ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 586 (1999) 234–240

Journal of Organometallic Chemistry

Reactivity of BH_3 and 9-BBN towards palladium(II) complexes of diphenylvinyl- and diphenylallyl-phosphine; X-ray structures of $[PdCl_2(PPh_2CH_2CH_2CH_3)]_2$ and $[PdCl_2(PPh_2CH_2CH{=}CH_2)]_2$

Simon J. Coles [a], Paul Faulds [b], Michael B. Hursthouse [a], David G. Kelly [b,*], Georgia C. Ranger [b], Andrew J. Toner [b], Neil M. Walker [b]

[a] *Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK*
[b] *Department of Chemistry and Materials, Manchester Metropolitan University, Chester Street, Manchester, M1 5GD, UK*

Received 8 April 1999

Abstract

Palladium(II) chloride complexes $PdCl_2L_2$ and $[PdCl_2L]_2$ have been prepared with the phosphine ligands $PPh_2CH{=}CH_2$ and $PPh_2CH_2CH{=}CH_2$. The reactions of $PdCl_2L_2$ complexes with thf·BH_3 afford equilibria in which the components may be identified by $^{31}P\{^1H\}$-NMR spectroscopy. $PdCl_2L_2$ and $[PdCl_2L]_2$ complexes and phosphine–borane adducts are observed. In addition, analogues of the $PdCl_2L_2$ and $[PdCl_2L]_2$ complexes are present in which one or both phosphine ligands have undergone alkene hydroboration. The reaction of $PdCl_2(PhCN)_2$ and the cyclic adduct formed between 9-BBN and $PPh_2CH_2CH{=}CH_2$ [cyclo-(9-borabicyclo[3.3.1]nonanyl)-propyl(diphenyl)phosphine] has been studied. Opening of the P–B dative bond occurs with the formation of a $[PdCl_2L']_2$ complex in which the phosphine ligand contains a pendant borane moiety. Hydrolysis in air yields the crystallographically characterised dimer $[PdCl_2(PPh_2CH_2CH_2CH_3)]_2$. The X-ray structure of the unsaturated analogue, $[PdCl_2(PPh_2CH_2CH{=}CH_2)]_2$, has also been obtained. Both compounds exist as symmetrical dimeric structures with terminal and asymmetric bridging halides.

Keywords: Phosphine–borane; Hydroboration; Alkenylphosphine; Palladium(II); Borabicyclononane

1. Introduction

Considerable current interest exists in the resolution of chiral tertiary phosphines via the formation of phosphine–borane adducts [1]. Although many phosphines may only react with boranes to form adducts, those possessing additional functionalities can offer alternative reaction pathways [2]. Moreover, given appropriate conditions a single borane moiety may react with both phosphine and a secondary functionality to afford cyclised products. The reactivity of ω-alkenyldiphenylphosphines towards BH_3 and 9-BBN has been investigated for vinyl-, allyl- and butenyl-substituted phosphines [3]. B–P donor/acceptor formation predominates, presumably due to the additional stability derived from the Umpolung [4]. When BH_3 is utilised, alkene hydroboration can only be achieved by the addition of a second equivalent of BH_3, whereas intramolecular hydroboration occurs with 9-BBN resulting in cyclised adducts [3]. The present study focuses on the effect of phosphine complexation on the reactivity of BH_3 and 9-BBN towards diphenylvinyl- and diphenylallylphosphines. Complexes of palladium(II) chloride were selected for this study as a general class of complexes for which synthesis, structure and ligand lability are firmly established [5–8].

2. Results and discussion

2.1. Synthesis of complexes with diphenylvinyl- and diphenylallylphosphine

The chemistry of tertiary phosphine complexes of palladium(II) has been extensively studied. Within the

* Corresponding author. Fax: +44-161-2476357.
E-mail address: d.g.kelly@mmu.ac.uk (D.G. Kelly)

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00283-1

present work further characterisation of the specific diphenylvinyl- and diphenylallyl-phosphine complexes has only been undertaken to provide $^{31}P\{^1H\}$-NMR data necessary for the elucidation of BH_3 and 9-BBN reactivity. Thus, the reported complex $PdCl_2(PPh_2CH{=}CH_2)_2$ (**1**) [8], as well as $PdCl_2(PPh_2CH_2CH{=}CH_2)_2$ (**2**) were prepared by the normal route of reacting two equivalents of phosphine with $PdCl_2(PhCN)_2$. As expected, both complexes exist as *cis* and *trans* isomers in solution.

The general class of *sym*-$[PdCl_2P]_2$ complexes has been known since the early studies of Mann et al. [9] The complexes $[PdCl_2(PPh_2CH{=}CH_2)]_2$ (**3**) and $[PdCl_2(PPh_2CH_2CH{=}CH_2)]_2$ (**4**) can be prepared by the 1:1 reaction of $PdCl_2(PhCN)_2$ and tertiary phosphine or by 1:1 reaction of **1** or **2** with $PdCl_2(PhCN)_2$. Compound **4** can also be isolated from the reaction of $NiCl_2(PPh_2CH{=}CH_2)_2$ (**5**) with two equivalents of $PdCl_2(PhCN)_2$. $^{31}P\{^1H\}$-NMR studies suggest that the modification of reaction stoichiometry in the latter affords **2** at 1:1 Ni:Pd ratios with no evidence for the formation of Ni_2 or NiPd dimeric species. In contrast to the very numerous crystallographic characterisations of $PdCl_2P_2$ complexes, those of *sym*-$[PdCl_2P]_2$ compounds are sparse. Hence, the X-ray structure of **4** has been obtained (Section 2.3).

BH_3 reactivity studies (Section 2.2) result in incomplete hydroboration of the available ω-alkenyl functionalities. Consequently, moderately complex $^{31}P\{^1H\}$-NMR data corresponding to unsaturated and hydroborated phosphines in a series of environments are observed. Isomerisation and equilibration renders the separation of these components impractical. Thus, to corroborate the assignment of the various species the $^{31}P\{^1H\}$-NMR chemical shifts of model systems have been obtained for comparative purposes. $PPh_2CH{=}CH_2/PPh_2CH_2CH_3$ and $PPh_2CH_2CH{=}CH_2/PPh_2CH_2CH_2CH_3$ provide suitable and readily available ligand combinations. The use of hydroborated vinyl and allyl derivatives in such studies would be ideal, however, the preference for phosphine–borane formation precludes this alternative.

The mechanisms of P-donor exchange [6], anion exchange [8] and isomerisation [10] in PdX_2P_2 have been examined in numerous publications. The present reactions do not aim to reiterate these studies, aiming simply to assign the $^{31}P\{^1H\}$-NMR resonances of the specific phosphine complexes relevant to the present work. Thus 2:1 molar ratios of $PPh_2CH{=}CH_2$:$PPh_2CH_2CH_3$ were reacted with $PdCl_2(PhCN)_2$ in a total phosphine:palladium ratio of 2:1. Data for *cis* and *trans* isomers of $PdCl_2L^I_2$, $PdCl_2L^{II}_2$ ($L^I = PPh_2CH{=}CH_2$; $L^{II} = PPh_2CH_2CH_3$) correspond to those reported by Nelson [7] and Grim [5], respectively, Table 1. Resonances with small upfield or downfield shifts from the these symmetrical complexes are assigned to $PdCl_2L^IL^{II}$ complexes in accord with earlier studies [6]. $^2J_{PP}$ coupling constants correspond well with published work [6,11]. Traces of *sym*-$[PdCl_2L^I]_2$ and *sym*-$[PdCl_2L^{II}]_2$ complexes are also observed as downfield resonances [5,12]. Reactions using $L^{III} = PPh_2CH_2CH{=}CH_2$ and $L^{IV} = PPh_2CH_2CH_2CH_3$ afford comparable data; *cis* and *trans* isomers of $PdCl_2L^{III}_2$, $PdCl_2L^{IV}_2$ and $PdCl_2L^{III}L^{IV}$, plus *sym*-$[PdCl_2L^{III}]_2$ and *sym*-$[PdCl_2L^{IV}]_2$ complexes being observed (Table 1). A zero $^2J_{PP}$ coupling for *trans*-$PdCl_2L^{III}L^{IV}$ is recorded, this may result from the pseudo-symmetry of the sterically and electronically similar allyl- and propyl-substituted phosphines or from ligand exchange processes. One notable feature of this work is that *trans*-$PdCl_2L^IL^{II}$ and *trans*-$PdCl_2L^{III}L^{IV}$ are formed at all, since Nelson and co-workers reported the formation of *cis*-only mixed phosphine complexes of relatively high thermodynamic stability and kinetic inertness [6]. However, it must be recognised that the latter involved phosphine exchange between $PdCl_2L^{\dagger}_2$ and $PdCl_2L^{\dagger\dagger}_2$

Table 1
$^{31}P\{^1H\}$-NMR data for equilibria obtained from the reaction of $PdCl_2(PhCN)_2$ with $PPh_2CH{=}CH_2/PPh_2CH_2CH_3$ and $PPh_2CH_2CH{=}CH_2/PPh_2CH_2CH_2CH_3$ mixtures

Complex	$^{31}P\{^1H\}$ δ (ppm)		Complex	$^{31}P\{^1H\}$ δ (ppm)	
	L^I [a]	L^{II} [a]		L^{III} [a]	L^{IV} [a]
Sym-$[PdCl_2L^I]_2$	25.7		*Sym*-$[PdCl_2L^{III}]_2$	30.3	
Sym-$[PdCl_2L^{II}]_2$		33.8	*Sym*-$[PdCl_2L^{IV}]_2$		32.5
Cis-$[PdCl_2L^I_2]$	21.8		*Cis*-$[PdCl_2L^{III}_2]$	24.7	
Cis-$[PdCl_2L^{II}_2]$		30.0	*Cis*-$[PdCl_2L^{IV}_2]$		27.7
Cis-$[PdCl_2L^IL^{II}]$	20.9 [b]	29.8 [b]	*Cis*-$[PdCl_2L^{II}L^{IV}]$	24.1 [b]	27.3 [b]
Trans-$[PdCl_2L^I_2]$	13.6		*Trans*-$[PdCl_2L^{III}_2]$	14.9	
Trans-$[PdCl_2L^{II}_2]$		19.0	*Trans*-$[PdCl^{IV}_2]$		15.9
Trans-$[PdCl_2L^IL^{II}]$	12.1 [c]	20.9 [c]	*Trans*-$[PdCl_2L^{III}L^{IV}]$	15.1 [b]	15.5 [b]

[a] L^I, $PPh_2CH{=}CH_2$; L^{II}, $PPh_2CH_2CH_3$; L^{III}, $PPh_2CH_2CH{=}CH_2$; L^{IV}, $PPh_2CH_2CH_2CH_3$.
[b] $^2J_{PP} = 0$ Hz.
[c] $^2J_{PP} = 556$ Hz.

complexes ($L^{\dagger}$, $L^{\dagger\dagger}$ = various P donors), rather than the reaction of tertiary phosphine mixtures with $PdCl_2(PhCN)_2$. Thus, within the two pairs of saturated/unsaturated phosphines used in the present study rates of PhCN displacement by these phosphines will be similar. Therefore, the isolation of *cis* and *trans* isomers of both symmetrically and unsymmetrically substituted phosphine complexes is not surprising.

2.2. Reactivity with BH_3 and 9-BBN

The reactivity of BH_3 with vinyl- and allyl-substituted phosphines has been investigated by Imamoto [2] and Schmidbaur [3]. Both ligands readily form phosphine–borane adducts with thf·BH_3 in preference to hydroboration of the alkene function. Moreover, internal hydroboration and cyclisation does not proceed even under forcing conditions, although additional free thf·BH_3 does result in alkene hydroboration. Thus, addition of thf·BH_3 to CH_2Cl_2 and $CHCl_3$ solutions of **1** and **2** offers the potential of metal reduction, phosphine–borane formation, or alkene hydroboration. In dilute (millimolar) solutions of **1** the addition of thf·BH_3 produces a series of $^{31}P\{^1H\}$-NMR resonances, Table 2. Using one equivalent of thf·BH_3 per mole of **1** phosphine abstraction from **1** to give phosphine–borane is the predominant reaction; the ligand-deficient palladium fragments dimerising to **3**. There is some evidence for limited BH_3 reactivity with the alkene groups of coordinated phosphines as evidenced by the assignment of $^{31}P\{^1H\}$-NMR resonances to $PdCl_2L^IL^V$ (L^I = $PPh_2CH{=}CH_2$; $L^V = PPh_2CH_2CH_2BH_2$). In view of the recognised lability of the general class of PdX_2P_2 complexes, it is perhaps surprising that redistribution of L^I and L^V does not occur to afford a mixture of $PdCl_2L^I_2$, $PdCl_2L^IL^V$ and $PdCl_2L^V_2$ based on statistical and thermodynamic factors. However, such exchanges may not be significant for $PdCl_2L^IL^V$ species, since similar mixed phosphine systems appear relatively inert [6].

On reacting four equivalents of thf·BH_3 with **1** phosphine abstraction to form phosphine–borane continues be a significant feature of reactivity. However, alkene hydroboration becomes more extensive with *cis* and *trans* $PdCl_2L^IL^V$ and $PdCl_2L^V_2$ being observed. Clearly product distribution is dependant on stoichiometry. There is also evidence for a concentration dependance; the use of similar reaction stoichiometries in neat thf·BH_3 or the addition of thf·BH_3 to 10^{-1}M CH_2Cl_2 solutions results in the reduction of **1** to metallic palladium and the isolation of phosphine–borane.

The reactivity of **2** with thf·BH_3 is broadly similar to that of **1**; at 1:1 ratios of complex and thf·BH_3 ligand abstraction to form phosphine–borane is the principal form of reactivity with alkene hydroboration being a secondary feature, although in this instance $[PdCl_2P]_2$ species could not be observed by $^{31}P\{^1H\}$-NMR (Table 3). 1:4 Complex:thf·BH_3 stoichiometries result in significantly more phosphine abstract ion and the clear evidence for the formation of $[PdCl_2P]_2$ species. Alkene hydroboration is more extensive with complexes containing both one and two hydroborated alkenes being observed. When compared with the reactivity of the vinyl phosphine complex, **1**, the hydroboration of alkene functionalities in **2** is less regioselective. For the former the α-PPh_2 group strongly influences BH_3 addition at the alkene function resulting only in $PPh_2CH_2CH_2BH_2$ (L^V) formation. As would be expected, this PPh_2 influence is less significant for the allyl substituted ligand. Although terminal BH_2 addition to afford $PPh_2(CH_2)_3BH_2$ (L^{VI}) still occurs most readily, there is also evidence for the presence of species containing $PPh_2CH_2CH(BH_2)CH_3$ (L^{VII}). Identification of these final species must be considered tentative, since assignments are made by analogy with the saturated/unsaturated mixed ligand systems described in Section 2.2.

Stoichiometric reactions of 9-BBN and **2** proceed in a similar manner to those of thf·BH_3. $^{31}P\{^1H\}$-NMR spectroscopy indicates the presence of unreacted **2**, the dimeric complex **4**, a phosphine–borane adduct (9.8 ppm) and the cyclised phosphine–borane adduct **6** (15.4 ppm) (Scheme 1). The isolation of a single palladium complex containing a hydroborated phosphine again appears to be precluded by the establishment of equilibria and by the potential for palladium reduction

Table 2
$^{31}P\{^1H\}$-NMR data for the reaction of **1** with one and four equivalents of thf·BH_3

Products	**1** + 1thf·BH_3	$^{31}P\{^1H\}$ δ (ppm)	**1** + 4thf·BH_3	$^{31}P\{^1H\}$ δ (ppm)
	L^I [a]	L^V [a]	L^I [a]	L^V [a]
Sym-$[PdCl_2L^I]_2$	26.0		25.9	
Sym-$[PdCl_2L^V]_2$		Absent		33.8
Cis-$[PdCl_2L^I_2]$	21.7		21.0	
Cis-$[PdCl_2L^V_2]$		Absent		30.7
Cis-$[PdCl_2L^IL^V]$	20.8 [b]	29.8 [b]	20.8 [b]	29.7 [b]
Trans-$[PdCl_2L^I_2]$	13.6		13.6	
Trans-$[PdCl_2L^V_2]$		Absent		19.2
Trans-$[PdCl_2L^IL^V]$	12.2 [c]	20.9 [c]	12.1 [b]	20.8 [b]
L^IBH_3, L^VBH_3	19.0 [d]		18.9 [d]	

[a] L^I, $PPh_2CH{=}CH_2$; L^V, $PPh_2CH_2CH_2BH_2$.
[b] $^2J_{PP} = 0$ Hz.
[c] $^2J_{PP} = 550$ Hz.
[d] Broad.

if these equilibria are shifted by the presence of high borane concentrations. Thus, an alternative reaction strategy using $PdCl_2(PhCN)_2$ and the cyclised adduct **6** was considered; since the latter contains no B–H bonding the potential for metal reduction is removed. $^{31}P\{^1H\}$-NMR data are consistent with the facile displacement of PhCN to form $PdCl_2L_2^{VIII}$ and $[PdCl_2L^{VIII}]_2$ complexes in which ring opening of the cyclic phosphine–borane, **6**, affords the phosphine ligand $PPh_2(CH_2)_3B(C_8H_{14})$ (L^{VIII}). Attempts to crystallise such species were unsuccessful although hydrolysis of the proposed dimer, $[PdCl_2L^{VIII}]_2$, affords the crystallographically characterised diphenylpropylphosphine dimer (**7**). Isolation of such a product in the presence of moisture accords with the known hydrolytic instability of hydroborated alkenes and with the insolubility of dimeric palladium(II) phosphine complexes noted by Grim and Keiter [5].

2.3. Crystallographic characterisation of 4 and 7

Strong structural analogies exist between **4** and **7**, the main chemical difference resulting from the presence of allyl and propyl phosphine substituents. Both structures contain centrosymmetric dimeric complexes in which each palladium exists in square planar geometry formed from a terminal chloride, a phosphine and two bridging chlorides. These bridging anions form almost orthogonal bonds to the palladium centres. The bridging Pd–Cl bond distances in both compounds are asymmetric with the longer bonds lying opposite the more strongly *trans* influencing phosphine ligand. Crystallisation produces two crystallograhically distinct, but chemically identical, molecules in the structure of **4**. The structure of **7** contains a single $[PdCl_2(PPh_2CH_2CH_2CH_3)]_2$ moiety. Selected bond lengths and angles for the two complexes are given in Table 4, whilst the two structures are shown in Figs. 1 and 2, respectively. Despite the early characterisation of $[PdCl_2(PBu^t_3)]_2$ [9] relatively few comparisons with **4** and **7** have been reported. A more recent characterisation of $[PdCl_2(PBu^t_3)]_2$, plus the X-ray diffraction study of $[PdCl_2(PPh_3)]_2$ indicate both compounds are similar to **4** and **7** [13,14], whilst the complex $[PdI_2(PPh_2CH{=}CH_2)]_2$ contains generally comparable features [12].

3. Experimental

3.1. Crystallographic characterisation

Data collection and structure solution for **4** and **7** were performed using previously described methods; resulting crystal data are given in Table 5 [15–17]. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 118821 Compound **4** and No. 118822 Compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [fax: +44-1223-336-033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

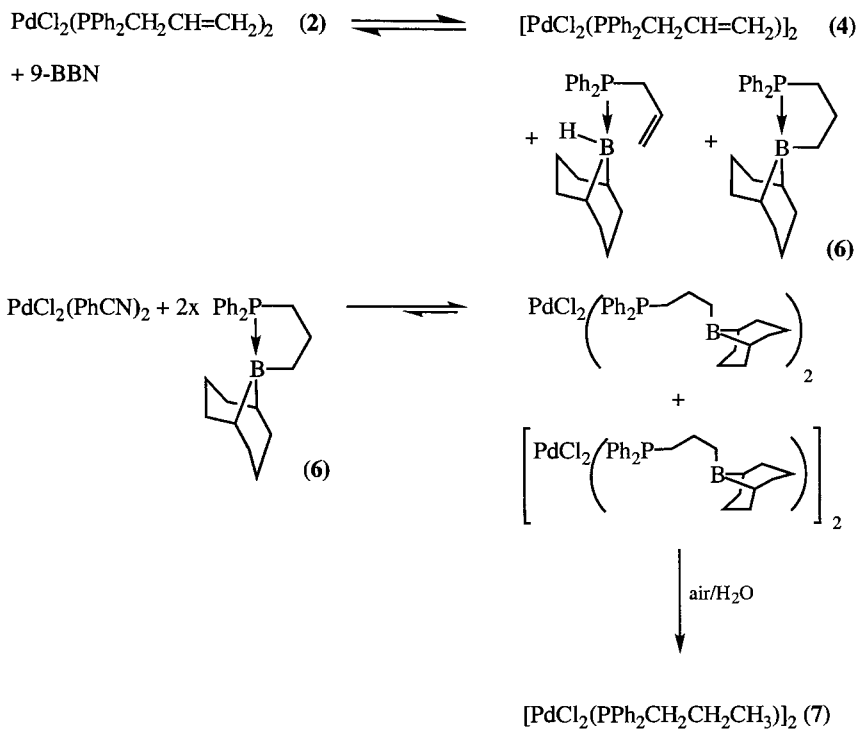
3.2. Synthesis

Commercial materials (including palladium and nickel salts, diphenylalkylphosphines, thf·BH_3 and 9-BBN) were used as received. $PPh_2CH{=}CH_2$ was pre-

Table 3
$^{31}P\{^1H\}$-NMR for the reaction of **2** with one and four equivalents of thf·BH_3

Products	**2**+1thf·BH_3	$^{31}P\{^1H\}$ δ (ppm)		**2**+4thf·BH_3	$^{31}P\{^1H\}$ δ (ppm)	
	L^{III} [a]	L^{VI} [a]		L^{III} [a]	L^{VI} [a]	L^{VII} [a]
Sym-$[PdCl_2L^{III}]_2$	Absent			29.8		
Sym-$[PdCl_2L^{VI}]_2$		Absent			32.3	
Cis-$[PdCl_2L_2^{III}]$	24.3			24.6		
Cis-$[PdCl_2L_2^{VI}]$		27.4			27.5	
Cis-$[PdCl_2L^{III}L^{VI}]$	24.3 [b]	27.0 [b]		24.4 [b]	27.2 [b]	
Cis-$[PdCl_2L^{III}L^{VII}]$	Absent	Absent		19.0 [b]		20.8 [b]
Trans-$[PdCl_2L_2^{III}]$	14.9			14.9		
Trans-$[PdCl_2L_2^{VI}]$		15.8			15.8	
Trans-$[PdCl_2L^{III}L^{VI}]$	15.1 [c]	15.4 [c]		15.1 [c]	15.4 [c]	
Trans-$[PdCl_2L^{III}L^{VII}]$	Absent	Absent		12.5 [b]		14.2 [b]
$L^{III}BH_3$, $L^{VI}BH_3$	15.9 [d]			15.9 [d]		

[a] L^{III}, $PPh_2CH_2CH{=}CH_2$; L^{VI}, $PPh_2(CH_2)_3BH_2$; L^{VII}, $PPh_2CH_2CH(BH_2)CH_3$.
[b] $^2J_{PP} = 0$ Hz.
[c] $^2J_{PP} = 556$ Hz.
[d] Broad.



Scheme 1. Reactivity of **2** with 9-BBN and of $PdCl_2(PhCN)_2$ with **6**.

pared by the Grignard route. $PPh_2CH_2CH{=}CH_2$ was synthesised by the reaction of $CH_2CH{=}CH_2Br$ with $LiPPh_2$. In each case the ^1H- and $^{31}P\{^1H\}$-NMR data ($CDCl_3$ 200 and 81 MHz, respectively) were comparable with literature values [18]. Solvents were dried by conventional methods, and reactions were performed under nitrogen using standard Schlenk-line techniques [19]. The following were all synthesised by published methods; $Pd(PhCN)_2Cl_2$ [20], $PdCl_2(PPh_2CH{=}CH_2)_2$ (**1**) [7], $NiCl_2(PPh_2CH{=}CH_2)_2$ (**5**) [21], and cyclo-(9-borabicyclo[3.3.1]nonanyl)-propyl(diphenyl)phosphine (**6**) [3].

Synthesis of **1**–**4** was by the following general method. $PdCl_2(PhCN)_2$ (0.4811 g; 1.255 mmol) is stirred in dry thf under reflux (5 cm^3). $Ph_2PCH_2CH{=}CH_2$ (0.58 g; 2.6 mmol) is dissolved in a similar volume of thf. Addition results in the formation of a yellow–green solution from which **2** precipitates on addition of Et_2O (25 cm^3) to the cooled thf solution. The solid is filtered and dried in vacuo before recrystallisation from CH_2Cl_2/Et_2O. Yield 0.67 g (85%).

$[PdCl_2(PPh_2CH_2CH{=}CH_2)_2]$ (**2**): Elemental analysis for $C_{30}H_{30}Cl_2P_2Pd$, expected C, 57.6; H, 5.1; found: C, 57.2; H, 4.8. ^1H (*cis*/*trans* not resolved): $\delta = 3.37$ (m, 2H, $PCH_2CH{=}CH_2$), 4.88 (d, 1H, $PCH_2CH{=}CH_2$), 5.02 (m, 1H, $PCH_2CH{=}CH_2$), 5.87 (m, 1H, $PCH_2CH{=}CH_2$), 7.20–7.72 (m, 10H, *Ph*$_2$P); $^{31}P\{^1H\}$ $\delta = 24.7$ and 14.9 (*cis*:*trans* 26:74). IR(KBr); ν(C=C) 1634 (s) cm^{-1}.

$[PdCl_2(PPh_2CH{=}CH_2)]_2$ (**3**): Elemental analysis for $C_{14}H_{13}Cl_2PPd$, expected C, 43.1; H, 3.3; found: C, 43.3; H, 3.2. ^1H: $\delta = 5.54$ (dd $^3J(HH) = 18.7$ Hz,

Table 4
Bond lengths and angles for **4** and **7**

Bonds lengths (Å) and angles (°)	Compound **4** [a]	Compound **7**
Metal centred		
Pd–Cl (terminal)	2.277(2), 2.275(2)	2.2684(7)
Pd–P	2.2222(2), 2.217(2)	2.2275(6)
Pd–Cl (bridging, *trans* to P)	2.420(2), 2.429(2)	2.4444(5)
Pd–Cl (bridging, *cis* to P)	2.309(2), 2.321(5)	2.3208(6)
P–Pd–Cl (terminal)	87.98(7), 92.04(6)	90.39(2)
P–Pd–Cl (bridging, *trans* to P)	176.89(7), 176.39(6)	176.36(2)
P–Pd–Cl (bridging, *cis* to P)	94.03(6), 90.85(6)	93.14(2)
Cl–Pd–Cl	94.04(6), 93.32(6)	94.52(2)
Allyl/*propyl function*		
P–C(13)	1.822(6), 1.839(6)	1.820(2)
C(13)–C(14)	1.451(11), 1.500(9)	1.518(4)
C(14)–C(15)	1.16(3), [b] 1.289(10)	1.519(4)
P–C(13)–C(14)	114.5(5), [b] 112.1(5)	115.19(18)
C(13)–C(14)–C(15)	133(2), [b] 124.6(8)	111.3(3)

[a] Data for two distinct molecules.
[b] Disordered site.

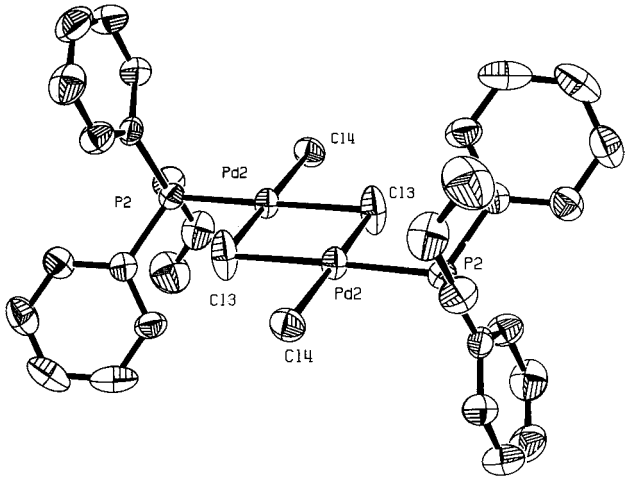


Fig. 1. Crystal structure of **4** (showing one of the chemically identical molecules).

^3J(HP) = 23.5 Hz, 1H, PCH=C*H*H), 6.18 dd ^3J(HH) = 12.1 Hz, ^3J(HP) = 43.6 Hz, 1H, PCH=C*H*H), 7.05 (ddd ^3J(HH) = 12.1 Hz, ^3J(HH) = 18.7 Hz, ^2J(HP) = 23.5 Hz, 1H, PC*H*=CH_2), 7.37–7.82 (m, 10H, *Ph*$_2$P); $^{31}P\{^1H\}$ $\delta = 25.7$.

$[PdCl_2(PPh_2CH_2CH=CH_2)]_2$ (**4**): Elemental analysis for $C_{15}H_{15}Cl_2PPd$, Expected C, 44.6; H, 3.7; Found: C, 44.4; H, 4.1. ^1H: $\delta = 3.41$ (s, 2H, PC*H*$_2$CH=CH_2), 4.88 (d ^3J(HH) = 16.9 Hz, 1H, PCH_2CH=C*H*H), 5.02 (d ^3J(HH) = 9.9 Hz, 1H, PCH_2CH=C*H*H), 5.87 (dd ^3J(HH) = 9.9 Hz, ^3J(HH) = 16.9 Hz, 1H, PC*H*=CH_2), 7.08–7.80 (m, 10H, *Ph*$_2$P); $^{31}P\{^1H\}$ $\delta = 30.3$. IR(KBr); ν(C=C) 1634 (s) cm^{-1}.

3.3. Reaction of $PdCl_2(PhCN)_2$ with mixed alkenyl/alkyl phosphines

The following is typical. $PdCl_2(PhCN)_2$ (0.2956 g; 1.54 mmol) is dissolved in thf (5 cm^3) under reflux. A mixture of PPh_2Et (0.1181 g; 0.55 mmol) and PPh_2CH=CH_2 (0.2109 g; 1.00 mmol) is dissolved in a similar volume of thf. Addition results in the formation of a yellow–green solution from which the phosphine complexes precipitate on addition of Et_2O (25 cm^3) to the cooled thf solution. Crude yield, 0.40 g (ca. 85%). The solid is extracted with $CDCl_3$ to afford a yellow–orange solution suitable for $^{31}P\{^1H\}$-NMR spectroscopy.

Table 5
Crystal data for **4** and **7**

	4	**7**
Colour and habit	Red block	Red block
Size (mm)	$0.12 \times 0.08 \times 0.07$	$0.60 \times 0.30 \times 0.20$
Formula	$C_{30}H_{30}Cl_4P_2Pd$	$C_{15}H_{17}Cl_2PPd$
a (Å)	7.982(2)	11.4519(2)
b (Å)	14.089(3)	9.21470(10)
c (Å)	14.459(3)	15.6374(3)
α (°)	96.33(3)	
β (°)	89.86(3)	96.5308(7)
γ (°)	97.68(3)	
V (Å^3)	1601.5(6)	1639.44(5)
Mo–K$_\alpha$, λ (nm)	0.71069	0.71069
System	Triclinic	Monoclinic
Space group	P-1	$P2(1)/c$
Z	2	4
Collection	FAST TV	Nonius KappaCCD
Total reflections	6724	24 245
Observed data [$I > 2\sigma(I)$]	3542	3103
2θ	$1.92 < 2\theta < 25.06$	$2.84 < 2\theta < 26.37$
Absorption correction	DIFFABS	SORTAV
Solution	Direct methods	Direct methods
Refinement	F^2 SHELXS-86	F^2 SHELXS-97
Hydrogen atoms	Riding	Riding
No. of parameters	353	174
R_1	0.0402	0.0241
wR_2	0.1074	0.0594

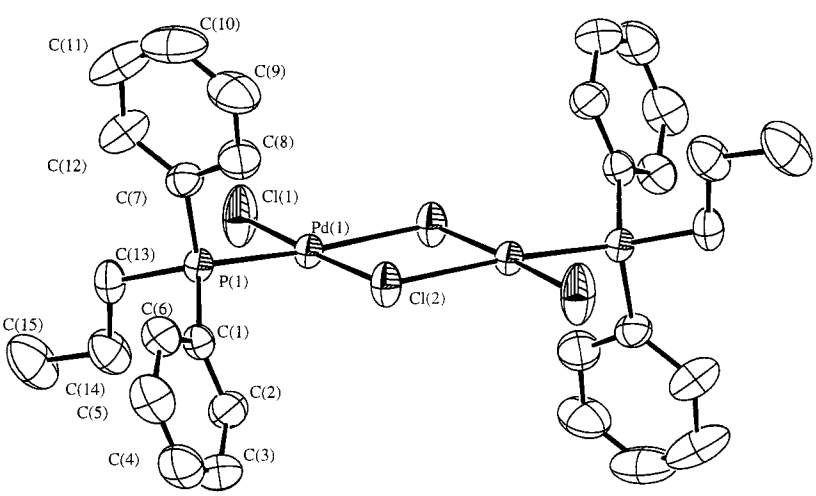


Fig. 2. Crystal structure of **7**.

3.4. Reaction of thf·BH_3 with **1** and **2**, and 9-BBN with **2**

Compound **1** (6.0 mg, 10 mmol) is placed in an NMR tube containing 2.0 cm^3 of dry degassed $CDCl_3$. thf·BH_3 (10 μl, 1 M thf·BH_3, 10 mmol) is added and the sealed tube heated to 60°C for 1 h. $^{31}P\{^1H\}$- and ^1H-NMR data are obtained upon cooling to ambient temperature. No significant spectral changes are observed after a further 7 days at ambient temperature.

3.5. Reaction of $PdCl_2(PhCN)_2$ and **6**

Compound **6** (0.190 g, 0.54 mmol) was added to a thf solution (5 cm^3) of $PdCl_2(PhCN)_2$ (0.105 g; 0.27 mmol). The solution changes from yellow to deep red in ca. 10 min. The solvent was removed in vacuo after 1 h and the solid redissolved in $CDCl_3$ (5 cm^3) for NMR analysis. On standing over ca. 7 days deep red crystals of **8** precipitated from solution.

$[PdCl_2(PPh_2CH_2CH_2CH_3)]_2$ (**7**): Elemental analysis for $C_{15}H_{17}Cl_2PPd$, expected C, 44.4; H, 4.2; found: C, 43.9; H, 4.3. ^1H: $\delta = 0.94$ (t, 3H, $PCH_2CH_2CH_3$), 2.36 (dd, 2H, $PCH_2CH_2CH_3$), 3.48 (dd, 2H, $PCH_2CH_2CH_3$), 7.37–7.81 (m, 10H, Ph_2P); $^{31}P\{^1H\}$ $\delta = 32.3$.

References

[1] M. Ohff, J. Holz, M. Quirmbach, A. Borner, Synthesis 10 (1998) 1391.

[2] (a) T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumozo, K. Sato, J. Am. Chem. Soc. 112 (1990) 5244. (b) T. Imamoto, E. Hirakawa, Y. Yamanoi, T. Inoue, K. Yamaguchi, H. Seki, J. Org. Chem. 60 (1995) 7697.

[3] H. Schmidbaur, M. Sigl, A. Schier, J. Organomet. Chem. 529 (1997) 323.

[4] A.H. Cowley, M.C. Damasco, J. Am. Chem. Soc. 93 (1971) 6815.

[5] S.O. Grim, R.L. Keiter, Inorg. Chim. Acta. 4 (1970) 56.

[6] A.W. Verstuyft, D.A. Redfield, L.W. Cary, J.H. Nelson, Inorg. Chem. 15 (1976) 1128.

[7] J.A. Rahn, M.S. Holt, M. O'Neil-Johnson, J.H. Nelson, Inorg. Chem. 27 (1988) 1316.

[8] J.A. Rahn, M.S. Holt, J.H. Nelson, Polyhedron 8 (1989) 897.

[9] (a) F.G. Mann, D. Purdie, J. Chem. Soc. (1935) 1549. (b) ibid (1936) 873. (c) F.G. Mann, A.F. Wells, J. Chem. Soc. (1938) 702.

[10] A.W. Verstuyft, L.W. Cary, J.H. Nelson, Inorg. Chem. 15 (1976) 3161 and references therein.

[11] J.G. Verkade, Coord. Chem. Rev. 9 (1973) 1.

[12] N.W. Alcock, W.L. Wilson, J.H. Nelson, Inorg. Chem. 32 (1993) 3193.

[13] P.A. Chaloner, S.Z. Dewa, P.B. Hitchcock, Acta Crystallogr. Sect. C. 51 (1995) 232.

[14] J. Vicente, M.C. Lagunas, E. Bleuel, M.C. Ramirez de Arellano, CCDC Ref. 183737 (1997).

[15] J.A. Darr, S.R. Drake, M.B. Hursthouse, K.M.A. Malik, Inorg. Chem. 32 (1993) 5704.

[16] G.M. Sheldrick, Acta. Crystallogr. Sect. A. 46 (1990) 467.

[17] G.M. Sheldrick, SHELX-93. University of Göttingen, Germany, 1993.

[18] L. Maier, in: L. Maier, G.M. Kosolapoff (Eds.), Organic Phosphorus Compounds, vol. 1, Wiley-Interscience, New York, 1972. Ch. 1 and references therein.

[19] S.J. Coles, M.B. Hursthouse, D.G. Kelly, A.J. Toner, N.M. Walker, J. Organomet. Chem. 580 (1999) 304.

[20] G.K. Anderson, M. Lin, Inorg. Synth. 28 (1990) 61.

[21] S.J. Coles, P. Faulds, M.B. Hursthouse, D.G. Kelly, G.C. Ranger, N. Walker, J. Chem. Res. (1999), 418 (S), 1811 (M).