Introduction

The coordination chemistry of phosphorus ylides $R_3P = CR'R''$ (R, R', R'' = alkyl, aryl, acyl, etc.) towards transition metals is now a well established research area in organometallic chemistry [1–3]. However, the synthesis of cyclic P-ylides or bis-ylides, and the study of their complexation to transition metals, is a less documented field; and very few examples have been reported in the literature [4–9], in spite of their practical importance [10–12].

As part of our ongoing research into α -stabilized ylides [13], we have undertaken the synthesis of new cyclic, stabilized ylides and bis-ylides through quaternization of the two P atoms of bis(diphenylphosphino)methane $[Ph_2PCH_2PPh_2 = dppm]$ with 1,3-dihalo derivatives (e.g. 1,3-dichloroacetone). In this way, we have been able to obtain the new cyclic, six-membered phosphonium-ylide 1 [(1,1,3,3,-tetraphenyl- $1\lambda^5, 3\lambda^5$ -1phosphonia-3-phosphorane-cyclohex-3-en-5-one)chloride]. We have also studied its reactivity towards deprotonating reagents and towards simple Pd(II) precursors. In addition, we have also studied the reactivity, with Pd(II) precursors, of the cyclic ylide-methanide [5methyl-1,1,3,3-tetraphenyl- $1\lambda^5$, $3\lambda^5$ -diphosphabenzene] [5a]. In the present contribution we report the results obtained.

^{*} Corresponding author. *E-mail addresses:* rafanava@posta.unizar.es (R. Navarro),

esteban@posta.unizar.es (E.P. Urriolabeitia).

2. Results and discussion

The reaction of dppm with 1,3-dichloroacetone for 12 h (1:1 molar ratio) in deoxygenated CHCl₃ at reflux temperature gives the cyclic ylide-phosphonium salt 1 (see Scheme 1) in good yield as a white solid, insoluble in most common organic solvents. The reaction occurs with quaternization of the two P atoms of the dppm moiety and spontaneous loss of HCl. The IR spectrum of 1 shows two intense absorptions at 1587 and 1568 cm^{-1} , showing the typical shift to low energy of a carbonyl group in resonance with an ylide function. This shift is frequently found in α -stabilized vlides Ph₃P= C(H)C(O)R [1-3,13]. The simultaneous presence of an ylide unit and a phosphonium moiety is clearly inferred from the NMR spectra of 1. The ¹H NMR spectrum of 1 shows, in addition to the aromatic resonances, three signals centered at 6.20 (t), 5.82 (d) and 5.10 ppm (d) of relative intensity 2:1:2; these resonances are attributed, respectively, to the PCH₂P, P=CH and PCH₂CO



Scheme 1.

protons. The ¹³C{¹H} NMR spectrum (APT: attached proton test) of 1 shows the carbonyl resonance at 170.1 ppm (negative phase), and the resonances attributed to the P=C(H), PCH_2 and PCH_2P carbons at, respectively, 70.0 ppm (dd, ${}^{1}J_{PC} = 103$ Hz, ${}^{3}J_{PC} = 9.5$ Hz, positive phase), 23.3 ppm (d, ${}^{1}J_{PC} = 46.6$ Hz, negative phase) and 12.3 (t, ${}^{1}J_{PC} = 45.4$ Hz, negative phase). The positions of the resonances, the respective values of the coupling constants ${}^{1}J_{PC}$ and the sign of the phase signal in the APT spectrum allows an unambiguous identification of all functional groups present in 1. Finally, the ${}^{31}P{}^{1}H{}$ NMR spectrum of 1 shows two broad resonances, centered at 18.4 and at 9.3 ppm, and attributed to the PCH₂ and P=C(H) groups, respectively. This attribution has been confirmed by ${}^{1}H{}^{31}P{}$ NMR measurements.

The synthesis of 1 merits comment. This facile process contrasts with that described for the related, acyclic, bisphosphonium salt [Ph₃PCH₂C(O)CH₂PPh₃]Cl₂, which must be performed with longer reaction times (up to 20 h) and in the presence of a huge excess of PPh₃ (molar ratio $PPh_3:1,3$ -dichloroacetone = 20:1) [14,15]. Probably, this very different behavior can be due to a greater stabilization of the six-membered structure in 1 by cyclization, compared with the acyclic structure. Moreover, it is surprising to observe the spontaneous loss of HCl in the synthesis of 1 under relatively mild conditions (CHCl₃, reflux, 12 h). We have reported a similar (loss of HCl) in the treatment result of $[Ph_3PCH_2C(O)CH_2PPh_3]Cl_2$, but under quite harsh conditions (refluxing 2-methoxyethanol, 22 h) [16], and with the difference that the amount of the corresponding ylide-phosphonium salt [Ph₃P=CHC(O)CH₂PPh₃]Cl obtained is just at trace level.

Compound 1 still presents two activated methylene groups, susceptible to deprotonation by an external base. When a suspension of 1 (CH₂Cl₂) was treated with a stoichiometric amount of NEt₃ (molar ratio 1:1), a clear colorless solution was obtained in a few seconds (see Scheme 1). The reaction was monitored by NMR (performed in CDCl₃ or CD₂Cl₂); and the ¹H NMR spectrum shows that the cation [HNEt₃]Cl is present in solution, indicating that deprotonation has taken place. In addition, two new species (2a and 2b), in 1/2 molar ratio, have been formed. The ³¹P{¹H} NMR spectrum of this solution shows three different signals, an AB spin system (doublets centered at 16.6 and 11.4 ppm; ${}^{2}J_{PP} =$ 38.4 Hz) and a singlet resonance at 8.9 ppm (relative intensity 1:1:1); no resonances attributed to the starting product 1 were found. The singlet resonance at 8.9 ppm is assigned to the new symmetric bis-ylide 2a (Scheme 1), due to the similarity of its chemical shift with that found for the ylide P atom in 1 (9.3 ppm), and which is formed by deprotonation of the methylene adjacent to the carbonyl group in 1. The AB spin system is assigned to the asymmetric ylide-methanide 2b, formed by

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deprotonation of the CH_2 group located between the two P atoms, and for which the resonance at 11.4 ppm is attributed to the ylide P atom [P=CHC(O)] while the signal at 16.6 ppm is assigned to the methanide P atom [$CH=PCH_2$].

The ¹H NMR spectrum shows resonances corresponding to the mixture **2a**:**2b** (1/2 molar ratio). For compound **2b**, the ylide proton P=C(H) appears at 3.85 ppm (d, ²J_{PH} = 12.6 Hz), the methanide proton P=C(H)-P at 3.36 ppm (dd, ²J_{PH} = 14.4 Hz, ²J_{PH} = 2.4 Hz), and the methylene protons PCH₂ at 3.18 ppm (d, ²J_{PH} = 12.0 Hz). For compound **2a**, the ylide protons P=C(H) appear at 3.73 ppm (d, ²J_{PH} = 25.8 Hz), while the resonance attributed to the PCH₂P protons is not observed, probably hidden by the signals of the protons of the [HNEt₃]⁺ cation.

Unfortunately, all attempts to isolate the compounds 2a and 2b in pure form from the reaction mixture were unsuccessful, since the product was always contaminated with ammonium salts. The same results were obtained when other classical deprotonating reagents, such as 1,8-bis(dimethylamino)naphthalene or other amines were employed. The use of Tl(acac) (acac = acetylacetonate), which allows the synthesis of the phosphonium-ylide [Ph₃P=CHC(O)CH₂PPh₃]ClO₄ starting from the bis-phosphonium salt $[Ph_3PCH_2C(O)CH_2PPh_3](ClO_4)_2$ [17], Ag(OOCCH_3), or hard bases (NaH, LiⁿBu) also fails to provide a satisfactory synthetic method to isolate the mixture 2a/ **2b** from the side products of the reaction. In our hands, the reaction with NEt₃ is the best choice for generating the 2a/2b mixture, and this can be used in situ.

Thus, the reaction of 1 with NEt₃ in CH₂Cl₂, followed by addition of PdCl₂(NCMe)₂ (1:1:1 molar ratio) to the colorless solution of the mixture 2a/2b produces an orange solution, from which product 3 precipitates as a yellow solid (see Scheme 1). The presence of two cischloride ligands can be inferred from the IR spectrum of 3, which shows two absorptions at 302 and 290 cm⁻¹, and the presence of coordinated ylide is inferred from the observation of a strong absorption at 1635 cm^{-1} , shifted to higher energies when compared with compound 1. Further spectroscopic characterization of 3 shows that it is actually a mixture of the symmetric complex 3a (generated by coordination of the two ylidic carbons of the bis-ylide 2a) and the asymmetric complex **3b** (a result of the coordination of the ylide and the methanide carbon atoms of 2b), in 1:2 molar ratio, the same ratio as that observed for compounds 2a and 2b.

The C,C-coordination of the bis-ylide in complex **3a** produces a loss of symmetry in the ylide, as reflected in the ¹H NMR spectrum of **3a**; the PC H_2 P protons appear at 5.54 and 5.34 ppm as an AB spin system—and split by coupling with the two chemically equivalent P atoms—while the ylidic protons are still chemically equivalent and appear as a broad singlet resonance at

4.05 ppm. Moreover, for compound **3b**, the ¹H NMR spectrum shows four different signals corresponding to the four chemically inequivalent protons of the different functional groups: (i) the PCH₂CO protons appear as an AB spin system coupled with ³¹P at very different chemical shifts (4.62 and 3.34 ppm); (ii) the methanide proton P₂C(H)Pd appears at 4.26 ppm as a triplet; (iii) the ylide proton PC(H)Pd appears at 3.64 ppm as a doublet.

The different natures of the carbon atoms in 3a and **3b** can be clearly distinguished in the ${}^{13}C{}^{1}H{}$ (APT) NMR spectrum of the mixture 3a/3b. Two resonances with negative phase are attributed to two methylene groups—the resonance at 32.6 ppm (d, ${}^{1}J_{PC} = 51$ Hz) to the PCH_2CO carbon of **3b** and the resonance at 22.4 (t, ${}^{1}J_{PC} = 52.9$ Hz) to the P₂CH₂ cabon atom of **3a**. And three signals with positive phase are assigned to the three types of coordinated CH atoms-a doublet at 30.7 ppm (${}^{1}J_{PC} = 53.1$ Hz) to the ylidic carbon atom in **3a**, another doublet at 20.9 ppm (${}^{1}J_{PC} = 54.9$ Hz) to the ylide carbon in **3b** and the triplet appearing at -13.4ppm (${}^{1}J_{PC} = 38.9$ Hz) to the methanide carbon atom, also in **3b**. As expected, the ${}^{31}P{}^{1}H{}$ NMR spectrum of **3** shows a singlet resonance for 3a, centered at 18.4 ppm, and an AB spin system for **3b** (8.8 and 7.7 ppm, ${}^{2}J_{PP} =$ 11.3 Hz). The molecular structure of 3b·3dmso has been determined by X-ray diffraction, and provides further structural characterization (see below).

Each of the components of the mixture 3a/3b seems to be quite robust, since the mixture does not show any noticeable signs of decomposition or evolution after treatment in refluxing 2-methoxyethanol for 24 h; and, moreover, the composition of the mixture remains virtually constant (3a:3b = 1:2). On the other hand, each complex, 3a and 3b, contains an activated methvlene group (3a between the two P atoms and 3b adjacent to the carbonyl unit) which, in principle, can be deprotonated. We have studied the reactivity of the mixture (3a:3b) towards some deprotonating reagents, such as (acac)AuPPh₃ and Hg(OOCCH₃)₂ (both reagents gave a very interesting reactivity in orthometallated ylides containing a phosphonium functionality) [18], but in both cases mixtures of the starting compounds were recovered.

More successful were the substitution reactions of the chloride ligands by neutral ligands L. The mixture **3a:3b** reacts with AgClO₄ (1:2 molar ratio) in NCMe to give the corresponding dicationic complexes [Pd-(NCMe)₂(bis-ylide)](ClO₄)₂ **4a** and [Pd(NCMe)₂(ylide-methanide)](ClO₄)₂ **4b** (Scheme 1). The molar ratio **4a:4b** was 1:2 (see Experimental). In the same way, the reaction of **3a:3b** with AgClO₄ (1:2 molar ratio) in acetone and, after filtration of the AgCl, further treatment of the resulting solution with pyridine (excess), afford a mixture of the complexes [Pd(py)₂(bis-ylide)](ClO₄)₂ **5a** and [Pd(py)₂(ylide-methanide)](ClO₄)₂

5b (Scheme 1). In this case the molar ratio obtained is 5a:5b = 3:1.

The characterization of the mixtures 4a:4b and 5a:5b has been carried out by analytical and spectroscopic methods. The IR spectrum of 4a:4b shows absorptions due to the NCMe ligands (2324, 2295 cm^{-1}) and to the carbonyl of the ylide groups (1667 cm^{-1}), while the IR spectrum of 5a:5b shows absorptions due to the pyridine ligands (1607 cm^{-1}) and to the carbonyl group of the ylide ligands (1658 cm⁻¹). The ¹H NMR spectrum of the mixture 4a:4b shows, in addition to the expected signals due to the Ph groups and the NCMe ligands, a pattern of resonances very similar to that described for the mixture 3a:3b—that is, seven different peaks corresponding to the seven different types of protons present in the two complexes (see Scheme 1 and Section 5). The same applies to the mixture 5a:5b, with understandable differences arising from the presence of pyridine ligands instead of NCMe. In addition, the ${}^{31}P{}^{1}H{}$ NMR spectrum of the mixture 4a:4b shows a singlet at 22.1 ppm, attributed to 4a, and two broad singlets at 17.3 and 11.8 ppm, assigned to 4b. Finally, the ${}^{31}P{}^{1}H{}$ NMR spectrum of the mixture 5a:5b shows a singlet at 20.9 ppm (5a), and two singlets at 13.7 and 12.2 ppm (**5b**).

The reaction of dppm with other 1,3-dihalo derivatives has also been studied. The reaction of dppm with 3chloro-2-chloromethyl-1-propene (1:1 molar ratio) in refluxing 1,2-dichloroethane gives the corresponding bis-phosphonium salt **6** (see Scheme 2) as a white solid. This phosphonium derivative has already been reported by Schmidbaur [5], although starting from different compounds (1,1-bis[(diphenylphosphino)methyl]ethene and CH_2I_2), and the yields are very similar. The present procedure is somewhat less complicated and less expensive, since it avoids the synthesis of the diphosphine 1,1-bis[(diphenylphosphino)methyl]ethene. The spectro-



scopic parameters of **6** are in good agreement with those reported in the literature [5b].

From a comparison of the syntheses of compounds 1 and 6, it seems clear that the presence of a carbonyl unit in 1 activates the adjacent methylene groups enough to allow a spontaneous deprotonation (probably, in the form of HCl), and that in further deprotonations (performed with soft bases under mild conditions) two possible reaction sites must be considered (leading to the formation of the isomers **a** and **b**). However, in the bis(phosphonium) 6 the presence of an olefin moiety does not produce a similar activating effect, and a cyclic compound with three methylene groups is obtained. The first deprotonation of 6 can also be produced under very mild conditions, but it is completely selective. A suspension of 6 reacts instantaneously with NEt₃ (1:1 molar ratio) in CHCl₃ to give a clear, colorless solution. The reaction can be monitored by NMR spectroscopy (solvent CDCl₃), and in this solution the only identified species are the methanide-phosphonium salt 6' and the expected salt [HNEt₃]Cl (see Scheme 2 and Section 5). The spectroscopic parameters of 6' (as the chloride salt, see Section 5) show clearly that deprotonation has taken place only at the methylene group between the two phosphorus atoms; the data are in good agreement with those reported in the literature for the corresponding iodide salt [5]. The only difference with the reported synthetic method is the base employed; in our procedure we obtain 100% spectroscopic yield using NEt₃, and in the published method the deprotonating reagents are LiⁿBu or triethylethyledenephosphorane. Our attempts to coordinate compound 6' to a Pd(II) center failed, probably due to the very poor nucleophilic character of the deprotonated carbon atom. Thus, the reaction of the chloride of 6' with $PdCl_2(NCMe)_2$ (1:2 molar ratio) results in the isolation of [6'][PdCl₄], and the reaction with the bis-solvate [Pd(dmba)(THF)₂](ClO₄)₂ (1:1 molar ratio; $dmba = C_6H_4CH_2NMe_2-C_N$ gives the dinuclear $[Pd(\mu-Cl)(dmba)]_2$ and the perchlorate of 6'.

The double deprotonation of 6 has been reported to 5-methyl-1,1,3,3-tetraphenyl- $1\lambda^5$, $3\lambda^5$ -diphosphagive benzene [5a], but no reactions with transition metals have been described. Moreover, very few reports concerning the reactivity of cyclic ylides with transition metals have appeared [4,7,8]. When a suspension of **6** in THF was treated with Li^tBu (1:2.2 molar ratio) a clear orange solution was formed. This solution-containing the 5-methyl-1,1,3,3-tetraphenyl- $1\lambda^5$, $3\lambda^5$ -diphosphabenzene derivative-was allowed to react with PdCl₂(NCMe)₂ (1:1 molar ratio) at 0 °C, resulting in the synthesis of 7 (see Scheme 2). Compound 7 was isolated, as an orange solid, after solvent evaporation, extraction of the residue with CH₂Cl₂ and precipitation with Et_2O (see Section 5). It gives correct elemental analysis and mass spectrum, and its IR spectrum shows

the presence of two *cis*-chloride ligands (two absorptions at 291 and 273 cm⁻¹).

The ¹H NMR spectrum of 7 shows all expected resonances for the proposed stoichiometry. The olefinic proton appears at 5.75 ppm (d, ${}^{2}J_{PH} = 20.4$ Hz), the methanide and ylidic protons appear at 2.72 ppm (broad singlet) and 2.67 ppm (d, ${}^{2}J_{PH} = 10.2$ Hz), respectively, and the methyl group appears at 2.48 ppm. The C,Ccoordination of the ylide-methanide ligand can be clearly seen in the ${}^{13}C{}^{1}H$ NMR spectrum (APT) of 7. There, the methanide carbon atom $[P_2C(H)Pd]$ appears at -17.5 ppm (dd, ${}^{1}J_{PC} = 52.1$ Hz, ${}^{1}J_{PC} = 40.0$ Hz), with positive phase, and strongly shifted to high field with respect to the corresponding resonance in the free ligand [5b] (-3.0 ppm, ${}^{1}J_{PC} = 109.1$ Hz), as expected for a hybridization change from sp² to sp³. The same arguments apply to the notable change in the values of the ${}^{1}J_{PC}$ coupling constants. Moreover, the ylidic carbon atom [PC(H)Pd] appears at 6.3 ppm (dd, ${}^{1}J_{PC} = 57.8$, ${}^{3}J_{PC} = 7.7$ Hz), also strongly shifted to high field with respect to its corresponding value in the free ligand (51.8 ppm, J = 120.54 Hz). On the other hand, the methyl carbon atom appears at virtually the same chemical shift (29.1 ppm, compared with 30.4 ppm in the free ligand) but with a different multiplicity (dd, ${}^{3}J_{PC} = 17.0$, ${}^{3}J_{PC} = 9.1$ Hz), reflecting the asymmetry of compound 7. The redistribution of the electron density after the C,C-coordination is also reflected in the olefinic fragment, which possesses now greater double bond character. The quaternary carbon atom appears now at 172.2 ppm (while in the free ligand it appears at 159.5 ppm) and the =CH carbon atom appears at 96.5 ppm (dd, =CH, ${}^{1}J_{PC} = 93.5$ Hz, ${}^{3}J_{PC} = 7.2$ Hz; compare with 51.8 ppm, J = 120.54 Hz in the free ligand). These downfield shifts are consistent with the putative greater double bond character. Finally, the ${}^{31}P{}^{1}H{}$ NMR spectrum shows two singlet peaks, centered at 10.2 and 7.7 ppm. The analysis of the molecular structure of 7. CHCl₃ by X-ray diffraction provides further structural information.

3. X-ray crystal structures of compounds 3b 3dmso and 7 CHCl₃

Fig. 1 shows a drawing of **3b**, relevant parameters concerning data collection and refinement are given in Table 1 and selected bond distances and angles are collected in Table 2. The Pd atom is located in a rhombically distorted square-planar environment, bonded to the two Cl atoms, the methanide carbon atom C(1) and the ylidic carbon atom C(2). The largest deviation from the best plane defined by Cl(1)–Cl(2)–Pd(1)–C(1)–C(2) corresponds to C(2) (+0.043 Å). The sum of the *cis*- bond angles about the Pd center is $360.0(3)^\circ$, which indicates the strict planarity of the



Fig. 1. Thermal ellipsoid plot of complex **3b**. Non-hydrogen atoms are drawn at the 50% probability level. H atoms have been omitted for clarity.

Crystal data for $3b \cdot 3dmso$ and $7 \cdot CHCl_3$

Table 1

Compound	3b ⋅ 3 dmso	$7 \cdot \text{CHCl}_3$
Empirical formula	C ₃₄ H ₄₁ Cl ₂ O ₄ P ₂ PdS ₃	C ₃₀ H ₂₆ Cl ₅ P ₂ Pd
Molecular weight	849.09	732.10
Data collection T (K)	173(2)	173(2) K
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.4199(13)	14.877(2)
b (Å)	12.1234(14)	13.989(2)
c (Å)	26.861(3)	15.616(3)
β (°)	93.928(2)	112.887(3)
V (Å ³)	3710.1(7)	2994.0(8)
Ζ	4	4
$D_{\rm calc} ({\rm Mg}\;{\rm m}^{-3})$	1.520	1.624
μ (Mo K α) (mm ⁻¹)	0.936	1.193
F(000)	1740	1468
Crystal size (mm)	$0.39 \times 0.25 \times 0.16$	$0.21 \times 0.15 \times 0.04$
θ Range (°)	1.52-28.65	1.60 - 28.78
Reflections collected	23 7 30	19 369
Reflections unique	8709 [0.1004]	7053 [0.0998]
$[R_{\rm int}]$		
Data/restraints/para- meters	8709/0/426	7052/0/380
R indices $[I > 2\sigma(I)]$	$R_1 = 0.0803, wR_2 =$	$R_1 = 0.0611, wR_2 =$
	0.1793	0.1033
R indices (all data)	$R_1 = 0.1358, wR_2 =$	$R_1 = 0.1362, wR_2 =$
	0.1970	0.1462
Goodness-of-fit	1.005	0.895
Largest difference peak and hole (e $Å^{-3}$)	1.672, -1.762	0.723, -0.676

 $R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; \ wR_{2} = [\Sigma \ w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma \ w(F_{o}^{2})^{2}]^{1/2}; \ \text{Goodness-of-fit} = [\Sigma \ w(F_{o}^{2} - F_{c}^{2})^{2} / (n_{\text{obs}} - n_{\text{param}})]^{1/2}.$

coordination environment. The atoms C(1) and C(2) are chiral, although, due to the centrosymmetric nature of the space group $(P2_1/n)$, the crystal as a whole is

Table 2 Bond lengths (Å) and angles (°) for **3b**·**3**dmso

Bond lengths			
Pd(1) - C(1)	2.099(6)	Pd(1)-C(2)	2.104(6)
Pd(1)-Cl(2)	2.3539(19)	Pd(1)-Cl(1)	2.3564(17)
P(1)-C(1)	1.781(6)	P(1)-C(2)	1.779(7)
P(1)-C(5)	1.796(7)	P(1)-C(11)	1.799(7)
P(2)-C(1)	1.760(7)	P(2)-C(17)	1.787(7)
P(2)-C(23)	1.790(7)	P(2)-C(4)	1.814(6)
C(2)-C(3)	1.452(9)	C(3)-O(1)	1.203(7)
C(3)-C(4)	1.541(10)		
Bond angles			
C(1) - Pd(1) - C(2)	77.4(2)	C(1) - Pd(1) - Cl(2)	169.75(17)
C(2)-Pd(1)-Cl(2)	92.37(18)	C(1) - Pd(1) - Cl(1)	93.82(17)
C(2) - Pd(1) - Cl(1)	170.42(18)	Cl(2)-Pd(1)-Cl(1)	96.38(7)
C(1)-P(1)-C(2)	95.1(3)	C(1) - P(1) - C(5)	111.2(3)
C(2)-P(1)-C(5)	111.4(3)	C(1)-P(1)-C(11)	117.0(3)
C(2)-P(1)-C(11)	114.0(3)	C(5)-P(1)-C(11)	107.8(3)
C(1)-P(2)-C(17)	110.4(3)	C(1)-P(2)-C(23)	110.1(3)
C(17)-P(2)-C(23)	109.7(3)	C(1)-P(2)-C(4)	108.2(3)
C(17) - P(2) - C(4)	109.5(3)	C(23) - P(2) - C(4)	109.0(3)
P(2)-C(1)-P(1)	111.5(3)	P(2)-C(1)-Pd(1)	103.5(3)
P(1)-C(1)-Pd(1)	84.5(2)	C(3)-C(2)-P(1)	118.3(5)
C(3)-C(2)-Pd(1)	103.0(4)	P(1)-C(2)-Pd(1)	84.4(2)
O(1)-C(3)-C(2)	122.7(7)	O(1)-C(3)-C(4)	117.4(7)
C(2)-C(3)-C(4)	119.8(5)	C(3)-C(4)-P(2)	118.3(5)

racemic. The absolute configurations shown in Fig. 1 are S [C(1)] and R [C(2)].

The bond distances Pd-Cl(1) [2.3564(17) Å] and Pd-Cl(2) [2.3539(19) Å] are identical, within experimental error, and fall in the range of distances found for this bond in similar environments (Cl-trans-C) [4,19]. The Pd-C bond distances Pd-C(1) [2.099(6) Å] and Pd-C(2) [2.104(6) Å] are also identical, within experimental error, and similar to those reported in other cyclic structures containing ylide and methanide C atoms linked to palladium [4]. The P-C bond distances show remarkable differences. While the P(1)-C(n) (n = 1, 2, 5, 11) bond distances are identical [range 1.779(7) - 1.799(7)Å], the P(2)–C(1) bond distance [1.760(7) Å] is shorter than the other P(2)-C(m) (m = 4, 17, 23) bond distances [range 1.787(7) - 1.814(6) Å]. This fact could be due to a partial double bond character in the P(2)-C(1) bond. On the other hand, the C(3)-C(4) bond distance [1.541(10) Å] is typical for a $\sigma(C-C)$ bond [20], while the C(2)–C(3) distance [1.452(9) Å] is shorter than that expected for the same type of bond. The C(3)-O(1)bond distance [1.203(7) Å] is typical for ylides derived from 1,3-dichloroacetone [18,21].

The bite angle of the ylide-methanide ligand C(1)–Pd(1)-C(2) is notably acute [77.4(2)°], as befits a fourmembered chelate ring; and similar values have been found in related complexes [4]. The presence of the four membered chelate ring introduces significant distortions in the molecule. The environments of both P atoms are tetrahedral [average of angles 109(3)° for P(1) and 109.5(3)° for P(2)] although for P(1) one of the angles C(1)–P(1)–C(2) [95.1(3)°] is rather different from the ideal value due to the coordination of C(1) and C(2) to the Pd atom. Similar trends can be observed for the coordinated carbon atoms. For instance, the bond angle P(1)–C(2)–Pd(1) is only 84.4(2)°. The basic skeleton of the ylide-methanide ligand adopts a pseudo-boat conformation, with the atoms C(2), C(3), C(1) and P(2) forming the base of the boat. These four atoms are almost coplanar, the RMS deviation from the best plane is 0.031 Å. The atoms located at the corners of the boat show higher deviations with respect to the same plane: 0.297(9) Å [C(4)] and 1.019(6) Å [P(1)]. The angle between the perpendiculars to the best least-square planes defined by [C(1), C(2), C(3), P(2)] and [Pd(1), Cl(1), Cl(2), C(1), C(2)] is 105.51(17)°.

Fig. 2 shows a drawing of the organometallic derivative 7, relevant parameters concerning the data collection and refinement are given in Table 1 and selected bond distances and angles are collected in Table 3. The structure as a whole is very similar to that of compound 3b. The palladium atom is located in a rhombically distorted square-planar environment, surrounded by the two Cl atoms, the methanide carbon atom C(1) and the vlidic carbon atom C(5). The coordination plane is defined by Cl(1)-Cl(2)-Pd(1)-C(1)-C(5) and the largest deviation from the best plane in this case is found at C5 (-0.087 Å). As described for **3b**, both carbon atoms C(1) and C(5) are chiral, and the crystal as a whole is racemic. The absolute configurations shown in Fig. 2 for these carbon atoms are R[C(1)] and S [C(5)]. The bond distances Pd-Cl(1) [2.377(2) Å] and Pd-Cl(2) [2.3544(15) Å] fall in the same range of distances found for this bond in similar environments (Cl-trans-C) [4,19], but are now different from each other, probably due to the different trans influences of the two carbon atoms. This fact is reflected



Fig. 2. Thermal ellipsoid plot of complex 7. Non-hydrogen atoms are drawn at the 50% probability level. H atoms have been omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for $7 \cdot CHCl_3$

Bond lengths			
Pd(1) - C(5)	2.066(5)	Pd(1)-C(1)	2.091(5)
Pd(1)-Cl(2)	2.3544(15)	Pd(1)-Cl(1)	2.377(2)
Pd(1) - P(1)	2.583(2)	C(1) - P(1)	1.761(6)
C(1)–P(2)	1.764(6)	C(2) - C(4)	1.364(7)
C(2)–P(2)	1.743(6)	C(3) - C(4)	1.502(7)
C(4)-C(5)	1.497(8)	C(5) - P(1)	1.752(6)
P(1)-C(6)	1.793(6)	P(1)-C(12)	1.815(6)
P(2)-C(24)	1.791(6)	P(2)-C(18)	1.813(6)
Bond angles			
C(5) - Pd(1) - C(1)	75.1(2)	C(5) - Pd(1) - Cl(2)	94.8(2)
C(1) - Pd(1) - Cl(2)	169.9(2)	C(5) - Pd(1) - Cl(1)	167.4(2)
C(1) - Pd(1) - Cl(1)	95.0(2)	Cl(2) - Pd(1) - Cl(1)	94.96(6)
C(5) - Pd(1) - P(1)	42.5(2)	C(1) - Pd(1) - P(1)	42.7(2)
Cl(2) - Pd(1) - P(1)	128.28(6)	Cl(1) - Pd(1) - P(1)	124.99(6)
P(1)-C(1)-P(2)	112.3(3)	P(1)-C(1)-Pd(1)	83.8(2)
P(2)-C(1)-Pd(1)	107.7(3)	C(4) - C(2) - P(2)	122.3(5)
C(2)-C(4)-C(5)	123.5(5)	C(2)-C(4)-C(3)	120.1(6)
C(5)-C(4)-C(3)	116.4(5)	C(4) - C(5) - P(1)	114.6(4)
C(4) - C(5) - Pd(1)	109.0(4)	P(1)-C(5)-Pd(1)	84.7(2)
C(5)-P(1)-C(1)	92.3(3)	C(5)-P(1)-C(6)	115.4(3)
C(1)-P(1)-C(6)	111.5(3)	C(5)-P(1)-C(12)	115.6(3)
C(1)-P(1)-C(12)	117.3(3)	C(6) - P(1) - C(12)	104.8(3)
C(5) - P(1) - Pd(1)	52.8(2)	C(1) - P(1) - Pd(1)	53.6(2)
C(6) - P(1) - Pd(1)	95.0(2)	C(12) - P(1) - Pd(1)	160.1(2)
C(2)-P(2)-C(1)	107.1(3)	C(2)-P(2)-C(24)	107.1(3)
C(1)-P(2)-C(24)	114.4(3)	C(2)-P(2)-C(18)	112.4(3)
C(1)-P(2)-C(18)	111.4(3)	C(24)-P(2)-C(18)	104.4(3)

in the Pd–C bond distances-Pd–C(1) [2.091(5) Å] and Pd–C(5) [2.066(5) Å]—in such a way that the shorter Pd–C bond distance has a longer Pd–Cl bond *trans* to it.

The expected structural changes in the 5-methyl-1,1,3,3-tetraphenyl- $1\lambda^5,3\lambda^5$ -diphosphabenzene ligand due to coordination are observed, as can be seen from a comparison of the two crystal structures [5a]. The P-C bond distances in the ring [P(1)-C(5): 1.752(6) Å; P(1)-C(1): 1.761(6) A; P(2)-C(1): 1.764(6) A; P(2)-C(2): 1.743(6) Å] are all elongated with respect to their corresponding values in the free ligand [1.729(3); 1.699(3); 1.695(3); 1.724(3) Å], while the endocyclic C-C bond distances-nearly identical in the free ligand [1.387(4) and 1.393(4) Å]—are now very different [C(5)-C(4): 1.497(8) Å and C(2)-C(4): 1.364(7) Å], theformer corresponding to a single $\sigma(C-C)$ bond and the latter to a double C=C bond. These facts match very well with the NMR data. The C-CH₃ bond distances are identical, within experimental error [1.502(7)] Å in 7 and 1.516(4) Å in the free ligand] [5a]. In addition, the structure of the ligand changes from a planar disposition in its free form to a pseudo-boat conformation in 7, similar to that described for 3b. In this case, the atoms C(1), C(4), C(5) and P(2) are coplanar, while C(2) atom deviates by -0.1004 Å from the best least-squares plane defined by the given atoms and P(1) deviates by -1.0425 Å from the same plane. The angle between the best least-squares planes defined by C(1)-C(4)-C(5)-P(2) and Cl(1)-Cl(2)-Pd(1)-C(1)-C(5) is 113.9°. The bite angle of the ligand C(5)-Pd(1)-C(1) is 75.1(2)°, very similar to that observed for **3b**. The four-membered chelate ring also gives distortions and deviations of the regular geometry around the P and coordinated C atoms, following similar trends to those described for **3b**. Finally, it is interesting to remark the presence of a contact between the chlorine atom Cl(1) and the aromatic proton H29A [2.614(8) Å].

4. Conclusion

A new cyclic ylide-phosphonium moiety **1** has been obtained by the facile quaternization of the two P atoms of dppm with 1,3-dichloroacetone, followed by loss of HCl. **1** presents two active methylene groups, and its reaction with NEt₃ produces deprotonation at the two possible sites. The reaction with Pd(II) complexes gives mixtures of derivatives with C,C-coordinated bis-ylide (**a**) and with C,C-bonded ylide-methanide (**b**). In contrast, the cyclic 5-methyl-1,1,3,3-tetraphenyl- $1\lambda^5$, $3\lambda^5$ diphosphabenzene bonds to Pd(II) to give the ylidemethanide complexes exclusively.

5. Experimental

5.1. 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. Ed.* 50 (1973) A335–A337.

5.2. General methods

Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyser. Infrared spectra (4000–200 cm⁻¹) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ¹H (300.13 MHz), ¹³C{¹H} (75.47 MHz, digital resolution: 0.545 HzpPT) and ${}^{31}P{}^{1}H{}$ (121.49 MHz, digital resolution 3.050 HzpPT) NMR spectra were recorded in CDCl₃, CD₂Cl₂ or dmso-d₆ solutions at room temperature (r.t.) (unless otherwise stated) on a Bruker ARX-300 spectrometer; ¹H and ¹³C{¹H} were referenced using the solvent signal as internal standard and ${}^{31}P{}^{1}H$ was externally referenced to H_3PO_4 (85%). Mass spectra (positive ion FAB) were recorded on a V.G. Autospec spectrometer from CH₂Cl₂ or dmso solutions. The following starting compounds have been obtained from commercial sources and used as supplied: 1,3-dichloroacetone, dppm, NEt₃, pyridine, Li^tBu and $H_2C=C(CH_2Cl)_2$. The complex [PdCl₂(NCMe)₂] has been prepared according to published procedures [22] with minor modifications (solvent change).

5.3. Synthesis of 1

To a solution of 1,3-dichloroacetone (1.003 g, 7.87 mmol) in deoxygenated CHCl₃ (20 ml), bis(diphenyl-phosphino)methane (dppm) (3.032 g, 7.87 mmol) was added. This solution was refluxed under an Ar atmosphere for 12 h. During this time a white solid precipitated. After cooling, the solid was filtered, washed with CHCl₃ (5 ml) and Et₂O (20 ml), air-dried and identified as **1**. Obtained: 2.658 g (70.3% yield). Compound **1** crystallizes with 2.5 molecules of water, which proved to be difficult to remove.

Anal. Calc. for $[C_{28}H_{25}ClOP_2] \cdot 2.5H_2O$: C, 64.68; H, 5.81. Found: C, 64.78; H, 5.49%. MS (FAB+) [m/z,(%)]: 439 (100%) $[(M-Cl)^+]$. IR (ν , cm⁻¹): 1587, 1568 ($\nu_{C=O}$). ¹H NMR (dmso-d₆, r.t.): δ (ppm), 8.04–7.53 (m, 20H, Ph), 6.20 (t, 2H, PCH₂P, ² J_{P-H} = 14.4 Hz), 5.82 (d, 1H, P=C(H), ² J_{P-H} = 9.3 Hz), 5.10 (d, 2H, PCH₂, ² J_{P-H} = 13.8 Hz). ³¹P{¹H} NMR (dmso-d₆, r.t.): δ (ppm), 18.4 (s, broad, PCH₂), 9.3 (s, broad, P=CH). ¹³C{¹H} NMR (dmso-d₆, r.t): δ (ppm), 170.1 (d, CO, ² J_{PC} = 11.1 Hz), 135.4 (s, C_{para}, Ph), 134.5 (s, C_{para}, Ph), 132.7 (d, C_{meta}, Ph, ³ J_{PC} = 10.4 Hz), 132.6 (d, C_{meta}, Ph, ³ J_{PC} = 10.0 Hz), 129.8 (d, C_{ortho}, Ph, ² J_{PC} = 13.3 Hz), 129.6 (d, C_{ortho}, Ph, ² J_{PC} = 13.0 Hz), 121.0 (d, C_{ipso}, Ph, ¹ J_{PC} = 95 Hz), 116.7 (d, C_{ipso}, Ph, ¹ J_{PC} = 89 Hz), 70.0 (dd, P=CH, ¹ J_{PC} = 103 Hz, ³ J_{PC} = 9.5 Hz), 23.3 (d, PCH₂, ¹ J_{PC} = 46.6 Hz), 12.3 (t, PCH₂P, ¹ J_{PC} = 45.4 Hz).

5.4. Spectroscopic characterization of the mixture 2a/2b

To a suspension of 1 in CDCl₃ (0.4 ml), NEt₃ was added until complete dissolution was obtained. The bisylide 2a and the ylide-methanide 2b were obtained instantaneously (1/2 molar ratio). The NMR measurements were carried out 5 min after mixture (time for locking and shimming).

¹H NMR (CDCl₃, r.t.): δ (ppm), 7.79–7.28 (m, Ph), 3.85 (d, P=CH, **2b**, ²J_{PH} = 12.6 Hz), 3.73 (d, P=CH, **2a**, ²J_{PH} = 25.8 Hz), 3.36 (dd, P=C(H)P, **2b**, ²J_{PH} = 14.4 Hz, ²J_{PH} = 2.4 Hz), 3.18 (d, PCH₂, **2b**, ²J_{PH} = 12.0 Hz); the resonance due to the PCH₂P protons was not observed, probably hidden by the [HNEt₃]⁺ signals. ³¹P{¹H} NMR (CDCl₃, r.t.): δ (ppm), 16.6, 11.4 (AB spin system, **2b**, ²J_{PP} = 38.4 Hz), 8.9 (s, **2a**).

5.5. Synthesis of 3

To a suspension of **1** (1.091 g, 2.30 mmol) in CH₂Cl₂ (20 ml), NEt₃ (0.323 ml, 2.30 mmol) was added dropwise, giving a clear, colorless solution. To this solution PdCl₂(NCMe)₂ (0.608 g, 2.30 mmol) was added, and the resulting orange solution was stirred at r.t. for 1 h. During this time, complex **3** precipitated as a yellow solid, which was filtered, washed with CH₂Cl₂ (5 ml) and Et₂O (20 ml) and air dried. Obtained: 1.016 g (71.7% yield). Molar ratio **3a/3b** = 1/2. Complex **3** crystallized with 3 molecules of H₂O. Repeated attempts to eliminate them by heating were unsuccessful (decomposition). Spontaneous crystallization from a concentrated dmso solution gave yellow crystals of **3b**·3dmso.

Anal. Calc. for C₂₈H₂₄Cl₂OP₂Pd·3OH₂: C, 50.20; H, 4.51. Found: C, 50.02; H, 4.34%. MS (FAB+) [m/z, (%)]: 616 (3%) $[M^+]$, 581 (40%) $[(M-Cl)^+]$, 439 (100%) $[(M-PdCl_2)^+]$. IR (v, cm⁻¹): 1635 (v_{C=0}), 302, 290 (v_{Pd-Cl}) . ¹H NMR (dmso-d₆, r.t.): δ (ppm), 8.49–7.25 (m, Ph, 3a+3b), 5.54 (pseudoq, P_2CH_2 , 3a, ${}^{2}J_{\text{HH}} \approx {}^{2}J_{\text{PH}} = 15.5 \text{ Hz}$), 5.34 (pseudoq, broad, P₂CH₂, **3a**, ${}^{2}J_{\text{HH}} = 15.5 \text{ Hz}$, ${}^{2}J_{\text{PH}} = 12.6 \text{ Hz}$), 4.62 (t, PCH₂CO, **3b**, ${}^{2}J_{\text{HH}} \approx {}^{2}J_{\text{PH}} = 13.8 \text{ Hz}$), 4.26 (pseudot, P₂CHPd, **3b**, ${}^{2}J_{\rm PH} = 5.8$ Hz), 4.05 (s, broad, PCHPd, **3a**), 3.64 (d, PCHPd, **3b**, ${}^{2}J_{PH} = 9.9$ Hz), 3.34 (dd, PCH₂CO, **3b**, ${}^{2}J_{\rm HH} = 13.8 \text{ Hz}, {}^{2}J_{\rm PH} = 12.0 \text{ Hz}). {}^{31}P{}^{1}H{} \text{NMR}$ (dmso d_{6} , r.t.): δ (ppm), 18.4 (s, broad, **3a**), 8.8, 7.7 (AB spin system, **3b**, ${}^{2}J_{PP} = 11.3$ Hz). ${}^{13}C{}^{1}H{}$ NMR (dmso-d₆, r.t.): δ (ppm), 181.8 (s, CO, **3b**), 167.8 (s, CO, **3a**), 134.3–121.1 (m, Ph, **3a**+**3b**), 32.6 (d, PCH₂, **3b**, ${}^{1}J_{PC} =$ 51 Hz), 30.7 (d, PCH, **3a**, ${}^{1}J_{PC} = 53.1$ Hz), 22.4 (t, P_2CH_2 , **3a**, ${}^1J_{PC} = 52.9$ Hz), 20.9 (d, PCH, **3b**, ${}^1J_{PC} =$ 54.9 Hz), -13.4 (t, P₂CH, **3b**, ${}^{1}J_{PC} = 38.9$ Hz).

5.6. Synthesis of 4

To a suspension of **3** (0.165 g, 0.268 mmol) in NCMe (20 ml), AgClO₄ (0.111 g, 0.536 mmol) was added, and the resulting mixture was stirred for 30 min with exclusion of light. After the reaction time, the white solid (AgCl) was filtered over Celite and the resulting pale yellow solution was evaporated to dryness. The oily residue was treated with Et₂O (20 ml), giving **4** as a white solid. Obtained: 0.184 g (83.1% yield). Molar ratio **4a/4b** = 1/2. Complex **4** was recrystallized from CH₂Cl₂/ Et₂O, giving colorless crystals of **4**·1.25CH₂Cl₂. These crystals were used for analytic and spectroscopic purposes. The amount of solvent of crystallization was quoted from the corresponding resonance in the ¹H NMR spectrum.

Anal. Calc. for $[C_{32}H_{30}Cl_2N_2O_9P_2Pd] \cdot 1.25CH_2Cl_2: C$, 42.84; H, 3.51; N, 3.00. Found: C, 42.68; H, 3.55; N, 2.95%. MS (FAB+) [m/z, (%)]: 645 (100%) $[(M - 2NCMe - ClO_4)^+]$. IR (ν , cm⁻¹): 2324, 2295 (ν_{CN}), 1667 ($\nu_{C=O}$). ¹H NMR (CD₂Cl₂, r.t.): δ (ppm), 8.21– 7.11 (m, Ph, **4a**+**4b**), 5.35 (pseudoq, P₂CH₂, **4a**, ${}^{2}J_{HH} \approx {}^{2}J_{PH} = 15$ Hz), 4.78 (pseudoq, broad, P₂CH₂, **4a**, ${}^{2}J_{HH} \approx {}^{2}J_{PH} = 15$ Hz), 4.72 (s, broad, P₂CHPd, **4b**), 4.55 (pseudot, PCH₂CO, **4b**, ${}^{2}J_{PH} \approx {}^{2}J_{HH} = 13.5$ Hz), 4.08 (s, broad, PCHPd, **4a**), 3.85 (d, PCHPd, **4b**, ${}^{2}J_{PH} =$ 7.2 Hz), 3.55 (dd, PCH₂CO, **4b**, ${}^{2}J_{HH} = 13.5$ Hz, ${}^{2}J_{PH} =$ 17.7 Hz), 2.50, 2.17, 2.10 (3s, NCMe, **4a**+**4b**). ${}^{31}P{}^{1}H{}^{3}$ NMR (CD₂Cl₂, r.t.): δ (ppm), 22.1 (s, broad, **4a**), 17.3, 11.8 (2s, broad, **4b**). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, r.t.): δ (ppm), 184.2 (s, CO, **4b**), 173.1 (s, CO, **4a**), 136.0–119.7 (m, Ph+NC, **4a**+**4b**), 33.0 (d, PCH₂, **4b**, ${}^{1}J_{PC} = 51.8$ Hz), 31.2 (d, PCH, **4a**, ${}^{1}J_{PC} = 48.3$ Hz), 25.2 (t, P₂CH₂, **4a**, ${}^{1}J_{PC} = 52.4$ Hz), 3.3 (s, NCMe, **4a**+**4b**); the resonances corresponding to one ylide carbon and to the methanide carbon (for **4b**) were not observed.

5.7. Synthesis of 5

To a suspension of **3** (0.271 g, 0.440 mmol) in acetone (15 ml), AgClO₄ (0.182 g, 0.880 mmol) was added, and the resulting mixture was stirred at r.t. for 30 min with exclusion of light. After the reaction time, the white solid (AgCl) was filtered and discarded. To the resulting pale yellow solution pyridine (0.57 ml, 1.8 mmol) was added, and stirring was continued for 30 min. During this time, **5** precipitated as a white solid, which was filtered, washed with Et₂O and air dried. Obtained: 0.196 g (49.4% yield). Molar ratio **5a/5b** = 3/1. The evaporation of the acetone solution gave an intractable residue, from which no identifiable products could be obtained.

Anal. Calc. for C₃₈H₃₄Cl₂N₂O₉P₂Pd: C, 50.60; H, 3.80; N, 3.11. Found: C, 50.69; H, 3.82; N, 3.29%. MS (FAB+) [*m*/*z*, (%)]: 803 (15%) [(*M*-ClO₄)⁺], 724 (60%) [(*M*-ClO₄-py)⁺], 645 (100%) [(*M*-ClO₄-2py)⁺]. IR (*v*, cm⁻¹): 1658 (*v*_{C=0}), 1607 (py). ¹H NMR (dmso-d₆, r.t.): δ (ppm), 8.48 (s, br, H_{ortho}, py, **5a**), 7.88-7.24 (m, Ph+py, **5a+5b**), 6.33 (pseudoq, P₂CH₂, **5a**, ²J_{HH} \approx ²J_{PH} = 15.3 Hz), 5.63 (pseudoq, broad, P₂CH₂, **5a**, ²J_{HH} \approx ²J_{PH} = 15.3 Hz), 5.29 (pseudot, PCH₂CO, **5b**, ²J_{PH} \approx ²J_{HH} = 15.0 Hz), 4.88 (s, broad, PCHPd, **5b**), 4.60 (s, broad, PCHPd, **5a**), 3.90 (s, broad, PCHPd, **5b**), 3.84 (pseudot, PCH₂CO, **5b**, ²J_{HH} \approx ²J_{PH} = 15.0 Hz). ³¹P{¹H} NMR (dmso-d₆, r.t.): δ (ppm), 20.9 (s, **5a**), 13.7, 12.2 (2s, broad, **5b**).

5.8. Synthesis of 6

To a solution of dppm (0.500 g, 1.30 mmol) in 15 ml of deoxygenated 1,2-dichloroethane, $H_2C=C(CH_2Cl)_2$ was added (0.150 ml, 1.30 mmol). This solution was refluxed (Ar atmosphere) for 24 h. Once cooled, the white precipitate of **6** was filtered, washed with Et₂O (20 ml) and dried in vacuo. Obtained: 0.329 g (50% yield). The product **6** crystallizes with two molecules of H_2O .

Anal. Calc. for $[C_{29}H_{28}Cl_2P_2] \cdot 2H_2O$: C, 63.86; H, 5.91. Found: C, 63.70; H, 5.81%. MS (FAB+) [m/z,(%)]: 437 (100%) $[(M-H-2Cl)^+]$. IR (v, cm⁻¹): 1645, 1624 ($v_{C=C}$), 1590 (Ph). ¹H NMR (dmso-d₆, r.t.): δ (ppm), 8.14 (m, 8H, H_{ortho}, Ph), 7.70 (m, 4H, H_{para}, Ph), 7.55 (m, 8H, H_{meta}, Ph), 6.61 (t, 2H, P₂CH₂, ²J_{PH} = 15.5 Hz), 5.96 (s, 2H, =CH₂), 4.98 (d, 4H, PCH₂, ²J_{PH} = 16.8 Hz). ³¹P{¹H} NMR (dmso-d₆, r.t.): δ (ppm), 15.5. ¹³C{¹H} NMR (dmso-d₆, r.t.): δ (ppm), 135.1 (s, C_{para}, Ph), 132.9 (d, C_{meta}, Ph, ³J_{PC} = 4.9 Hz), 129.7 (d, C_{ortho}, Ph, ²J_{PC} = 6.5 Hz), 127.5 (t, =C, ²J_{PC} = 11 Hz), 126.9 (t, =CH₂, ³J_{PC} = 10 Hz), 117.8 (d, C_{ipso}, Ph, ¹J_{PC} = 94.3 Hz), 26.9 (dd, PCH₂, ¹J_{PC} = 58.2 Hz, ³J_{PC} = 9 Hz), 13.9 (t, P₂CH₂, ¹J_{PC} = 41 Hz).

5.9. Spectroscopic characterization of 6'

To a suspension of **6** in CDCl₃ (0.4 ml), NEt₃ was added until complete dissolution was attained. The ylide-phosphonium salt **6**' was obtained instantaneously. The NMR measurements were carried out 5 min after mixture (time for locking and shimming).

¹H NMR (CDCl₃, r.t.): δ (ppm), 7.76–7.69 (m, 8H, H_{ortho}, Ph), 7.56–7.45 (m, 12H, H_{meta} + H_{para}, Ph), 5.00 (t, 2H, =CH₂, ⁴J_{PH} = 3.9 Hz), 3.84 (d, 4H, PCH₂, ²J_{PH} = 16.8 Hz), 1.30 (t, 1H, P₂CH, ²J_{PH} = 4.2 Hz). ³¹P{¹H} NMR (CDCl₃, r.t.): δ (ppm), 15.6 (s). ¹³C{¹H} NMR (CDCl₃, r.t.): δ (ppm), 134.7–127.2 (m, Ph), 125.4 (t, =C, ²J_{PC} = 10 Hz), 120.8 (t, =CH₂, ³J_{PC} = 10 Hz), 119.4 (d, C_{ipso}, Ph, ¹J_{PC} = 84 Hz), 33.0 (d, PCH₂, ¹J_{PC} = 58.5 Hz), -3.7 (t, P₂CH, ¹J_{PC} = 108.4 Hz).

5.10. Synthesis of 7

To a suspension of **6** (0.250 g, 0.49 mmol) in dry THF (20 ml), Li^tBu (0.72 ml of a 1.5 M solution, 1.1 mmol) was added, giving, in few seconds, an intense orange solution. This solution was stirred at r.t. for 15 min, and then cooled on an ice bath. PdCl₂(NCMe)₂ (0.123 g, 0.49 mmol) was added to the cool solution, the mixture was stirred for 30 min, and then the bath was removed and the solvent was evaporated to dryness. The residue was extracted with CH₂Cl₂ (2 × 10 ml), filtered, and the combined yellow solution was evaporated to small volume (≈ 2 ml). By Et₂O addition (20 ml) and stirring, 7 was obtained as a yellow–orange solid, which was filtered, washed with Et₂O (10 ml) and dried. Obtained: 0.239 g (79.3% yield).

Anal. Calc. for $[C_{29}H_{26}Cl_2P_2Pd]$: C, 56.75; H, 4.27. Found: C, 56.68; H, 4.25%. MS (FAB+) [m/z, (%)]: 577 (50%) $[(M-Cl)^+]$. IR (ν, cm⁻¹): 1560 (ν_{C=C}+Ph), 291, 273 (ν_{Pd-Cl}). ¹H NMR (CD₂Cl₂, r.t.): δ (ppm), 8.58–6.89 (m, 20H, Ph), 5.75 (d, 1H, =C(H)P, ²J_{PH} = 20.4 Hz), 2.72 (s, broad, 1H, P₂C(H)Pd), 2.67 (d, 1H, PC(H)Pd, ²J_{PH} = 10.2 Hz), 2.48 (s, 3H, Me). ³¹P{¹H} NMR (CD₂Cl₂, r.t.): δ (ppm), 10.2 (s, PPh₂), 7.7 (s, PPh₂). ¹³C{¹H} NMR (CD₂Cl₂, r.t.): δ (ppm), 172.2 (s, =C), 135.0–122.0 (m, Ph), 96.5 (dd, =CH, ¹J_{PC} = 93.5 Hz, ³J_{PC} = 7.2 Hz), 29.1 (dd, CH₃, ³J_{PC} = 17.0 Hz, ³J_{PC} = 9.1 Hz), 6.3 (dd, C-ylide, PdC(H)P, ¹J_{PC} = 57.8 Hz, ³J_{PC} = 7.7 Hz), -17.5 (dd, C-methanide, PdC(H)P₂, ¹J_{PC} = 52.1 Hz, ¹J_{PC} = 40.0 Hz).

5.11. X-ray crystallography

Crystals of the complex $3b \cdot 3dmso$ of adequate quality for X-ray measurements were obtained by spontaneous crystallization from a concentrated dmso solution of the crude complex $3 \cdot 3H_2O$. Crystals of $7 \cdot CHCl_3$ of adequate quality for X-ray mesurements were obtained by slow vapour diffusion of Et₂O into a CHCl₃ solution of complex 7. One crystal of each compound was mounted at the end of a quartz fiber and covered with epoxy.

5.11.1. Data collection

A single crystal of dimensions $0.39 \times 0.25 \times 0.16$ mm (**3b**·3dmso) or $0.21 \times 0.15 \times 0.04$ mm (7·CHCl₃) was mounted in a random orientation. In both cases, data collection was performed at T = -100 °C on a Bruker Smart CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected based on three ω -scan runs (starting $\omega = -30^{\circ}$) at values $\phi = 0$, 90 and 180° with the detector at $2\theta = 30^{\circ}$. For each of these runs, frames (606, 435 and 230, respectively) were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the program SAINT [23] and the integrated intensities were corrected for absorption with SADABS [24].

5.11.2. Structure solution and refinement

The structures were solved and developed by Patterson and Fourier methods [25]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and treated as riding atoms, except for those of the methyl groups (complex 7), which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the C-C(methyl)bonds treated as variables. Each hydrogen 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_{0}^{2} , and no reflections were omitted in the least-squares calculations [26]. During the refinement of 3b-3dmso one of the solvent regions was found to be so severely disordered that we were not able to build up a sensible model for it. The effects of this solvent were removed by the squeeze algorithm of the program PLATON [27]. One of the other solvent regions was also disordered, but in this case it was possible to refine a model in which two dmso congeners share the site. In the structure of 7. CHCl₃, the interstitial chloroform molecule was found to be disordered in such a way that the carbon atom and one chlorine could be refined with full occupancy, but that the other two chlorine atoms were disordered over more than one site each. In order to achieve the best fit to the average electron density observed by X-ray diffraction, we modeled the latter two chlorine atoms as three partially occupied sites each, maintaining proper stoichiometry. Given the disorder, however, we do not believe that the geometric parameters derived for this moiety are useful descriptors for the shape of the chloroform molecule. Crystallographic calculations were done on an AlphaStation (OPEN/VMS V6.2).

6. Supplementary material

Tables giving complete data collection parameters, atomic coordinates, complete bond distances and angles and thermal parameters for $3b \cdot 3dmso$ and $7 \cdot CHCl_3$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 183568 and 183569 for $3b \cdot 3dmso$ and $7 \cdot CHCl_3$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.uk or www: http://www.ccdc.cam.ac.uk).

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