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New mono- and di-phosphido-bridged Pd^I dimers. Formation of tertiary dialkyl(allyl) phosphines from an allyl complex with a secondary phosphine *

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Abstract

Depending upon the experimental conditions, Cy_2PH reacts with $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ (**1**) giving different Pd^I dimers. $[Pd_2(\mu\text{-}PCy_2)(\mu,\eta^3\text{-}C_3H_5)(PCy_2H)_2]$ (**2**) can be isolated in high yield when performing the reaction with low ratios of phosphine to **1** in acetone, where complex **2** is only sparingly soluble. Higher ratios of phosphine to **1** and apolar solvents favour the formation of the diphosphido-bridged dimer $[\{Pd(\mu\text{-}PCy_2)(PCy_2H)\}_2]$ (**3**); minor amounts of $[Pd_2(\mu\text{-}PCy_2)_2(PCy_2H)(PCy_2allyl)]$ (**4**) and $[\{Pd(\mu\text{-}PCy_2)(PCy_2allyl)\}_2]$ (**5**) were observed as by-products of the reaction. Multinuclear NMR characterization of complexes **2–5** is reported.

Keywords: Palladium; Metal–metal bonds; Phosphide-bridges; Allyl; Dimers; Insertion

1. Introduction

$[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ (**1**) has been successfully employed in the synthesis of tertiary phosphine complexes of Pd^0 [1,2]. Careful control of the reaction conditions allowed the isolation of Pd^I dimeric derivatives of tertiary phosphines with bridging allyl and cyclopentadienyl functionalities [3].

We recently investigated the reactivity of complex **1** with the secondary phosphine P^tBu_2H; the formation of either the mononuclear Pd^0 complex $[Pd(P^tBu_2H)_3]$ [4] or the dimeric Pd^I derivative $[Pd(\mu\text{-}P^tBu_2)(P^tBu_2H)_2]$ [5] was observed, depending upon the reaction temperature, the solvent, and the reagent ratio. The interest in the chemistry of phosphido-bridged dimers stems from their structural flexibility that can bring together metals with a variety of environments. Phosphido-bridged palladium dimers could be special, in view of the well known catalytic properties of mononuclear Pd compounds. We report here the reaction of complex **1** with PCy_2H to give the π-allyl derivative $[Pd_2(\mu\text{-}PCy_2)(\mu,\eta^3\text{-}C_3H_5)\text{-}(PCy_2H)_2]$ (**2**) [6]. Further reaction of complex **2** with PCy_2H gives the bis-phosphido-derivative $[Pd(\mu\text{-}PCy_2)(PCy_2H)]_2$, (**3**). Complex **3** can be prepared alternatively by direct reaction of complex **1** with an excess of PCy_2H. Two dimeric by-products often found to contaminate complex **3** were identified as $[Pd_2(\mu\text{-}PCy_2)_2(PCy_2H)(PCy_2allyl)]$ (**4**) and $[\{Pd(\mu\text{-}PCy_2)(PCy_2allyl)\}_2]$ (**5**) which trap the product of allylation of the secondary phosphines.

2. Results and discussion

As an acetone solution of PCy_2H was dropped at 20°C into an acetone solution of $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ (**1**) (P/Pd molar ratio 1.5), the solution changed quickly from red to bright yellow and a yellow solid precipitated within a few minutes. After workup, a

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* Dedicated to Professor Fausto Calderazzo, in the occasion of his 65th birthday, in recognition of his high example of moral and scientific rigour.

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crystalline product was isolated in 75% yield and was characterized by elemental and spectroscopic analyses as $[Pd_2(\mu\text{-}PCy_2)(\mu,\eta^3\text{-}C_3H_5)(PCy_2H)_2]$ (**2**): The IR spectrum (Nujol, KBr) exhibited (P–H) at 2275 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectrum of benzene solutions of **2** shows a triplet at δ 137.5 ppm and a doublet at δ 15.6 ppm, indicating the presence of three phosphorus ligands in a ratio 1:2. The coupled spectrum and the observation of a significant NOE on the high-field resonance indicate that this is due to two secondary phosphines while the value of the chemical shift of the low-field resonance suggests a phosphido bridging a Pd–Pd moiety [7a].

The ^1H NMR spectrum (Fig. 1) shows the typical pattern of the *H*P function (δ 4.77 ppm) in a system containing two strongly-coupled magnetically non-equivalent secondary phosphines. Neglecting all further couplings, the main features of this multiplet are those of the A part of an $[AX]_2$ (A = P–*H*, X = *P*–H) spin system [8], comprising two main resonances (at 5.07 and 4.48 ppm in Fig. 1) with half intensity of the multiplet, and four pairs of resonances symmetrically arranged around ν_A (δ 4.77 ppm). These overlap in two pairs one within and one outside the main doublet (the broad signals at 5.18, 4.98, 4.56 and 4.36 ppm). The coupling with the methyne hydrogens of the cyclohexyl rings and with the bridging phosphide cause further splittings that are resolved in the two main signals (see insert of Fig. 1). Analysis of the ^{31}P and ^1H spectra allowed the measurement of $^1J_{PH}$ (293 Hz), $^4J_{PH}$(< 1 Hz), $^3J_{P\mu H}$ (9.6 Hz). $^3J_{HH\alpha}$ (5.3 Hz), $^3J_{PP'}$ (105 Hz) and $^2J_{PP\mu}$ (53 Hz).

In the ^1H NMR spectrum, two other groups of resonances can be observed besides the complex overlapping multiplets spanning 2.2–1.0 ppm and due mainly to the cyclohexyl protons. One, at lower field, comprises two multiplets centred at 3.55 and 3.47 ppm with integrated ratio corresponding to 2 and 1 hydrogen atoms, respectively. The second one shows two multiplets centred at 2.61 and 2.50 ppm, (ratio 1:1). A 2D ^1H correlation experiment showed that the signals at 3.55 and 3.45 ppm are coupled together and that both are coupled with other resonances at 1.75 ppm. These signals can be assigned to the *syn*, *meso* and *anti* protons of a μ,η^3-allyl functionality bridging the two metal atoms, by comparison with the values reported for related systems such as $[Pd_2(\mu,\eta^3\text{-}C_3H_5)(PCy_3)_2(\mu\text{-}SPh)]$ [9a], $[Pd_2(\mu,\eta^3\text{-}C_3H_5)(PMe_3)_2(\mu\text{-}SPh)]$ [9b], and $[Pd_2(\eta^5\text{-}C_5H_5)(\mu,\eta^3\text{-}C_3H_4R)L_2]$ [3a].

The two multiplets at 2.61 and 2.50 ppm have been identified by means of a 2D ^1H-^{31}P correlation experiment, as the methyne protons of the phosphido-bridge. The appearance of two distinct resonances for these two hydrogen atoms implies that the allyl moiety is rigid on the NMR time scale, in contrast with what is observed for other dimeric compounds with bridging allyl moieties [10]. This correlation experiment showed also that $^1J_{PH}$ and $^2J_{PP\mu}$ are of opposite sign. Since $^1J_{PH}$ is positive, [11] $^2J_{PP\mu}$ must be negative.

The ^{13}C NMR spectrum and a ^1H-^{13}C correlation experiment performed in the 'reverse mode' confirm these assignments, since they show the resonance of the *meso*-carbon of the π-allyl at 92.0 ppm ($^1J_{CH}$ = 145

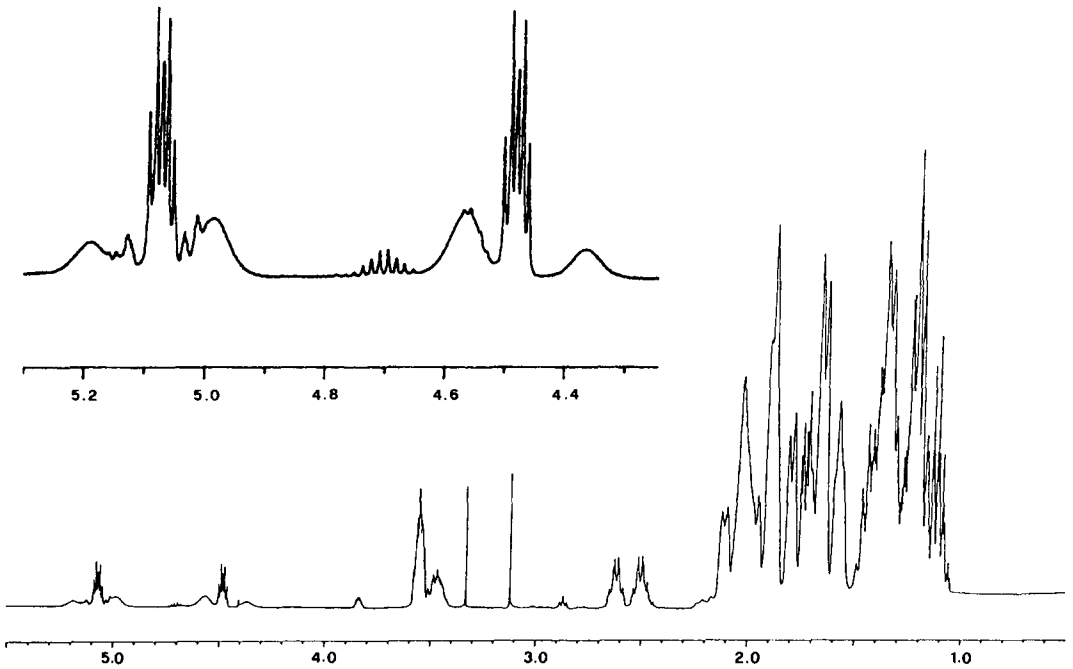
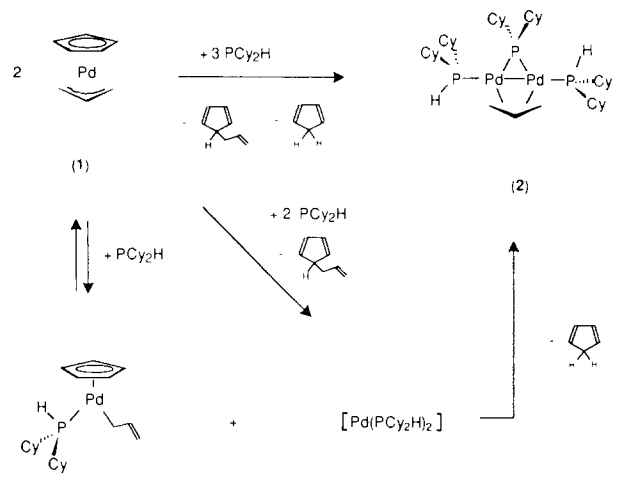
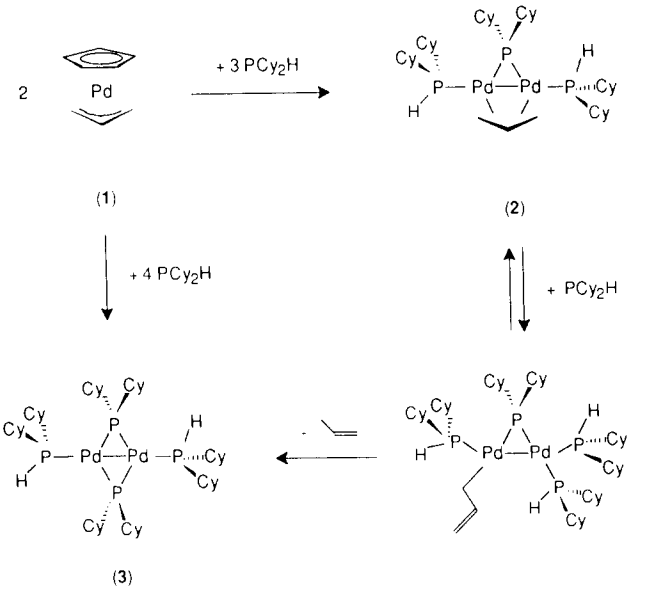


Fig. 1. 1D ^1H NMR spectrum of a solution of compound **2** (500 MHz, 303 K, benzene-d_6).



Scheme 1.



Scheme 2.

Hz) and show also that both the ^{1}H resonances at 3.55 and 1.75 ppm are coupled to a single carbon at 31.7 ppm [3a,12]. The other resonances in the ^{13}C spectrum are more difficult to assign since they appear as overlapping second-order multiplets between 36 and 25 ppm.

Scheme 1 shows our proposal for the formation of complex **2**, in strict analogy with the mechanism of the Werner reaction [1,3] of $[Pd(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(PR_3)]$ with $[Pd(PR_3)_2]$ giving the Pd^1 dimers $[Pd_2(\mu,\eta^5\text{-}C_5H_5)(\mu,\eta^3\text{-}C_3H_5)(PR_3)_2]$ [1,3], the structural analogy of which with complex **2** is obvious. In our system a proton-transfer from a secondary phosphine to the cyclopentadienyl group causing loss of C_5H_6 and the formation of the phosphido-ligand (both allylcyclopentadiene and cyclopentadiene were detected as products of the reaction) accounts for the only significant difference from the Werner dimers.

Similar reactions of $[Pd(\eta^3\text{-}C_3H_5)(PR_3)(X)]$ (X = SR or OAc) with $[Pd(PR_3)_2]$, giving the related dimers $[Pd_2(\mu,\eta^3\text{-}C_3H_5)(\mu\text{-}X)(PR_3)_2]$, have been reported [9].

Complex **2** reacts with an equimolar amount of PCy_2H in dimeltoxyethane (DME). The solution slowly changed from the original yellow to orange and then to red and a red solid was isolated and characterized as $[\{Pd(\mu\text{-}PCy_2)(PCy_2H)\}_2]$ (**3**). Complex **3** was also obtained by the reaction of complex **1** with a twofold molar excess of the phosphine in DME. Complex **1** is rapidly and quantitatively transformed to complex **2** which then slowly gives complex **3** as demonstrated by $^{31}P\{^{1}H\}$ NMR spectra.

Complex **3** is believed to form (Scheme 2) by addition of a phosphine to complex **2**, with the allyl ligand switching from μ,η^3-bridging to η^1-terminal coordination. Subsequent elimination of propene (identified by GC in the reaction mixture) gives the diphosphido-bridged derivative.

The $^{31}P\{^{1}H\}$ NMR spectrum of compound **3** shows two sharp first-order triplets at $\delta = 238.0$ and 14.2 ppm ($J_{PP} = 39$ Hz). Their integrated intensity ratio obtained from a spectrum decoupled without NOE is 1 : 1. The significant NOE effect exhibited by the high-field resonance suggests that compound **3** is a dimer containing two terminal secondary phosphines and two phosphides bridging the two metal atoms in a symmetrical arrangement similar to that found in the X-ray crystal structure of the t-butyl analogue $[\{Pd(\mu\text{-}P^tBu_2)(P^tBu_2H)\}_2]$ [5]. The low-field part of the ^{1}H spectrum shows the resonances of the *H*–P function ($\delta = 5.07$ ppm) with the main pair of signals exhibiting a more complex pattern compared to compound **2**, due to the presence of two phosphido-ligands (Fig. 2). Selective decoupling of the ^{31}P resonances (Fig. 3) and partial computer simulations of the $[AXYM_2Z_2]_2$ spin system (A = *H*–P,

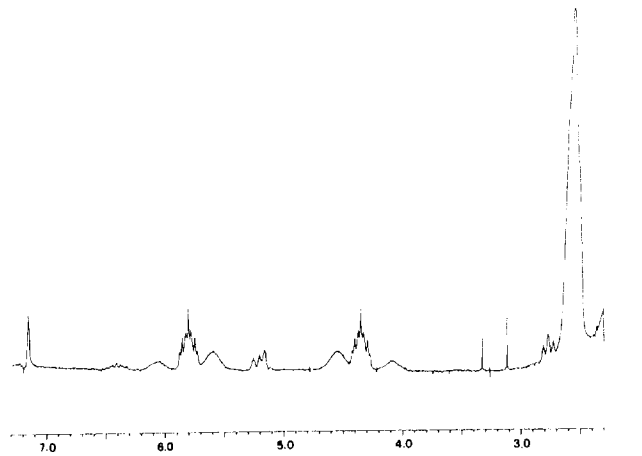


Fig. 2. 1D ^{1}H NMR spectrum of a solution of compound **3** (200.13 MHz, 295 K, benzene-d_6).

X = H–*P*, Y = P_μ, M = *H*–C–P_t, Z = *H*–C–P_μ) allowed a better estimate of the structural parameters [$^1J_{HP}$ = 290 Hz, $^4J_{HP'}$ = 1 Hz, $J_{PP'}$ = 93 Hz, $^3J_{HH\alpha}$ = 4.3 Hz, $J_{HP\mu}$ = 11 Hz].

A 2D ^{1}H-^{31}P correlation experiment performed in the reverse mode indicated that the proton resonance at 2.5 ppm belongs to the phosphide cyclohexyl rings, and confirmed that $^1J_{PH}$ and $^2J_{PP\mu}$ are of opposite sign.

With both the synthetic procedures of Scheme 2 the reagent conversion is quantitative and complex **3** is formed in > 80% yields, but only occasionally of high purity, as can be seen also from the above spectra. Two other dinuclear compounds were often found to contaminate the main product and they have been identified as [$Pd_2(\mu$-$PCy_2)_2(PCy_2H)(PCy_2$ allyl)] (**4**) and [{$Pd(\mu$-$PCy_2)(PCy_2$ allyl)}$_2$] (**5**). ^{1}H and ^{31}P{^{1}H} NMR spectra of a typical reaction mixture are shown in Fig. 4. The ^{31}P{^{1}H} spectrum shows at low field three sharp triplets at δ 238.0 ppm ($^2J_{PP}$ = 39 Hz), 234.1 ppm ($^2J_{PP}$ = 40 Hz), 229.7 ppm ($^2J_{PP}$ = 40 Hz) and two sets of overlapping multiplets around 38–36 and 15–13 ppm. The low-field region is the most sensitive for the recognition of differences among these compounds, and on this basis, three main products (relative ratio 1/1.8/ca. 0.8) containing phosphides and two terminal phosphines can be recognized. One of these is compound **3** (triplets at δ 238.0 and 14.2 ppm). As for the other two compounds, the integration of the signals in a decoupled spectrum without NOE indicates that the multiplet at medium field is a superposition of a doublet of triplets (δ 37.1 ppm, J = 99 and 40 Hz) and of a triplet (δ 36.2 ppm, J = 40 Hz) whose intensity ratios with respect to the resonances at 234.1 and 229.7 ppm are 1:2 and 1:1, respectively. In the high-field region, the triplet at 14.2 ppm due to compound **3** overlaps with the low-field part of a doublet of triplets (δ 13.6 ppm J = 99 and 40 Hz), whose intensity is one half of that of the signal at 234.1 ppm. A ^{31}P 2D correlation experiment confirmed the assignments of the resonances (Fig. 5) to compounds **3**, **4** and **5**, indicating that the two new products contain respectively one and two phosphines other than PCy_2H as terminal ligands. In addition, Fig. 5 shows that the phosphido-signal at 234.1 ppm is a doublet of doublets that appears as a triplet due to the accidental coincidence of the coupling constants with the two different phosphines. These values, similar to those of **3** and **5** indicate a structural similarity of the three compounds.

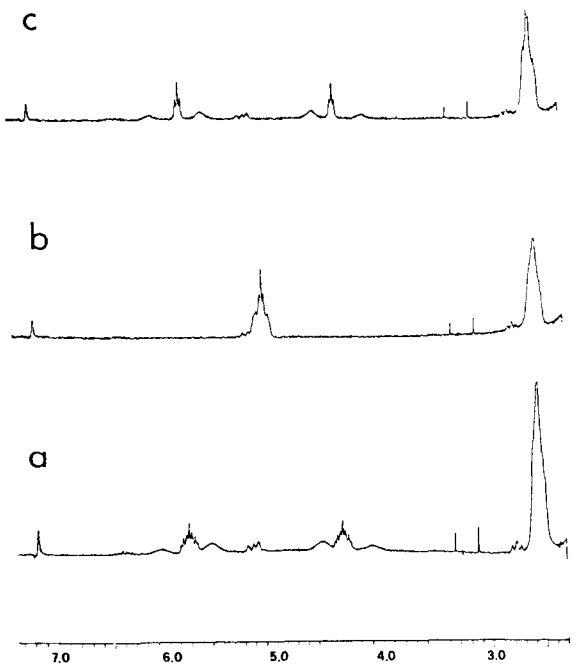


Fig. 3. 1D ^{1}H NMR decoupling from ^{31}P of compound **3** (200.13 MHz, 295 K, benzene-d_6): a) coupled to ^{31}P; b) ^{31}P selective decoupling at 14.2 ppm; c) ^{31}P selective decoupling at 238.0 ppm.

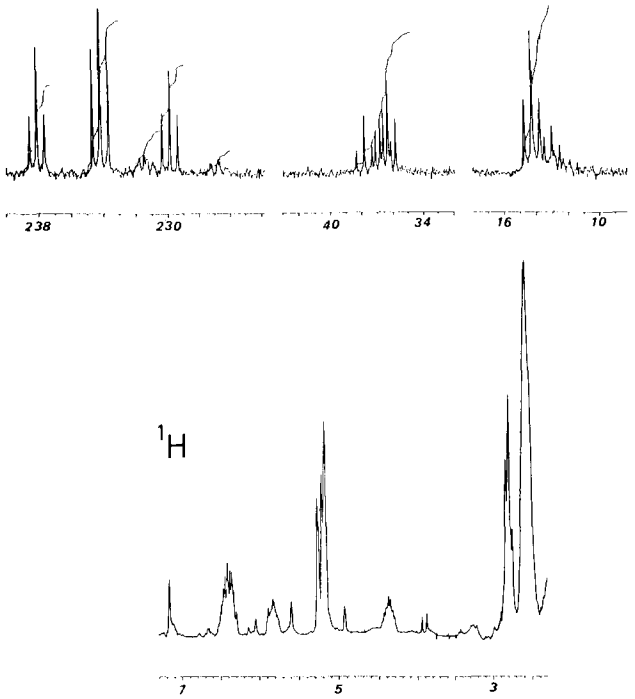


Fig. 4. Bottom: 1D ^{1}H NMR spectrum of a reaction mixture containing **3**, **4** and **5** (200.13 MHz, 295 K, benzene-d_6). Top: 1D ^{31}P{^{1}H} NMR spectrum of a solution of a reaction mixture containing **3**, **4** and **5** (81.015 MHz, 295 K, benzene-d_6).

The coupled ^{31}P NMR spectrum showed that the new ligands are tertiary phosphines and the nature of the third substituent on the phosphorus atoms has been clarified by a 2D ^{1}H homonuclear correlation experiment and a 2D ^{1}H-^{31}P correlation experiment. The ^{1}H NMR spectrum is very difficult to assign, with the superposition of the signals of at least three main species, but the complex multiplet at 6.4 ppm and the resonances at 5.3–5.1 ppm (Fig. 4) suggests the presence of a η^1-allyl moiety [13]. The 2D ^{1}H COSY spectrum shows that these signals are coupled together, and also with the multiplet at 2.8 ppm. The

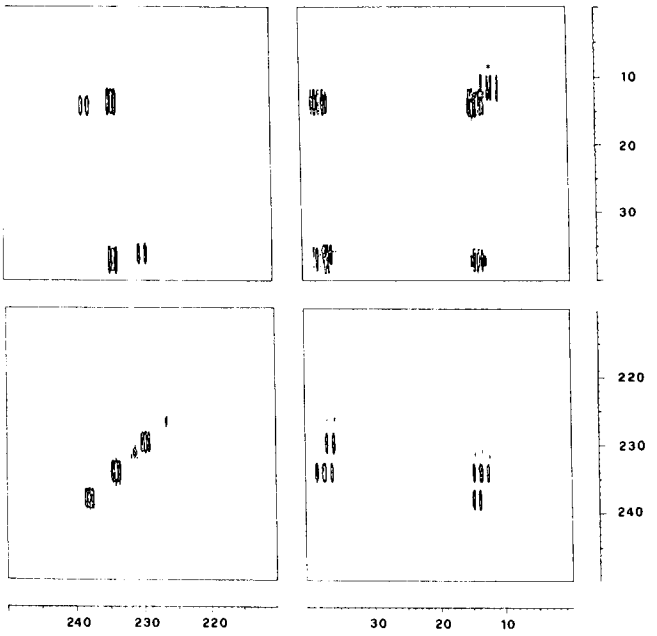


Fig. 5. 2D $^{31}P\{^1H\}$ correlation experiment of a reaction mixture containing **3**, **4** and **5** (81.015 MHz, 295 K, benzene-d_6). 128 transients have been recorded (SW 24000 Hz, 4 K data points) for 256 t_1 increments. Data have been zero-filled to 2 K in F_1 and sine-bell and sine-bell squared weighting functions have been applied in F_2 and in F_1, respectively. The diagonal peak marked with * is due to an impurity.

possibility that the allyl fragment is directly bound to the metal can be excluded because of the symmetry of the $^{31}P\{^1H\}$ NMR spectrum. Moreover, the coupling constant between the terminal phosphines in compound **4** is very similar to that observed in compound **3** (99 vs. 93 Hz). The ^1H-^{31}P 2D correlation experiment confirms that the allyl is directly bound to phosphorus.

As shown in Fig. 6, the phosphines at 38–36 ppm are both coupled with the allyl resonances while all the other signals show coupling with the *H*–P hydrogen of the secondary phosphines, apart from the upfield phosphido-signal that belongs to compound **5**, which contains two tertiary phosphines. Fig. 6 confirms that $^1J_{HP}$ and $^2J_{PP\mu}$ have opposite signs, as have $^2J_{HP}$ and $^3J_{PP'}$.

A $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture of **3**, **4** and **5** showed signals at δ ca. 137.2, 115.1, 38.8 and 36.7 ppm, besides overlapping multiplets spanning 34–24 ppm. The two downfield signals are slightly broadened (137.2 ppm) or doubled (115.1 ppm), as expected for a mixture of structurally related compounds. A DEPT experiment indicated that the two downfield signals are assignable to CH and CH_2, respectively, and they therefore arise from the methyne and terminal methylene carbon atoms of the η^1-allyl moieties. The chemical shifts are closer to those observed for free [14] and bound [15] P(η^1-allyl)$(Cy)_2$ [$-CH_2-C(H)=CH_2$ 137.5 and 134.5 ppm; $-CH_2-C(H)=CH_2$ 115.5 and 117.0 ppm] than to those observed for the η^1-allyl fragment directly bound to a metal (see for instance 148.1 and 100.0 ppm for [Pd(η^1-allyl)(μ,η^3-allyl)PMe_3]) [12,13], which is further support for the structural characterization.

The P–P′ coupling constants between the terminal phosphines are very similar to those observed for other Pd–Pd moieties bridged by a phosphide in trinuclear clusters (see for instance $[Pd_3(\mu\text{-}PCy_2)_2(\mu\text{-}EPh)(PCy_2H)_2(EPh)]$ [(**6**), E = S; (**7**), E = Se][16] 89 Hz, or $[Pd_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(PEt_3)_3]^+$ (**8**) 93 Hz and related derivatives) [17] while the values reported for dimeric compounds show a greater range of values, e.g. 200 Hz in $[Pd_2(\mu\text{-}PPh_2)(\mu\text{-dppm})(PPh_3)_2]^+$ (**9**) [18], or 49 Hz in $[Pd_2(\mu\text{-}P^tBu_2)(\mu\text{-}P^tBu_2H)(P^tBu_2H)_2]^+$ (**10**) [19]. However, both the last compounds are distorted observed due to the chelating diphosphine or the bridging secondary phosphine. In contrast, the absolute magnitude of the coupling between the terminal and bridging phosphorus atoms increases on passing from the trimers **6** and **7** (−28, −26 Hz, estimated from computer simulations) [16] or **8** (−11 Hz) [17] to the dimers discussed here. All the experimental results indicate a negative sign for this coupling when the phosphide bridges a metal–metal interaction, at variance from what is obtained for other dimers without a Pd–Pd bond [7b]. Due to the symmetry, we could obtain no information on the sign of $^3J_{P\mu P\mu}$.

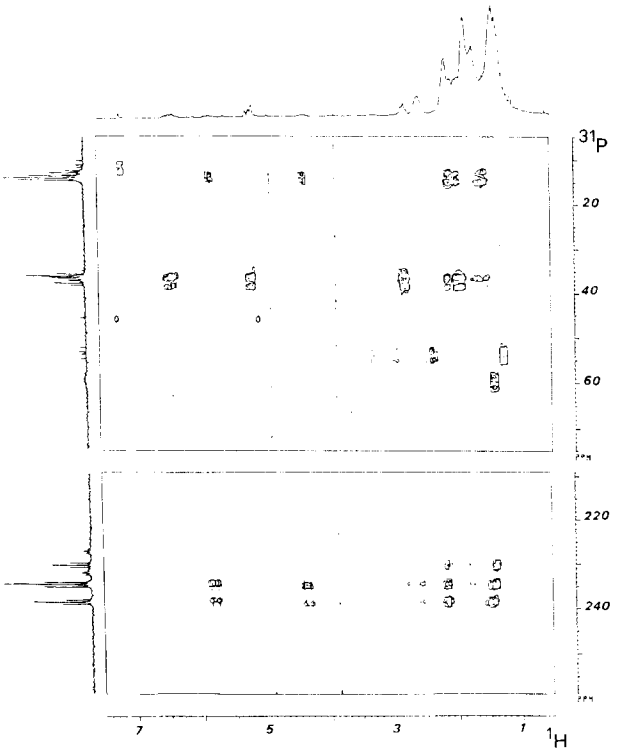
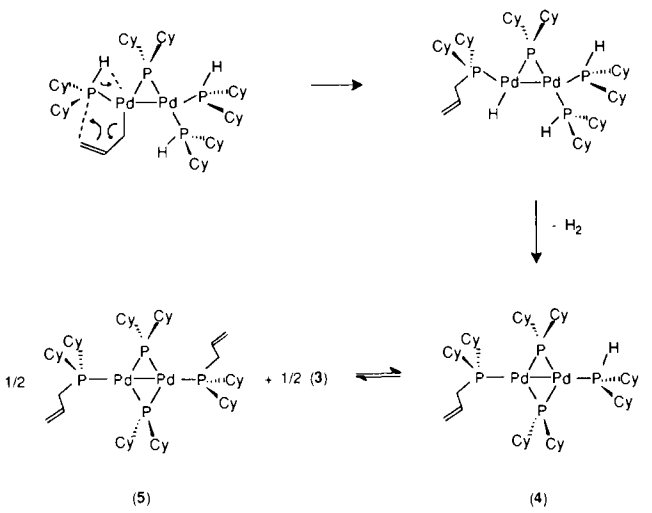


Fig. 6. 2D ^1H-^{31}P reverse heteronuclear correlation experiment of a reaction mixture containing **3**, **4** and **5**. 72 transients have been recorded (SW2 = 1600 Hz, 1024 data points) for 512 t_1 increments (SW1 = 24000 Hz). Data have been zero-filled to 1 K in F_1 and sine-bell weighting functions have been applied in both dimensions.



Scheme 3.

In the absence of a mechanistic study concerning the reaction of **2** with PCy_2H giving **4** and **5**, we can only make assumptions as regards the reaction pathway. The net result of the reaction is the transformation of a Pd-coordinated secondary phosphine into a Pd-coordinated tertiary allylphosphine, in other words, the breaking of a P–H bond and the formation of a P–C bond.

Our recent studies on palladium complexes with secondary phosphine have shown the requirements for Pd to activate the P–H bond. These include a Pd–H–P agostic interaction as in $[Pd_2(\mu\text{-}P^tBu_2)(\mu\text{-}P^tBu_2H)(P^tBu_2H)_2]CF_3SO_3$ [19] and the transformation of Pd-coordinated secondary phosphines into bridging phosphide with concomitant dihydrogen evolution, as in the synthesis of $[\{Pd(\mu\text{-}P^tBu_2)(P^tBu_2H)\}_2]$ [4,5].

If these factors are considered in respect of the system reported in this paper the formation of **4** can reasonably be explained by the reaction path reported in Scheme 3 (dihydrogen evolution was confirmed by GC analysis). The formation of **4** also accounts for the presence in the reaction mixture of small amounts of **5**, which can be related to **4** through the equilibrium shown in the lower part of Scheme 3. In contrast, the ability of complexes $[(\eta^3\text{-}C_3H_5)Pd(L)(X)]$ (L = tertiary phosphine, X = OAc, OPh, or halogen) to promote the allylation of tertiary phosphine ligands producing phosphonium salts is well known [9a]. In the present case, the activation of the P–H bond and the possible hydride transfer and H_2 elimination lead to the stabilization of a neutral derivative instead of a phosphonium salt.

Though metal-mediated P–C bond cleavage is much more frequent [20] the formation of new P–C bonds from metal-phosphido-derivatives has some precedent in other metal systems [21].

3. Experimental section

3.1. General data

All preparations and manipulations were carried out under purified dinitrogen using standard Schlenk techniques. Solvents were purified by refluxing them over an appropriate drying agent, and were distilled prior to use. $[CpPd(\eta^3\text{-}C_3H_5)]$ was prepared as described [22] and sublimed prior to use; PCy_2H was prepared according to the literature [23]. IR spectra were recorded as Nujol mulls (KBr) on a Perkin Elmer 1725X FT-IR spectrophotometer. Benzene-d_6 solutions of compounds **2**, **3** and of isolated reaction mixtures were prepared dissolving 15 mg or 80 mg of the products in 500 μl of the solvent under dinitrogen for recording ^1H or heteronuclear NMR spectra. The solutions were also degassed by freeze-thaw cycles. Apart from a ^1H 1D spectrum of compound **2** recorded on a Bruker AM500 at 303 K, all the NMR measurements were performed at 295 K on a Bruker AC200 spectrometer operating at 200.13, 81.015 and 50.327 MHz for ^1H, ^{31}P, and ^{13}C, respectively. The instrument is equipped with a 5 mm inverse probe. A BSV3 unit with a second synthesizer and a power amplifier allows decoupling and pulsing at heteronuclear frequencies while observing ^1H. The length of the 90° pulses through the BSV3 unit was 11 μs for ^{31}P, and 35 μs for ^{13}C. The HMQC [24] pulse sequence was used for the 2D ^1H-^{31}P NMR experiments performed in the reverse mode (D2 = 25 ms), while the BIRD [25] pulse sequence (D4 = 0.17 s) has been used for the 2D ^1H-^{13}C reverse experiment. Further details are reported as captions to the figures. Computer simulations were performed using a modified version of the UEA NMR Basic program with no iterative procedure.

3.2. Preparation of $[Pd_2(\mu\text{-}PCy_2)(\mu\text{-}\eta^3\text{-}C_3H_5)(PCy_2H)_2]$ (2)

PCy_2H (434.5 mg, 2.19 mmol) was added to a red-coloured acetone (50 ml) solution of $[CpPd(\eta^3\text{-}C_3H_5)]$ (310.4 mg, 1.46 mmol). The solution quickly turned bright yellow and a yellow crystalline solid started to precipitate in a few minutes. The suspension was left for 3 h at −30°C, and the yellow solid was filtered off and vacuum dried, yielding 420 mg (71%) of complex **2**. Anal. Calcd. for $C_{39}H_{73}P_3Pd_2$: C, 55.3; H, 8.68. Found: C, 55.0; H, 8.59%.

NMR ^1H δ 4.77 [2H, m, $^1J_{HP}$ 293 Hz, $^4J_{HP} < 1$ Hz, $^3J_{HP\mu}$ 9.6 Hz, $^3J_{HH}$ 5.3 Hz, 2 *H*–P], 3.55 [2H, m, 2 H *syn*-allyl], 3.47 [1H, m, H *meso*-allyl], 2.61–2.50 [*H*–C_α–P_μ], 2.02–2.03 [*H*–C_α], 1.75 [H *anti*-allyl]; $^{31}P\{^1H\}$ δ 15.5 ppm [2 P, d, $^2J_{PP\mu}$ 53 Hz, 2 P_t], 137.5 [1 P, t, 1 P_μ]; $^{13}C\{^1H\}$ δ 92.0 [1 C, d, $^1J_{CH}$ = 145 Hz, CH_2–*C*H–CH_2], 31.7 [2 C, m, *C*H_2–CH–CH_2].

3.3. Preparation of $[\{Pd_2(\mu\text{-}PCy_2)(PCy_2H)\}_2]$ (3)

Method a): PCy_2H (49 mg, 0.247 mmol) was added to a yellow solution of complex **2** (192 mg, 0.226 mmol) in DME (25 ml). The solution slowly turned red and was left for 3 days at room temperature and then overnight at −30°C. The red solid which precipitated was filtered off and vacuum-dried (142 mg, 0.141 mmol, 62.6% yield). Anal. Calcd. for $C_{48}H_{90}P_4Pd_2$: C, 57.4; H, 9.04. Found: C, 56.9; H, 9.00%. NMR: ^1H δ 5.07 [2H, m, $^1J_{HP}$ 290 Hz, $^4J_{HP}$ 1 Hz, $^3J_{HP\mu}$ 11 Hz, $^3J_{HH}$ 4.3 Hz, 2 *H*–P] 2.55 [2H, m, *H*–C_α–P_μ]; $^{31}P\{^1H\}$ δ 14.2 ppm [2 P, t, $^3J_{PP'}$ 93 Hz, $^2J_{PP\mu}$ − 39 Hz, 2 P_t], 238.0 [2 P, t, 2 P_μ].

Method b): PCy_2H (0.98 g, 4.94 mmol) was added to a solution of $CpPd(\eta^3\text{-}C_3H_5)$ (335 mg, 1.564 mmol) in DME (50 ml). The solution was heated under reflux for 3 h and the solvent was evaporated, leaving a red oil. After addition of acetone (30 ml) and vigorous stirring, the oil solidified and was filtered off and vacuum-dried. IR and NMR spectra were identical to those of a sample prepared by method a), though variable amounts (5–30%) of complexes **4** and **5** were found as by-products. NMR: Compound **4** ^1H δ 6.4 [m, *H*–C(=CH_2)–CH_2–], 5.3–5.1[m, H–C(=C*H*$_2$)–CH_2–], 2.8 [m, H–C(=CH_2)–C*H*$_2$–]; $^{31}P\{^1H\}$ δ 13.6 [1 P, dt, $^3J_{PP'}$ 99 Hz, $^2J_{PP\mu}$ −40 Hz, 1 P_t], 37.1 [1 P, dt, $^3J_{PP'}$ 99 Hz, $^2J_{PP\mu}$ −40 Hz, 1 P_t], 234.1 ppm [2 P, t, $^2J_{PP\mu}$ −40 Hz, 2 P_μ]. Compound **5** ^1H δ 6.4 [m, *H*–C(=CH_2)–CH_2–], 5.3–5.1 [m, H–C(=C*H*$_2$)–CH_2–], 2.8 [m, H–C(=CH_2)–C*H*$_2$–]; $^{31}P\{^1H\}$ δ 36.2 [2 P, t, $^2J_{PP\mu}$ −40 Hz, 2 P_t], 229.7 ppm [2 P, t, $^2J_{PP\mu}$ −40 Hz, 2 P_μ].

Supplementary material available

1D $^{13}C\{^1H\}$ and 2D ^1H phase sensitive correlation NMR spectra of complex **2**, 1D $^{31}P\{^1H\}$ and 2D ^1H-^{31}P reverse heteronuclear correlation NMR spectra of complex **3**, 2D ^1H magnitude correlation NMR spectrum of a reaction mixture containing **3**, **4** and **5** (5 pp).

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References and notes

[1] (a) H. Werner, *Angew. Chem. Int. Ed. Engl., 16* (1977) 1; (b) G. Parker and H. Werner, *Helv. Chim. Acta, 56* (1973) 2819.
[2] (a) S. Otsuka, T. Yoshida, M. Matsumoto and K. Nakatsu, *J. Am. Chem. Soc., 98* (1976) 5850; (b) T. Yoshida and S. Otsuka, *Inorg. Synth., 19* (1979) 101; (c) T. Yoshida and S. Otsuka, *Inorg. Synth., 28* (1990) 113.
[3] (a) A. Kühn and H. Werner, *J. Organomet. Chem., 179* (1979) 421; (b) H. Werner and A. Kühn, *Chem. Ber., 113* (1980) 2291.
[4] P. Leoni, *Organometallics, 12* (1993) 2432.
[5] P. Leoni, M. Sommovigo, M. Pasquali, P. Sabatino and D. Braga, *J. Organomet. Chem., 423* (1992) 263.
[6] The preparation of complex **2** has been briefly described by M. Pasquali, F. Marchetti, P. Leoni, T. Beringhelli and G. D'Alfonso, *Gazz. Chim. It., 11* (1993) 659.
[7] (a) A.J. Carty, S.A. MacLaughlin, D. Nucciarone, in J.G. Verkade and L.D. Quin (eds.), *Methods in Stereochemical Analysis*, vol. 8. p. 559 New York, 1987; (b) p. 609 and references therein.
[8] H. Gunther, in *NMR Spectroscopy*, J. Wiley and Sons, New York, 1980 p. 171.
[9] (a) T. Yamamoto, M. Akimoto, O. Saito and A. Yamamoto, *Organometallics, 5* (1986) 1559; (b) K. Osakada, Y. Ozawa and A. Yamamoto, *J. Organomet. Chem., 399* (1990) 341; (c) K. Osakada, T. Chiba, Y. Nakamura, T. Yamamoto and A. Yamamoto, *Organometallics, 8* (1989) 2602.
[10] See for instance R. Benn, A. Rufinska and G. Schroth, *J. Organomet. Chem., 217* (1981) 91.
[11] K.R. Dixon, in J. Mason (ed.), *Multinuclear NMR*, Plenum Press, New York, 1987, p. 390; J.G. Verkade and J.A. Mosbo, in J.G. Verkade and L.D. Quin (eds.), *Methods in Stereochemical Analysis*, VCH, New York, 1987, vol. 8, p. 425.
[12] P.W. Jolly and R. Mynott, *Adv. Organomet. Chem., 19* (1981) 257.
[13] See for instance B. Henc, P.W. Jolly, R. Salz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard and C. Kruger, *J. Organomet. Chem., 191* (1980) 449 and references therein.
[14] R. Mynott, personal communication.
[15] K. Jonas, E. Deffense and D. Habermann, *Angew. Chem. Suppl.*, (1983) 1005.
[16] M. Sommovigo, M. Pasquali, M. Marchetti, P. Leoni, T. Beringhelli, *Inorg. Chem., 33* (1994) 2651.
[17] K.R. Dixon and A.D. Rattray, *Inorg. Chem., 17* (1978) 1099.
[18] N. Hadj-Bagheri, J. Browning, K. Dehghan, K.R. Dixon, N.J. Meanwell and R. Vefghi, *J. Organomet. Chem., 396* (1990) C47.
[19] (a) A. Albinati, F. Lianza, M. Pasquali, M. Sommovigo, P. Leoni, P.S. Pregosin and H. Ruegger, *Inorg. Chem., 30* (1991) 4690; (b) P. Leoni, M. Pasquali, M. Sommovigo, F. Laschi, P. Zanello, A. Albinati, F. Lianza, P.S. Pregosin and H. Ruegger, *Organometallics, 12* (1993) 1702.
[20] (a) M. Sommovigo, M. Pasquali, P. Leoni, D. Braga and P. Sabatino, *Chem. Ber. 124* (1991) 97; (b) P.E. Garrou, *Chem. Rev., 85* (1985) 171.
[21] R.T. Baker, J.C. Calabrese, R.L. Harlow and I.D. Williams, *Organometallics, 12* (1993) 830, and references therein.
[22] Y. Tatsuno, T. Yoshida and S. Otsuka, *Inorg. Synth., 19* (1979) 220.
[23] (a) K. Issleib and A.Z. Brack, *Anorg. Allg. Chem., 277* (1954) 258; (b) K. Issleib and A. Tzschach, *Chem. Ber., 92* (1959) 704; (c) E.C. Ashby, R.N. DePriest and W.-Y. Su, *Organometallics, 3* (1984) 1718.
[24] A. Bax, R.H. Griffey and B.L. Hawkins *J. Magn. Reson., 55* (1983) 301.
[25] A. Bax and S. Subramamian, *J. Magn. Reson., 67* (1986) 565.