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Journal of Organometallic Chemistry 602 (2000) 151–157

Journal of Organometallic Chemistry

Reactivity of Pd(II) complexes containing the orthometallated C,C-chelating ligand C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$ towards deprotonating reagents. Part 2☆

Susana Fernández, 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

Received 31 January 2000; accepted 1 March 2000

Abstract

The reaction of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(\mu\text{-}Cl)]_2(ClO_4)_2$ (**1**) with the deprotonating reagent NBu_4OH (1:2.5 molar ratio, room temperature (r.t.)) and subsequently with monodentate ligands L (1:4 molar ratio) or bidentate ligands L–L (1:2 molar ratio) gives the cationic complexes $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3)(L)_2](ClO_4)$ (L = PPh_3 (**2**), $H_2NCH_2CH{=}CH_2$ (**3**)) or $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3)(L\text{–}L)](ClO_4)$ (L–L = dppm (**4**), $Ph_2PCH_2PPh_2C(H)COPh$ (**5**), NC_5H_4-2-CO–N=PPh_3 (**6**)). In complexes **2**–**6** the orthometallated-ylide ligand is coordinated through the arylic carbon and through one ylidic carbon, and contains a free ylide fragment –C(H)=PPh_3. The reaction of **1** with NBu_4OH (1:2.5 molar ratio, r.t.) and with $[PPh_2CH_2PPh_2CH_2COMe]ClO_4$ (1:2 molar ratio) gives $[Pd(PPh_2CH_2PPh_2CHC(O)Me)_2](ClO_4)_2$ (**7**) and the ylide–phosphonium salt $[Ph_3P{=}C(H)COCH_2PPh_3]ClO_4$. The reaction seems to occur through protonation of the orthometallated-ylide ligand by the acid protons of the phosphonium unit. All complexes were characterized on the basis of their spectroscopic data. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Orthometallated; Deprotonation; Phosphoylides

1. Introduction

We have reported recently the synthesis [1] of Pd(II) complexes containig the C,C-orthometallated ligand $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(L)(L')]^{n+}$ (see Fig. 1)

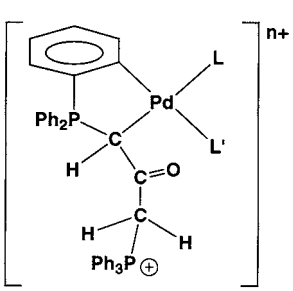


Fig. 1.

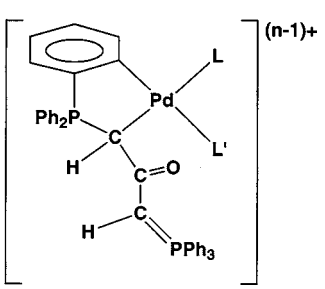


Fig. 2.

and their reactivity towards different deprotonating reagents [2]. In all cases studied, the dangling phosphonium group –CH_2PPh_3 was deprotonated, generating a non-coordinated free ylide group –C(H)=PPh_3, that is, complexes of stoichiometry $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{-}COCH{=}PPh_3)(L)(L')]^{(n-1)+}$ could be obtained (see Fig. 2). The subsequent reaction of these last complexes with an electrophilic metal center allowed to the obtention of di- and trinuclear heterometallic derivatives, in

☆ Part 1, see Ref. [2].

* Corresponding author.

E-mail addresses: rafanava@posta.unizar.es (R. Navarro), esteban@posta.unizar.es (E.P. Urriolabeitia)

PII: S0022-328X(00)00143-1

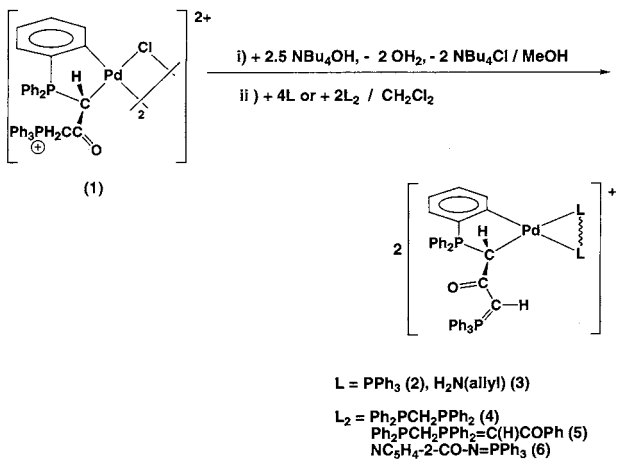
which the orthometallated ylide group was acting as a C,C,C-terdentate ligand, chelating the palladium centre through two carbon atoms — the cyclometallated and one ylidic — and bridging through the two ylidic carbon atoms the palladium and the other metal (see Fig. 3). This C,C,C-bonding mode was unknown for the ylides. Although the orthometallation of the ylides is not an unknown reaction [3,4], the contribution to the chemistry of bis-ylides or related phosphino–ylides remains scarce [5,6].

The reported [2] synthetic method of free ylide derivatives $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3)(L)(L')]^{(n-1)+}$ could not be adequate if the ancillary ligands L or L′ possess acidic protons or could react themselves with the deprotonating reagent. Thus, the reaction of the starting complex $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(L)(L')]^{n+}$ with the deprotonating reagent could result in competitive processes – namely, the deprotonation of the phosphonium group or the deprotonation or transformation of the ancillary ligand. For instance, coordinated ligands such as dppm ($Ph_2PCH_2PPh_2$), allylamine or the phosphonium–ylides $PPh_2CH_2PPh_2{=}C(H)C(O)R$ are prone to react themselves with deprotonating agents such as NBu_4OH or $Na[N(SiMe_3)_2]$.

Due to these facts, and also due to our interest in the preparation of complexes containing the orthometallated fragment and a free ylide group, we have developed an alternative method to synthesise derivatives $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3)(L)(L')]^{m+}$ with different L and L′. This method extends the scope of stoichiometries available for different ligands, L and L′ in the aforementioned complexes. In this paper we report the obtained results using this method and some of its practical limitations.

2. Results and discussion

The reaction of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)\text{–}CH_2\text{-}PPh_3)(\mu\text{-}Cl)]_2(ClO_4)_2$ (**1**) with the deprotonating reagent NBu_4OH (1:2.5 molar ratio) in MeOH results in a fast colour change from yellow to orange and in the gradual dissolution of the initial suspension to give an orange solution. Further stirring of this solution at room temperature (r.t.) produces the precipitation of a pale yellow solid [7]. The solvent was evaporated and the residue redissolved in methylene chloride, in which a clear orange solution was obtained. This solution is the starting point for further preparations, since its treatment with monodentate ligands L (**1**:L = 1:4 molar ratio) or bidentate ligands L–L (**1**:L_2 = 1:2 molar ratio) allows the synthesis of complexes containing the orthometallated-free ylide ligand $[C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)\text{–}C(H){=}PPh_3]$ (see Eq. (1)).



(1)

In a first attempt we have performed the reaction with PPh_3 (1:4 molar ratio). This reaction results in the formation of the cationic mononuclear complex $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)\text{–}C(H){=}PPh_3)(PPh_3)_2](ClO_4)$ (**2**), which was isolated in analytical pure form after evaporation of the CH_2Cl_2, washing of the residue with water (in order to eliminate the tetrabutylammonium salts) and with Et_2O.

The characterisation of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)\text{–}C(H){=}PPh_3)(PPh_3)_2](ClO_4)$ (**2**) has been carried out by analytical and spectroscopic methods. The presence of the free ylide unit –C(O)–C(H)=PPh_3 is inferred from the IR spectrum since the stretch ν_{CO} (ylide) appears at 1524 cm^{-1}, a typical region for this situation [2]. The NMR spectra of **2** provide more structural information. The ^{1}H-NMR spectrum shows a doublet resonance at 3.80 ppm, attributed to the methine proton [–C(*H*)=P] with a value of the coupling constant $^2J_{P\text{–}H}$ of 26 Hz, the $^{31}P\{^1H\}$-NMR spectrum shows a doublet resonance at 15.11 ppm attributed to the phosphorus of the free ylide group [–C(H)=*P*], and the $^{13}C\{^1H\}$-NMR spectrum shows a doublet of quartets at 56.07 ppm, attributed to the ylidic carbon [–*C*(H)=P]. The value of the coupling constant $^1J_{P\text{–}C}$ = 108 Hz is typical for the presence of the free ylide unit [2].

The observation of four different resonances in the $^{31}P\{^1H\}$-NMR spectrum (relative intensities 1:1:1:1) shows the presence of four chemically unequivalent P atoms in the molecule, two of the C,C-chelating or-

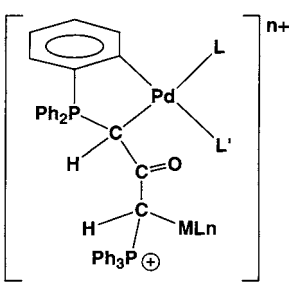
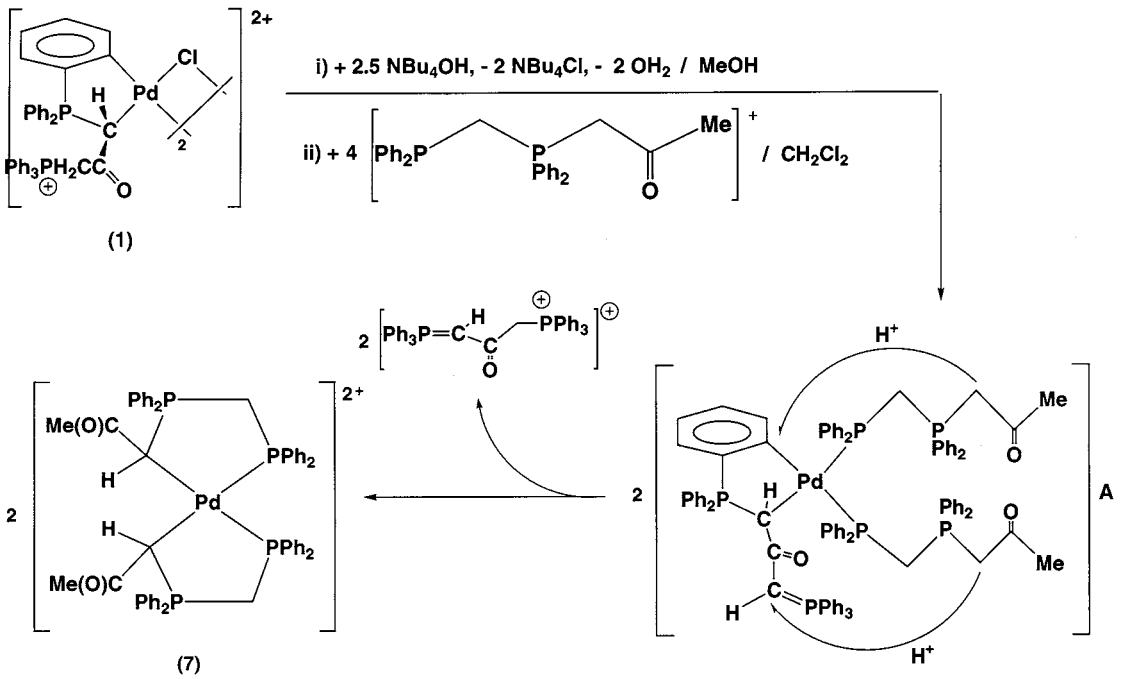


Fig. 3.



Scheme 1.

thometallated ylide and two mutually *cis* PPh_3 ligands. The orthometallated carbon atom appears at 171.51 ppm as a doublet of doublets of doublets, and the values of the coupling constants $^2J_{PtransC} = 123$ Hz and $^2J_{PcisC} = 34$ Hz show clearly the mutual *cis* arrangement of the phosphine ligands.

It is interesting to remark the presence in **2** of two mutually *cis* phosphine ligands which are also *trans* to two carbon atoms. According with the antisymbiotic behaviour of the Pd(II) centre [8–11] and the transphobic effect [12], or reluctance of a phosphine ligand to be in *trans* to an arylic carbon atom, the complex **2** should be really unstable. However, complex **2** is very stable and the presence of the phosphine *trans* to the aryl carbon atom is not only stable but sometimes can not be avoided. For instance, complex **2** can be identified in the reaction of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(Cl)(PPh_3)](ClO_4)$ with $Na[N(SiMe_3)_2]$. We have reported recently [2] that this reaction gave a mixture of products which were not identified: complex **2** is one of them. An additional example is provided by the fact that $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(Cl)(PPh_3)](ClO_4)$ exist as a single isomer [1] with the PPh_3 *trans* to the ylidic carbon. However its deprotonated, neutral, form $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3)(Cl)(PPh_3)]$ is obtained as a mixture of two geometric isomers [2], *cis* and *trans*, with the most abundant being that containing the PPh_3 *trans* to the orthometallated carbon. A plausible explanation for the stability of **2** could be that the reductive elimination would be slow owing to the high energy of the derived four-membered organic product [13].

However, the easiness of synthesis of **2** contrast with the impossibility found in the synthesis of the related $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)CH_2PPh_3)(PPh_3)_2](ClO_4)_2$. Thus, the reaction of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)CH_2\text{-}PPh_3)(NCMe)_2](ClO_4)_2$ with two equivalents of PPh_3 in CH_2Cl_2 results in the substitution of the NCMe ligand *trans* to the ylidic carbon and the formation of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)CH_2PPh_3)(NCMe)(PPh_3)](ClO_4)_2$, already described by us [1], together with some amounts of the hydrolysis products $[Pd(\mu\text{-}OH)(PPh_3)_2](ClO_4)_2$ — characterised by comparison with the reported spectral data [14] — and mono-ylide $[Ph_3P{=}C(H)COCH_2PPh_3]ClO_4$.

In the same way as that described for **2**, **1** reacts with NBu_4OH (1:2.5 molar ratio) and allylamine $H_2N\text{–}CH_2\text{–}C(H){=}CH_2$ (1:4 molar ratio) (see Eq. (1)) resulting in the formation of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)C(H){=}PPh_3)(NH_2\text{–}CH_2\text{–}C(H){=}CH_2)_2](ClO_4)$ (**3**) as a yellow solid, which has been characterised on the basis of its analytical and spectroscopic data. The IR spectrum of **3** shows the ν(CO) of the ylide at 1511 cm^{-1} and also shows absorptions at 3299 and 3269 cm^{-1} corresponding to the ν(NH) stretch, suggesting the presence of coordinated amine. The $^{31}P\{^1H\}$-NMR spectrum shows the presence of an AX spin system centred at 20.32 ppm (P-in-ring) and 15.33 ppm [–C(H)=*P*]. The ^1H-NMR spectrum shows the expected two sets of resonances attributed to the chemically unequivalent allylamine groups and a doublet of doublets at 3.64 ppm attributed to the free ylidic proton [–C(*H*)=P]. This last resonance shows a value of the coupling constant $^2J_{P\text{–}H}$ of 24.3 Hz. All these facts

confirm the proposed stoichiometry and the validity of the synthetic method.

We have also attempted reactions with monodentate ligands but using a lower molar ratio Pd:ligand (1:2) in order to obtain mononuclear derivatives with only one L coordinated and aiming to force the coordination of the carbonyl oxygen in the position *cis* to the coordinated ylidic carbon. However, these reactions did not give the expected results. For instance, when $L = PPh_3$, the reaction results in the formation of a complex mixture in which the only identified product was **2**. Due to this fact, these type of reactions were not investigated further.

Other chelating ligands, symmetrical and asymmetrical, were employed with successful results. The reaction of **1** with NBu_4OH and dppm results in the formation of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)C(H)\text{=}PPh_3)(Ph_2PCH_2PPh_2)](ClO_4)$ (**4**) as a white solid, and the reaction with the phosphino–ylide $Ph_2PCH_2PPh_2$=C(H)COPh gives $[Pd(C_6H_4\text{ - }2\text{ - }PPh_2C(H)\text{–}C(O)C(H)\text{=}PPh_3)(Ph_2PCH_2PPh_2C(H)C(O)Ph)](ClO_4)$ (**5**). Complex **4** was obtained in analytically pure form after concentration of the CH_2Cl_2 solution and precipitation with Et_2O, while **5** was recrystallized from MeOH. The characterisation of **4** and **5** was carried out by examination of the same parameters as those employed for **2** and **3**, that is, (i) the position of the ν(CO) of the ylide; (ii) the chemical shift of the methine resonance [–C(*H*)=P] and the value of the coupling constant $^2J_{P\text{–}H}$ in the ^{1}H-NMR spectrum; (iii) the chemical shift of the ylidic phospohorus [–C(H)=*P*] in the $^{31}P\{^1H\}$-NMR spectrum; and (iv) the chemical shift of the ylidic carbon [–*C*(H)=P] and the value of the coupling constant $^1J_{P\text{–}C}$ in the $^{13}C\{^1H\}$-NMR spectrum (see Section 4).

Complex **4**, as well as complexes **2** and **3**, contains only one chiral centre and was obtained as the racemic mixture. Complex **5** could be obtained as the mixture of two geometric isomers, P-*trans*-to-C_{ylide} and P-*trans*-to-C_{aryl}, each geometric isomer containing two chiral centers, thus expecting a maximum of four diastereoisomers (each one as the racemic mixture of two enantiomers). However, the spectroscopic data for **5** show the presence of a single diastereoisomer in which the phosphino–ylide is P,C-bonded to the palladium centre, as represented in Fig. 4, being the phosphorus *trans* to the orthometallated carbon atom. This arrangement of ligands can be inferred from the $^{13}C\{^1H\}$-NMR in which the orthometallated carbon appears at 175.58 ppm as a doublet of doublet of doublets. The value of the large coupling constant $^2J_{P_{trans}C} = 133$ Hz is indicative of a P-*trans*-to-C_{aryl} disposition [1]. In addition, this geometric isomer should be obtained as the mixture of two diastereoisomers (*RR*/*SS*) and (*RS*/*SR*) but only one is detected. It seems clearly established that in five-membered metallacycles containing a bulky substituent, this substituent is directed to an axial disposition. For instance, in complexes with the C,N-chelating ligand C_6H_4–C(H)Me–NMe_2, the α-methyl group is invariably in an axial position [15–20] and in complexes with the P,C-bonded phosphino–ylide ligand $Ph_2PCH_2PPh_2$=C(H)COR, the C(O)R group is also axially directed [21–23]. Following that, we propose a structure for complex **5** as that represented in Fig. 4, in which both bulky groups attached to the ylidic carbons are in an axial disposition but in opposite sides of the molecular plane, in order to minimise steric repulsions, and both hydrogen atoms are in equatorial dispositions. Additional evidences can be obtained from the $^1H\text{–}^1H$ NOESY spectrum, in which a strong NOE cross-peak is observed between the resonance at 4.91 ppm (attributed to the ylidic proton Pd–C(*H*)–C(O)Ph) and the resonance at 8.29 ppm (attributed to the H_{ortho} proton of the metallated C_6H_4 ring). Obviously, Fig. 4 represents only one enantiomer of **5** and the product as a whole is the racemic mixture. Once again, complex **5** represents an example of a stable P-*trans*-to-C_{aryl} arrangement of ligands.

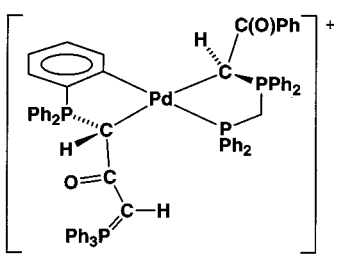


Fig. 4.

On the other hand, **1** reacts cleanly with NBu_4OH and the imino–phosphorane NC_5H_4-2-C(O)–N=PPh_3 resulting in the formation of the mononuclear derivative $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{–}C(O)C(H)\text{=}PPh_3)(NC_5H_4\text{-}2\text{-}C(O)\text{–}N\text{=}PPh_3)](ClO_4)$ (**6**), according with its elemental analysis and mass spectrum. This iminophosphorane ligand has shown to behave as a versatile coordinating group, and three different coordination modes has been characterised in Pd(II) and Pt(II) complexes [23]. In the case of complex **6**, the comparison of the spectral data (see Section 4) with those reported previously [23] allows to determine that the iminophosphorane ligand is N,N-coordinated. The absorption corresponding to the ν_{CO} of the iminophosphorane appears at 1578 cm^{-1}, and the $^{31}P\{^1H\}$-NMR spectrum shows the resonance corresponding to the –N=PPh_3 group as a singlet at 25.75 ppm. The presence of the orthometallated-free ylide ligand can be inferred from the spectroscopic data as for complexes **2**–**5**. Two geometric isomers can also be expected for complex **6**, that with N(py)-*trans*-to-C_{aryl} and that with N(py)-*trans*-to-C_{ylide}. The $^1H\text{–}^1H$ NOESY spectrum provides the additional structural information because a strong NOE interaction between the H_6 proton of the pyridine ligand and the ylidic

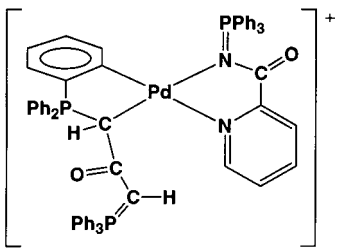


Fig. 5.

proton reveals their mutual *cis* disposition, as represented in Fig. 5. Finally, since complex **6** has only a chiral center, the complex is obtained as the racemic mixture.

When complex **1** is allowed to react with NBu_4OH and the phosphine–phosphonium salt $[Ph_2PCH_2PPh_2CH_2COMe]ClO_4$ in the usual molar ratios, an interesting redistribution reaction occurs (see Scheme 1), instead of the expected P-coordination of the two phosphine moieties. The reaction was performed in MeOH–CH_2Cl_2 (see Section 4) and in the subsequent workup and crystallisation from MeOH two fractions were separated. The first fraction, insoluble in MeOH, contains a small quantity of unreacted phosphonium and a product characterised as $[Pd(PPh_2CH_2PPh_2CHC(O)Me)_2](ClO_4)_2$ (**7**) on the basis of its analytical and spectral data (see Section 4). The second fraction, precipitated with Et_2O, contains almost exclusively the ylide–phosphonium salt $[Ph_3P{=}C(H)C(O)CH_2\text{-}PPh_3](ClO_4)$ [1].

Product **7** shows, in the IR spectrum, a strong absorption at 1637 cm^{-1}, attributed to the ν_{CO} of the carbonyl group –C(H)–*C*(*O*)–Me. No absorptions were found around 1520 cm^{-1}, typical region of the ylide –C(H)–*C*(*O*)–C(H)=PPh_3. The $^{31}P\{^1H\}$-NMR spectrum shows the presence of an AA′XX′ spin system and the ^1H-NMR show the resonances attributed to the ylidic proton Pd–C(*H*), the diastereotopic protons of the PC*H*$_2$P fragment and a doublet for the methyl group –C(O)–*Me*.

With these data we propose that **7** has a geometry P-*cis*-to-P since the reaction should begin by mutual *cis* P-coordination of the two phosphine ends of the phosphine–phosphonium ligands (intermediate **A** in Scheme 1) and then protonation of the Pd–C_{aryl} bond by the acidic phosphonium group. The bis-ylide thus generated can deprotonate the remaining phosphonium moiety, thus forming a new ylide which coordinates immediately giving **7**, and obtaining $[Ph_3P{=}C(H)C(O)CH_2PPh_3](ClO_4)$ as the protonation product of the bis-ylide. In this case, the acidity of the protons of the phosphonium group is strong enough to promote undesirable side reactions. This strong acidity could be a limiting factor when using this method and could reduce its scope of applicability.

3. Conclusions

The reactivity of **1** with NBu_4OH and different mono- and bidentate ligands has been explored. This type of reaction allows the synthesis, in very mild conditions, of complexes containing the orthometallated fragment and the dangling free ylide group with ligands, which could also react themselves with the deprotonating reagent. Moreover, the method tolerates the presence of functional groups attached to the donor atom.

4. Experimental

4.1. 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 Ref. [24]).

4.2. General procedures

Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over benzophenone ketyl, dichloromethane and chloroform over P_2O_5, acetonitrile over CaH_2, methanol over magnesium and *n*-hexane and toluene over sodium. 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), $^{13}C\{^1H\}$ (75.47 MHz) and $^{31}P\{^1H\}$ (121.49 MHz)-NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at r.t. (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). The two dimensional ^1H–^1H NOESY experiments for complexes **5** and **6** were performed at a measuring frequency of 300.13 MHz. The data were acquired into a 512 × 1024 matrix, and then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive ion FAB) were recorded on a V.G. autospec spectrometer from CH_2Cl_2 solutions. The starting complex $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ (**1**), was prepared according to published methods [1].

4.3. *[Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)(PPh_3)$_2$][ClO_4] (2)*

To a yellow suspension of $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ (**1**) (0.160 g, 0.097

mmol) in MeOH (15 ml), was added an aqueous solution of NBu_4OH (40% wt) (159 μl, 0.243 mmol). The suspension becomes orange and after 5 min all solids were dissolved. This solution was stirred for 1 h at r.t., and during this time a pale yellow solid precipitated. The resulting suspension was evaporated to dryness and the residue extracted with CH_2Cl_2 (20 ml), giving a yellow solution. Any remaining solid material at this stage was filtered and discarded. To this solution was added PPh_3 (0.102 g, 0.390 mmol) and the solution stirred for 2 h at r.t. After this time the solvent was evaporated to dryness and the residue was washed with H_2O (2 × 20 ml) and Et_2O (2 × 20 ml), giving **2** as a yellow solid. Obtained: 0.190 g (74% yield).

Anal. Calc. for $C_{75}H_{61}ClO_5P_4Pd$ (1308.06 g mol^{-1}): C, 68.87; H, 4.70. Found: C, 68.28; H, 4.36%. MS [*m*/*z*, %]: 945 [(M–PPh_3–ClO_4)$^+$, 15%]. IR (*ν*, cm^{-1}): 1524 (ν_{CO} ylide). ^{1}H-NMR (CD_2Cl_2): *δ* 7.88–6.66 (m, 59H, Ph + C_6H_4), 4.03 (dddd, 1H, C(H)–Pd, $^3J_{Ptrans-H} = 14$, $^2J_{P-H} = 7.2$, $^3J_{Pcis-H} = 5.1$, $^4J_{P-H} = 2.1$ Hz), 3.80 (d, 1H, C(H)=P, $^2J_{P-H} = 26$ Hz). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): *δ* 35.73 (dd, PPh_3 *trans* to C ylide, $^2J_{P-P} = 31$, $^3J_{P-P} = 20$ Hz), 26.75 (dd, PPh_3 *cis* to C ylide, $^3J_{P-P} = 27$ Hz), 26.11 (ddd, C_6H_4-2-PPh_2, $^3J_{P-P} = 27$, $^4J_{P-P} = 6$ Hz), 15.11 (d, C(H)=PPh_3). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): *δ* 186.24 (quart, CO, $^2J_{P-C} \cong {}^3J_{P-C} = 4.6$ Hz), 171.51 (ddd, C_1, C_6H_4, $^2J_{PtransC} = 123$, $^2J_{PcisC} = 34$, $^2J_{PC} = 7.3$ Hz), 141.56–125.10 (Ph + C_6H_4), 56.07 (dq, C(H)=P, $^1J_{PC} = 108.1$, $^3J_{P-C} \cong {}^4J_{P-C} = 3.8$ Hz), 49.14 (ddd, C(H)Pd, $^1J_{P-C} = 63.8$, $^2J_{Ptrans-C} = 43$, $^2J_{Pcis-C} = 17.1$ Hz).

4.4. [Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)($H_2NCH_2CH=CH_2$)$_2$][ClO_4] (3)

Complex **3** was synthesised in the same way as those described for **2**: **1** (0.158 g, 0.096 mmol), NBu_4OH (157 μl, 0.240 mmol), allylamine (28 μl, 0.385 mmol). Obtained: 0.133 g (77% yield).

Anal. Calc. for $C_{45}H_{45}ClN_2O_5P_2Pd$ (897.66 g mol^{-1}): C, 60.21; H, 5.05; N, 3.12. Found: C, 59.21; H, 4.97; N, 2.65%. MS [*m*/*z*, %]: 683 [(M − $2NH_2CH_2CHCH_2$–ClO_4)$^+$, 100%]. IR (*ν*, cm^{-1}): 3299, 3269 (ν_{NH}), 1511 (ν_{CO} ylide). ^{1}H-NMR ($CDCl_3$): *δ* 8.04–6.99 (m, 29H, Ph + C_6H_4), 5.72 (m, 1H, CH_{cent}, allyl), 5.30, (m, 1H, CH_{cent}, allyl), 5.05 (d, 1H, CH_{trans}, allyl, $^3J_{H-H} = 16$ Hz), 4.93 (d, 1H, CH_{cis}, allyl, $^3J_{H-H} = 10.5$ Hz), 4.73 (d, 1H, CH_{trans}, allyl, $^3J_{H-H} = 17$ Hz), 4.65 (d, 1H, CH_{cis}, allyl, $^3J_{H-H} = 10.2$ Hz), 3.91 (dd, 1H, C(H)–Pd, $^2J_{P-H} = 6$, $^4J_{P-H} = 2.1$ Hz), 3.64 (dd, 1H, C(H)=P, $^2J_{P-H} = 24.3$, $^4J_{P-H} = 0.9$ Hz), 3.36 (m, 1H, NH_2), 3.15 (m, 2H, NCH_2), 2.97 (m, 1H, NH_2), 2.78 (m, 4H, NCH_2 + NH_2). $^{31}P\{^1H\}$-NMR ($CDCl_3$): *δ* 20.32 (d, C_6H_4-2-PPh_2, $^4J_{P-P} = 11$ Hz), 15.33 (d, C(H)=PPh_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): *δ* 189.89 (pseudot, CO, $^2J_{P-C} = 4$ Hz), 164.16 (d, C_1, C_6H_4, $^2J_{PC} = 23$ Hz), 46.77 (dd, C(H)=P, $^1J_{PC} = 116$, $^3J_{P-C} = 9$ Hz), 35.23 (dd, C(H)Pd, $^1J_{P-C} = 47$, $^3J_{P-C} = 18$ Hz).

4.5. [Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)($Ph_2PCH_2PPh_2$)][ClO_4] (4)

Complex **4** was synthesised in the same way as those described for **2**: **1** (0.158 g, 0.096 mmol), NBu_4OH (157 μl, 0.240 mmol), $Ph_2PCH_2PPh_2$ (0.074 g, 0.192 mmol). Obtained: 0.191 g (85% yield).

Anal. Calc. for $C_{64}H_{53}ClO_5P_4Pd$ (1167.87 g mol^{-1}): C, 65.82; H, 4.57. Found: C, 65.13; H, 4.26%. MS [*m*/*z*, %]: 1067 [(M − ClO_4)$^+$, 100%]. IR (*ν*, cm^{-1}): 1511 (ν_{CO} ylide). ^{1}H-NMR ($CDCl_3$): *δ* 7.94–6.88 (m, 49H, Ph + C_6H_4), 4.39 (m, 1H, Pd–C(H)P), 4.16 (ddd, 1H, PCH_2P, $^2J_{H-H} = 16$, $^2J_{P-H} = 10$, $^2J_{P-H} = 8$ Hz), 3.88 (dt, 1H, PCH_2P, $^2J_{P-H} = 9$ Hz), 3.37 (d, 1H, C(H) = P, $^2J_{P-H} =$ 24.6 Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): *δ* 25.18 (ddd, C_6H_4-2-PPh_2, $^3J_{P-Ptrans} = 26$, $^3J_{P-Pcis} = 23$, $^4J_{P-P} = 8$ Hz), 14.50 (d, C(H)=PPh_3, $^4J_{P-P} = 8$ Hz), − 19.36 (dd, PPh_2 *cis* to C ylide, $^2J_{P-P} = 49$, $^3J_{P-P} = 23$ Hz), − 30.54 (dd, PPh_3 *trans* to C ylide, $^2J_{P-P} = 49$, $^3J_{P-P} = 26$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): *δ* 188.11 (m, CO), 168.76 (dd, C_1, C_6H_4, $^2J_{PtransC} = 130$, $^2J_{PcisC} = 26$ Hz), 141.99–125.66 (Ph + C_6H_4), 44.81 (m, C(H)Pd).

4.6. [Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)($Ph_2PCH_2PPh_2$C(H)COPh)][ClO_4] (5)

Complex **5** was synthesised in the same way as those described for **2** except that the product was recrystallised from MeOH: **1** (0.158 g, 0.096 mmol), NBu_4OH (157 μl, 0.240 mmol), $Ph_2PCH_2PPh_2$=C(H)COPh (0.096 g, 0.192 mmol). Obtained: 0.185 g (75% yield).

Anal. Calc. for $C_{72}H_{59}ClO_6P_4Pd$ (1286.00 g mol^{-1}): C, 67.24; H, 4.62. Found: C, 66.85; H, 4.25%. MS [*m*/*z*, %]: 1185 [(M − ClO_4)$^+$, 100%]. IR (*ν*, cm^{-1}): 1605 (ν_{COPh} ylide), 1505 ($\nu_{COCH=P}$ ylide). ^{1}H-NMR ($CDCl_3$): *δ* 8.29 (t, 1H, H_6, C_6H_4, $^4J_{P-H} = 6.9$ Hz), 8.15–6.65 (m, 53H, Ph + C_6H_4), 4.91 (t, 1H, Pd–C(*H*)COPh, $^2J_{P-H} = {}^4J_{P-H} = 5$ Hz), 4.74 (ddd, 1H, PCH_2P, $^2J_{P-H} = 17$, $^2J_{H-H} = 15$, $^2J_{P-H} = 9$ Hz), 4.01 (dt, 1H, PCH_2P, $^2J_{P-H} = 9$ Hz), 3.53 (dt, 1H, C(H)–Pd, $^2J_{P-H} = 9.9$, $^4J_{P-H} = {}^4J_{H-H} = 5$ Hz), 3.02 (d, 1H, C(H) = P, $^2J_{P-H} =$ 25.2 Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): *δ* 36.77 (d, Pd–PPh_2, $^2J_{P-P} = 73$ Hz), 25.27 (d, C_6H_4-2-PPh_2, $^4J_{P-P} = 36$ Hz), 15.78 (dd, Pd–C(H)(COPh)*P*Ph_2), 14.33 (s, C(H)=PPh_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): *δ* 196.11 (d, *C*OPh, $^2J_{P-C} = 3.2$ Hz), 187.55 (t, CO, $^2J_{P-C} = 4.2$ Hz), 175.58 (ddd, C_1, C_6H_4, $^2J_{PtransC} = 133$, $^2J_{PcisC} = 32$, $^2J_{PC} = 6.3$ Hz), 139.06–121.51 (Ph + C_6H_4), 54.02 (dd, C(H)=P, $^1J_{P-C} = 108$, $^3J_{P-C} = 5.5$ Hz), 41.02 (ddd, C(H)Pd, $^1J_{P-C} = 38$, $^2J_{P-C} = 17.3$, $^3J_{P-C} = 5.4$ Hz), 38.83 (d, Pd–*C*(H)COPh, $^1J_{P-C} = 57$ Hz), 33.20 (dd, PCH_2P, $^1J_{P-C} = 66$, $^1J_{PC} = 11$ Hz).

4.7. [Pd(C_6H_4-2-$PPh_2C(H)COC(H)=PPh_3$)-(NC_5H_4-2-CO–N=PPh_3)](ClO$_4$) (6)

Complex **6** was synthesised in the same way as those described for **2**: **1** (0.158 g, 0.096 mmol), NBu_4OH (157 μl, 0.240 mmol), NC_5H_4-2-CO–N=PPh_3 (0.073 g, 0.192 mmol). Obtained: 0.200 g (90% yield).

Anal. Calc. for $C_{63}H_{50}ClN_2O_6P_3Pd$ (1165.87 g mol^{-1}): C, 64.90; H, 4.32; N, 2.40. Found: C, 64.28; H, 4.33; N, 2.54%. MS [m/z, %]: 1065 [$(M-ClO_4)^+$, 100%]. IR (ν, cm^{-1}): 1578 (ν_{CO} iminophosphorane), 1525 (ν_{CO} ylide). ^{1}H-NMR ($CDCl_3$): δ 8.69 (d, 1H, H_6, py, $^3J_{H-H}=4.8$ Hz), 8.55 (d, 1H, H_3, py, $^3J_{H-H}=7.2$ Hz), 8.02 (td, 1H, H_4, py, $^3J_{H-H}=7.2$, $^4J_{H-H}=1.2$ Hz), 7.87–7.07 (m, 42H, Ph + C_6H_4), 6.90 (m, 1H, H_5, py), 6.83 (m, 1H, $H_{5'}$, C_6H_4), 6.63 (d, 1H, $H_{6'}$, C_6H_4, $^3J_{H-H}=7.8$ Hz), 3.83 (dd, 1H, C(H)–Pd, $^2J_{P-H}=6.6$, $^4J_{P-H}=4.5$ Hz), 3.63 (d, 1H, C(H)=P, $^2J_{P-H}=24.9$ Hz). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 27.83 (d, C_6H_4-2-PPh_2, $^4J_{P-P}=1.6$ Hz), 25.75 (s, –N=PPh_3), 14.66 (d, C(H)=PPh_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 187.98 (t, CO, $^2J_{P-C}=2.6$ Hz), 177.40 (d, CO–N=P, $^2J_{P-C}=8$ Hz), 161.52 (d, C_2, py, $^3J_{P-C}=24$ Hz), 153.54 (d, C_1, C_6H_4, $^2J_{PC}=24$ Hz), 149.76 (s, C_6, py), 139.22 (s, C_4, py), 137.30 (d, C_2, C_6H_4, $^1J_{P-C}=114$ Hz), 135.08 (d, C_6H_4, $J_{P-C}=16$ Hz), 134.22 (d, C_6H_4, $J_{P-C}=9$ Hz), 133.59–128.76 (m, Ph + C_6H_4), 128.15, 127.17 (2s, C_3+C_5, py), 126.40 (d, Ph, C_{ipso}, $J_{P-C}=86$ Hz), 125.13 (d, Ph, C_{ipso}, $J_{P-C}=96$ Hz), 125.09 (d, C_6H_4, $J_{P-C}=12$ Hz), 54.05 (dd, C(H)=P, $^1J_{PC}=109$, $^3J_{P-C}=5.6$ Hz), 33.97 (dd, C(H)Pd, $^1J_{P-C}=42$, $^3J_{PC}=17$ Hz).

4.8. cis-[Pd($Ph_2PCH_2PPh_2CHCOMe)_2$](ClO$_4$)$_2$ (7)

Complex **7** was synthesised in the same way as those described for **2**, except that the product was precipitated in MeOH after washing with water: **1** (0.158 g, 0.096 mmol), NBu_4OH (157 μl, 0.240 mmol), [$Ph_2PCH_2PPh_2CH_2COMe$](ClO$_4$) (0.207 g, 0.384 mmol). Obtained: 0.270 g. This product was characterised as a mixture of **7** and the phosphonium–ylide [Ph_3P=C(H)$COCH_2PPh_3$]ClO_4. Pure **7** was obtained by recrystallisation of this mixture from CH_2Cl_2–MeOH. Obtained: 0.126 g (55% yield).

Anal. Calc for $C_{56}H_{52}Cl_2O_{10}P_4Pd{\cdot}CH_2Cl_2$ (1271.122 g mol^{-1}): C, 53.85; H, 4.28. Found: C, 54.27; H, 4.01%. MS [m/z, %]: 1087 [$(M-ClO_4)^+$, 6%]. IR (ν, cm^{-1}): 1637 (ν_{CO}). ^{1}H-NMR (CD_2Cl_2): δ 7.84–7.11 (m, 20H, Ph), 5.75 (m, 1H, C(H)Pd), 4.66 (ddd, 1H, PCH_2P, $^2J_{H-H}=15.6$, $^2J_{P-H}=18$, $^2J_{P-H}=11.1$ Hz), 4.32 (m, broad, PCH_2P, 1H), 2.14 (d, 3H, –C(O)Me, $^4J_{P-H}=0.9$ Hz). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 41.17, 32.05 (AA′XX′ spin system, $^2J_{A-X}=55$, $^3J_{A-X'}=-12$, $^2J_{A-A'}=29.64$, $^4J_{X-X'}=0$ Hz).

Acknowledgements

Funding by the Dirección General de Enseñanza Superior (Spain, project PB95-0003-C02-1) is gratefully acknowledged, and we thank Professor J. Forniés for invaluable logistical support.

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