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Addition of organic halides to bis{(2-vinylphenyl)diphenylphosphine}palladium(0). X-Ray structure of the chelate σ-alkylpalladium(II) complex $\overline{\mathrm{PdI}\{o\text{-}\mathrm{CH(CH_3)C_6H_4PPh_2}}\}$-$\{(E)\text{-}o\text{-}\mathrm{Ph_2PC_6H_4CH{=}CHC_6H_5}\}$

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Abstract

Iodobenzene adds to the palladium(0) complex $\mathrm{Pd(VP)_2}$ (**2**) (VP = (2-vinylphenyl)diphenylphosphine, $o\text{-}\mathrm{CH_2{=}CHC_6H_4PPh_2}$) to give the planar palladium(II) complex $\overline{\mathrm{PdI}\{o\text{-}\mathrm{CH(CH_3)C_6H_4PPh_2}}\}\{(E)\text{-}o\text{-}\mathrm{Ph_2PC_6H_4CH{=}CHC_6H_5}\}$ (**5**), which has been characterized by NMR (^{1}H, ^{31}P) spectroscopy and by single crystal X-ray analysis. Crystals of **5** are triclinic, space group $P\bar{1}$, *a* 13.404(5); *b* 13.850(6), *c* 14.158(7) Å, α 118.39(3), β 92.28(4), γ 95.58(3)°, *Z* 2; 2139 data with $I > 2\sigma(I)$ were refined to *R* 0.087, R_w 0.049. The complex contains a five-membered chelate σ-alkyl group (Pd–P(1) 2.279(6), Pd–C(1) 2.05(3) Å) and monodentate *P*-bonded *E*-(2-styrylphenyl)diphenylphosphine (Pd–P(2), 2.346(7) Å). **5** is believed to be formed by a sequence of oxidative addition, phenyl migration from palladium to one of the vinyl groups, and β-hydride transfer from one P-donor ligand to the other. Bromobenzene reacts with **2** to give the bromo analogue of **5** together with an unidentified minor isomer. Allyl bromide gives $\mathrm{PdBr(\eta^3\text{-}C_3H_5)(VP)}$ containing monodentate *P*-bonded VP, but the products of reaction of **2** with methyl iodide and benzyl bromide have not been fully characterized.

Introduction

The sequence of *cis*-addition of an olefin to a $\mathrm{Pd^{II}}$-C-σ-bonded complex RPdX and *cis*-elimination of Pd and HX from the resulting adduct leads to vinylic hydrogen substitution on the olefin (eq. 1) and is a synthetically useful transforma-

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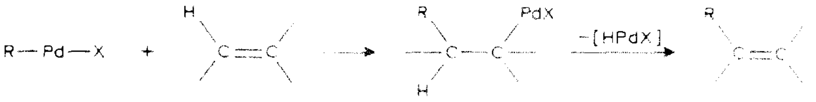
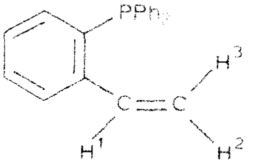
tion in organic chemistry [1–4]. One of the most practical of the many ways in



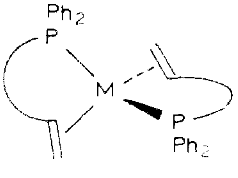
(1)

which the transient Pd^{II}–C σ-bonded complex can be formed is the oxidative addition of an aryl or vinylic halide to a tertiary phosphine-palladium(0) complex. The latter can be conveniently generated in situ by reduction of a catalytic amount of a palladium(II) precursor $Pd(O_2CMe)_2L_2$ (L = PPh_3, P(*o*-tolyl)$_3$) and the vinylic substitution reaction is performed in the presence of a base, such as a tertiary amine, to remove hydrogen halide. Aryl, vinylic and benzylic halides, and methyl iodide oxidatively add to $Pd(PPh_3)_4$ to give *trans*-$PdRX(PPh_3)_2$, the order of reactivity being Cl < Br < I [5–8]; it has also been shown that *trans*-$PdBr(C_6H_5)(PPh_3)_2$ reacts with an excess of styrene or methyl acrylate on heating to give the expected vinylic substitution products *trans*-stilbene or methyl cinnamate [9], although no intermediates were isolated.

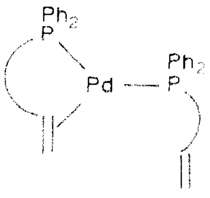
The potentially chelating olefinic tertiary phosphine (2-vinylphenyl)diphenylphosphine (*o*-$CH_2{=}CHC_6H_4PPh_2$), abbreviated VP *, forms complexes of general formula $M(VP)_2$ with zerovalent metals of the nickel triad (M = Ni, Pd, Pt) [10]. Single crystal X-ray structural analysis shows that the nickel(0) and platinum(0) complexes are tetrahedrally coordinated monomers (**1**) containing two bidentate ligands, so that the metal atom in each case has an 18*e*-configuration. In contrast, the metal atom in the palladium(0) complex in the solid state is approximately trigonally coordinated by one bidentate ligand and one *P*-bonded, monodentate ligand (structure **2**); thus the metal atom in **2** has a 16*e*-configuration and is



VP



(**1a**, M = Pt;
1b, M = Ni)



(**2**)

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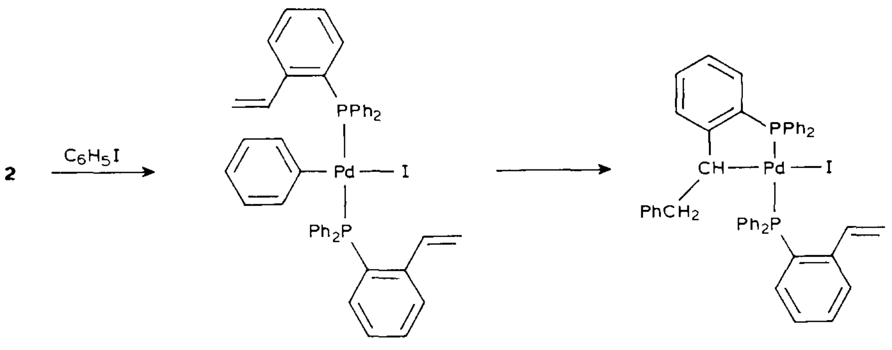
* In earlier publications we named this ligand as *o*-styryldiphenylphosphine and abbreviated it as SP. This nomenclature is not strictly correct and will not be used here, owing to the possibility of confusion with the ligand (2-styrylphenyl)diphenylphosphine, *o*-$C_6H_5CH{=}CHC_6H_4PPh_2$, which appears in the present work.

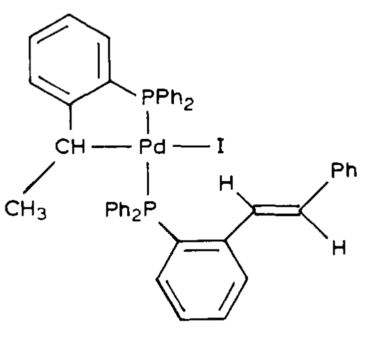


(3) (4)

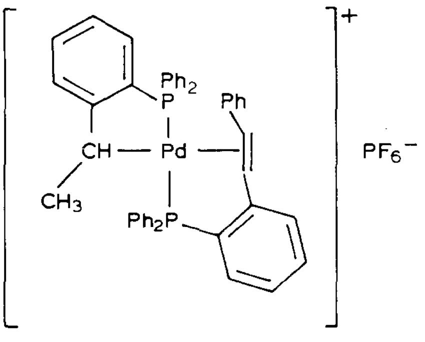
Scheme 1

coordinatively unsaturated. This suggests that **2** might undergo oxidative addition with an organic halide such as iodobenzene to give initially a η^1-phenylpalladium(II) complex **3**, and that the phenyl group in **3** could subsequently migrate to one of the adjacent vinyl groups to give an isolable palladocycle **4** (Scheme 1). We report here our studies of this type of reaction.

Iodobenzene reacts with **2** in refluxing benzene to give a yellow, crystalline 1 : 1 adduct in 66% yield. The IR spectrum shows a weak band at 1620 cm^{-1} assignable to ν(C=C) of an uncoordinated double bond and the $^{31}P\{^1H\}$ NMR spectrum consists of an AB quartet, the magnitude of $^2J(PP)$ (383 Hz) being consistent with the presence of mutually *trans*-, inequivalent phosphorus atoms [11]. However, the ^1H NMR spectrum in CD_2Cl_2 does not contain the characteristic pair of doublets in the region δ 4.5–5.5 ppm due to the CH_2 protons of an uncoordinated vinyl group, nor does it show the ABX pattern expected from the benzylic and methine protons of structure **4**. Apart from the aromatic multiplets in the region δ 6.7–8.3 ppm, there is only a multiplet at δ 3.73 ppm and an approximate quartet at δ 1.04 ppm; this pattern broadens and shifts slightly at −90 °C, but no other peaks appear. On ^{31}P-decoupling, the last two signals simplify to a quartet and a doublet (J 7 Hz), respectively, suggestive of the presence of a $CHCH_3$ group. The observations are consistent with structure **5**, isomeric with **4**, containing a five-membered metallacycle $Pd\{o\text{-}CH(CH_3)C_6H_4PPh_2\}$ and the ligand (2-styrylphenyl)diphenylphosphine, $o\text{-}Ph_2PC_6H_4CH{=}CHC_6H_5$, coordinated to palladium through its phosphorus



(5)

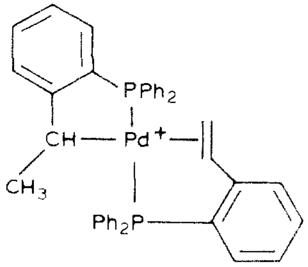


(6)

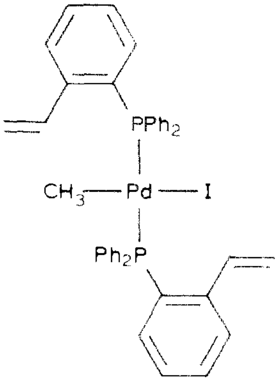
atom only. This has been confirmed by a single crystal X-ray structural analysis (see below), which also shows the aryl groups to be mutually *trans* about the free double bond. The olefinic protons of this ligand are presumably buried beneath the aromatic proton resonances e.g. δ(CH=CH) for *trans*-stilbene in $CDCl_3$ is 7.1 ppm [12].

Treatment of **5** with $AgPF_6$ in dichloromethane/acetone removes iodide ion to give a yellow crystalline salt **6** in which the double bond of (2-styrylphenyl)diphenylphosphine, (*E*)-*o*-$C_6H_5CH{=}CHC_6H_4PPh_2$, is presumably coordinated to palladium. There is no band at 1620 cm^{-1} due to free olefin in the IR spectrum of **6** but the presence of PF_6^- is evident from the strong, broad absorption at 840 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows an AB quartet (^2J(PP) 331 Hz) typical of mutually *trans* ^{31}P nuclei and the $^1H\{^{31}P\}$ NMR spectrum contains a quartet at δ 3.89 ppm and a doublet at δ 1.24 ppm (*J*(HH) 7 Hz) due to the $CHCH_3$ group. These NMR parameters are similar to those observed for the closely related cation **7**, which is formed by treatment of **2** with HBF_4 or HPF_6 [10], and which exhibits β-vinyl proton resonances at δ 5.50 and δ 4.70 ppm. Surprisingly, although the olefinic proton resonances of **6** would be expected to be upfield of the aromatic signals as a result of coordination, we were unable to locate them with certainty, even when the spectrum was recorded at −90 °C. Possibly the styryl group of **6** is more weakly bound to palladium than is the vinyl group of **7** and is undergoing rapid, reversible dissociation in solution.

A yellow compound is also obtained from the reaction of **2** with bromobenzene in refluxing benzene, whereas chlorobenzene is unreactive. The elemental analysis of the bromo compound corresponds to a 1 : 1 adduct, but the NMR spectra show the presence of two main components that could not be separated by crystallization.



(**7**)



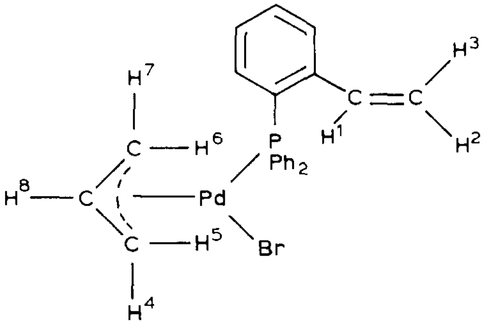
(**8**)

The $^{31}P\{^1H\}$ NMR spectrum contains two AB quartets in a ratio of ca. 7/3 with similar chemical shifts and coupling constants (δ(P_A) 20.3, δ(P_B) 44.6, *J*(AB) 385 Hz (major product); δ(P_A) 22.1, δ(P_B) 41.4, *J*(AB) 391 Hz (minor product)). The ^1H NMR spectrum shows multiplets at δ 1.05 and δ 3.52 ppm which simplify on ^{31}P decoupling to a doublet and a quartet respectively. These are assigned to the $CHCH_3$ group of the bromo analogue of **5**, which is the major product, but there are also other resonances, including pairs of doublets in the regions δ 5.8–6.0 and δ 2.8 ppm, which cannot be assigned. All the signals broaden at −60 °C but there are no other obvious changes.

Methyl iodide reacts with **2** in benzene at room temperature to give a yellow solid which, according to NMR spectroscopy, contains two species. The main product is believed to be the methylpalladium(II) complex **8** containing two mutually *trans*, *P*-bonded monodentate (2-vinylphenyl)diphenylphosphine ligands. The ^{1}H NMR spectrum in CD_2Cl_2 shows a triplet due to Pd-CH_3 at δ 0.16 ppm (J(PH) 7.0 Hz) cf. *trans*-[PdI(CH_3)(PPh_3)$_2$] δ 0.18 ppm (J(PH) 5.0 Hz) [5] and a pair of doublets at δ 5.09 and δ 5.58 ppm (J(HH) 10, 17 Hz respectively) which can be assigned to the β-protons H^2 and H^3 of the uncoordinated vinyl group of **8**. A sharp singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 31.0 ppm due to the equivalent ^{31}P nuclei of **8**. The $^{31}P\{^1H\}$ NMR spectrum also shows an AB quartet ($\delta(P_A)$ 21.5, $\delta(P_B)$ 42.4 ppm; J(AB) 383 Hz) indicative of a palladium(II) complex containing mutually *trans*, inequivalent ^{31}P nuclei; this complex (**9**) could arise by transfer of the methyl group of **8** to one of the vinyl groups and could be structurally similar to **4** or **5**. The $^1H\{^{31}P\}$ NMR spectra of different samples of the isolated compound contain various other resonances, including a doublet at δ 0.76 (J(HH) 7 Hz) and a doublet at δ 5.1 (J(HH) 11 Hz) which may arise from **9**, but the data are insufficient to provide structural information.

Samples of the yellow product obtained from **2** and methyl iodide which have not been passed down an alumina column also contain small amounts of the methiodide of (2-vinylphenyl)diphenylphosphine, $[VPMe]^+I^-$, as evidenced by the presence of a doublet at δ 2.89 ppm (J(PH) 13 Hz) in the ^{1}H NMR spectrum and a singlet at δ 21.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

The reactions of **2** with allyl bromide and benzyl bromide differ from those described above in that one molecule of the olefinic tertiary phosphine is eliminated; the yellow adducts PdBr(allyl)(VP) (**10**) and PdBr(benzyl)(VP) (**11**) are isolated in 60–70% yield. The ^{1}H NMR spectrum of **10** in CD_2Cl_2 at room temperature exhibits a pair of doublets at δ 5.16 and δ 5.63 ppm (J(HH) 10.9, 17.6 Hz respectively) due to the β-protons H^2 and H^3 of an uncoordinated vinyl group. The latter overlaps with a quintet centred at δ 5.5 ppm (J(HH) 10.1 Hz) assignable to the central proton H^8 of a fluxional allyl group, the remaining protons of which appear as two broad resonances in the regions δ 3.2–3.6 ppm and δ 4.2–4.7 ppm. At −90 °C all five of the resonances expected for an asymmetrically bound η^3-allyl ligand are observed (see Experimental), the pattern being generally similar to that reported for PdCl(η^3-C_3H_5)(PPh_3) at 34 °C [13] and at −50 °C [14]. The vinyl resonances do not change at −90 °C, so the double bond of VP remains free,



(10)

consistent with the structure shown. The broadening of the resonances due to the terminal allylic protons at room temperature may be a $\eta^3 \leftrightarrow \eta^1$ process induced by traces of VP, which is liberated in the reaction of **2** with allyl bromide.

The ^{1}H NMR spectrum of PdBr(benzyl)(VP) (**11**) in CD$_2$Cl$_2$, both at room temperature and at −90 °C, shows four broad, overlapping multiplets in the region δ 2–3 ppm, a broad multiplet at ca. δ 4.7 ppm, and aromatic multiplets in the region δ 6.8–8.0 ppm in the approximate ratio 20/1/4. These spectra clearly show the absence of a free vinyl group, and this is confirmed by the IR spectrum, which contains no ν(C=C) band at 1620 cm^{-1}. However, it is unclear from the data whether the benzyl group is *trihapto*, as in [PdCl(η^3-CH$_2$C$_6$H$_5$)]$_2$ [15] and [Pd(η^3-CH$_2$CH$_6$H$_5$)(PEt$_3$)$_2$]BF$_4$ [16], or *monohapto*, as in PdX(η^1-CH$_2$C$_6$H$_5$)L$_2$ (X = Cl, Br; L = PEt$_3$, PPh$_3$) [7,15,16]. The ^{31}P{^{1}H} NMR spectrum consists of two closely spaced singlets of different intensity, which suggests that two species are present in solution. More work is needed to establish the nature of complex **11**.

The reactions of the various organic halides with Pt(VP)$_2$ (**1a**) and Ni(VP)$_2$ (**1b**) have also been investigated briefly, but no tractable products could be obtained.

Crystal structure of PdI{o-$\overline{\mathrm{CH(CH_3)C_6H_4PPh_2}}$}{($E$)-$o$-Ph$_2PC_6H_4$CH=CHC$_6H_5$} (5)

The molecular structure is shown in Fig. 1 together with the numbering scheme. Relevant metrical data are summarized in Tables 1 and 2; fractional atomic coordinates are in Table 3. The five-membered P–C chelate ring, the monodentate P-bonded (2-styrylphenyl)diphenylphosphine, and the iodine atom form an essen-

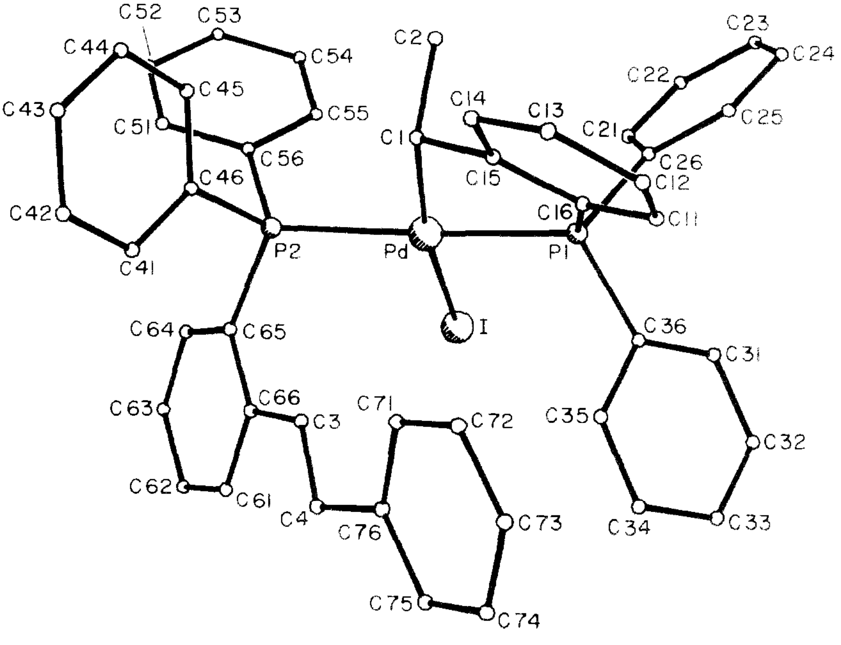


Fig. 1. Molecular geometry of PdI{o-$\overline{\mathrm{CH(CH_3)C_6H_4PPh_2}}$}{($E$)-$o$-Ph$_2PC_6H_4$CH=CHC$_6H_5$} (5).

Table 1

Selected bond lengths (Å) in $\overline{\mathrm{PdI}\{o\text{-}\mathrm{CH(CH_3)C_6H_4PPh_2}}\}\{(E)\text{-}o\text{-}\mathrm{Ph_2PC_6H_4CH{=}CHC_6H_5}\}$ (**5**) (with estimated standard deviations in parenthesis)

Pd–I	2.684(4)	Pd–P(1)	2.279(6)
Pd–P(2)	2.346(7)	Pd–C(1)	2.05(3)
P(1)–C(16)	1.78(3)	P(1)–C(26)	1.82(3)
P(1)–C(36)	1.79(3)	P(2)–C(46)	1.72(3)
P(2)–C(56)	1.78(2)	P(2)–C(65)	1.78(2)
C(1)–C(2)	1.57(5)	C(1)–C(15)	1.57(3)
C(3)–C(4)	1.45(6)	C(3)–C(66)	1.46(3)
C(4)–C(76)	1.46(4)		

tially planar coordination array about the palladium atom. The chelate ring adopts an envelope conformation with a hinge angle of 29.5 °. The methyl group occupies an axial site, as is the case also in the octahedral manganese(I) complex $\overline{\mathrm{Mn}\{o\text{-}\mathrm{CH(CH_3)C_6H_4PPh_2}}\}\mathrm{(CO)_4}$ [17]; in contrast, the methyl group in the octahedral ruthenium(II) complex $\overline{\mathrm{RuBr}\{o\text{-}\mathrm{CH(CH_3)C_6H_4PPh_2}}\}\mathrm{(CO)_3}$ is equatorial [18]. As expected, the phosphorus atoms are mutually *trans*, the Pd–P distance in the chelate ring (2.279(6) Å) being significantly shorter than the Pd–P bond length for the monodentate *P*-bonded tertiary phosphine (2.346(7) Å). A similar effect is observed in the trigonal bipyramidal, zerovalent iron complex $\mathrm{Fe(CO)_2(VP)_2}$ [19], whereas the Pd–P distances in the approximately trigonal planar, zerovalent palladium complex $\mathrm{Pd(VP)_2}$ (**2**) are equal within experimental error [9]. Presumably as a consequence of the high *trans*-influence of the Pd–C σ-bond, the Pd–I bond length (2.684(4) Å) is significantly greater than the Pd–I distances characteristic of iodide

Table 2

Bond angles (°) in $\overline{\mathrm{PdI}\{o\text{-}\mathrm{CH(CH_3)C_6H_4PPh_2}}\}\{(E)\text{-}o\text{-}\mathrm{Ph_2PC_6H_4CH{=}CHC_6H_5}\}$ (**5**) (with estimated standard deviations in parenthesis)

I–Pd–P(1)	93.6(2)	I–Pd–P(2)	93.0(2)
P(1)–Pd–P(2)	173.0(3)	I–Pd–C(1)	171.0(9)
P(1)–Pd–C(1)	81(1)	P(2)–Pd–C(1)	93(1)
Pd–P(1)–C(16)	106.3(9)	Pd–P(1)–C(26)	117.3(6)
C(16)–P(1)–C(26)	106(1)	Pd–P(1)–C(36)	119.2(7)
C(16)–P(1)–C(36)	103(1)	C(26)–P(1)–C(36)	104(1)
Pd–P(2)–C(46)	117.8(6)	Pd–P(2)–C(56)	112.9(9)
C(46)–P(2)–C(56)	98(1)	Pd–P(2)–C(65)	113(1)
C(46)–P(2)–C(65)	106(1)	C(56)–P(2)–C(65)	108(1)
Pd–C(1)–C(2)	106(2)	Pd–C(1)–C(15)	111(2)
C(2)–C(1)–C(15)	109(2)	C(4)–C(3)–C(66)	128(3)
C(3)–C(4)–C(76)	120(3)	C(1)–C(15)–C(14)	115(2)
C(1)–C(15)–C(16)	126(2)	P(1)–C(16)–C(11)	134.1(8)
P(1)–C(16)–C(15)	105.9(8)	P(1)–C(26)–C(21)	117.9(6)
P(1)–C(26)–C(25)	122.1(6)	P(1)–C(36)–C(31)	126.9(8)
P(1)–C(36)–C(35)	113.0(8)	P(2)–C(46)–C(41)	121.8(8)
P(2)–C(46)–C(45)	118.1(8)	P(2)–C(56)–C(51)	119(1)
P(2)–C(56)–C(55)	121(1)	P(2)–C(65)–C(66)	119.7(7)
C(3)–C(66)–C(61)	115(2)	C(3)–C(66)–C(65)	125(2)
C(4)–C(76)–C(71)	121(2)	C(4)–C(76)–C(75)	119(2)

Table 3

Fractional atomic coordinates ($\times 10^4$) and temperature factors (Å $\times 10^2$)

Atom	x	y	z	U [a]
Pd	3403(2)	2422(2)	588(1)	64(1)
I	2988(1)	489(2)	591(1)	79(1)
P(1)	4055(5)	3347(6)	2351(5)	68(4)
P(2)	2703(5)	1684(6)	−1202(5)	65(4)
C(1)	3943(24)	3901(23)	678(25)	98(20)
C(2)	5058(24)	3807(23)	374(24)	110(20)
C(3)	882(29)	2205(26)	208(24)	117(20)
C(4)	106(36)	2658(33)	924(26)	157(27)
C(11)	4046(17)	5716(23)	3800(16)	122(22)
C(12)	4003(17)	6751(23)	3873(16)	167(28)
C(13)	3929(17)	6850(23)	2938(16)	184(45)
C(14)	3899(17)	5914(23)	1929(16)	138(25)
C(15)	3942(17)	4878(23)	1855(16)	117(24)
C(16)	4015(17)	4779(23)	2791(16)	81(20)
C(21)	5696(21)	2206(18)	2026(14)	96(23)
C(22)	6674(21)	2055(18)	2251(14)	130(23)
C(23)	7309(21)	2921(18)	3094(14)	148(26)
C(24)	6967(21)	3938(18)	3711(14)	128(24)
C(25)	5989(21)	4089(18)	3486(14)	75(18)
C(26)	5354(21)	3223(18)	2644(14)	78(16)
C(31)	3779(14)	2764(16)	4013(21)	92(19)
C(32)	3157(14)	2599(16)	4705(21)	124(22)
C(33)	2158(14)	2805(16)	4711(21)	138(24)
C(34)	1782(14)	3177(16)	4026(21)	141(27)
C(35)	2404(14)	3343(16)	3335(21)	93(21)
C(36)	3402(14)	3137(16)	3328(21)	66(14)
C(41)	1520(16)	2877(19)	−1745(16)	157(31)
C(42)	1381(16)	3664(19)	−2071(16)	153(32)
C(43)	2203(16)	4172(19)	−2319(16)	138(28)
C(44)	3164(16)	3892(19)	−2241(16)	148(26)
C(45)	3303(16)	3105(19)	−1915(16)	154(30)
C(46)	2481(16)	2597(19)	−1667(16)	72(15)
C(51)	3312(14)	634(17)	−3242(22)	100(20)
C(52)	3963(14)	55(17)	−3999(22)	141(29)
C(53)	4829(14)	−237(17)	−3675(22)	150(25)
C(54)	5044(14)	51(17)	−2593(22)	115(24)
C(55)	4393(14)	630(17)	−1836(22)	85(18)
C(56)	3527(14)	922(17)	−2160(22)	73(16)
C(61)	−50(15)	399(24)	−926(18)	113(22)
C(62)	−190(15)	−654(24)	−1826(18)	121(30)
C(63)	537(15)	−979(24)	−2558(18)	117(21)
C(64)	1404(15)	−251(24)	−2389(18)	101(24)
C(65)	1545(15)	802(24)	−1488(18)	63(15)
C(66)	818(15)	1127(24)	−757(18)	67(16)
C(71)	1089(18)	4532(27)	1980(22)	160(26)
C(72)	1223(18)	5584(27)	2883(22)	148(31)
C(73)	602(18)	5830(27)	3714(22)	170(33)
C(74)	−154(18)	5025(27)	3644(22)	218(38)
C(75)	−288(18)	3973(27)	2742(22)	211(41)
C(76)	333(18)	3727(27)	1910(22)	132(14)

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[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor

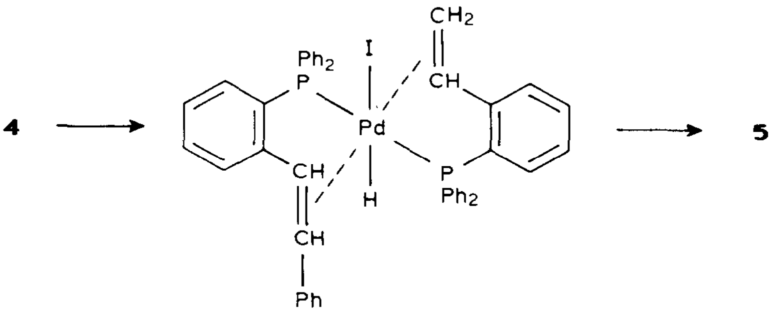
trans to iodide in palladium(II) complexes, e.g. 2.592(3) Å in the monoclinic form of *trans*-$PdI_2(PMe_2Ph)_2$ [20], 2.587(1) Å in *trans*-$PdI_2(PPh_3)_2$ [21], and 2.587(6) Å in *trans*-PdI_2(t-BuNC)$_2$ [22]. The Pd–C bond length (2.05(3) Å) is in the normal range cf. 2.05(2) Å in *trans*-Pd{OC(O)OH}$(CH_3)(PEt_3)_2$ [23], 2.061(3) Å in *trans*-$PdCl(CH_2SCH_3)(PPh_3)_2$ [24], and 2.071(3) Å in PdCl{*o*-$Ph_2PC_6H_4CH$–CH=$C(CH_3)C_6H_4PPh_2$-*o*} [25].

Discussion

The reaction of $Pd(VP)_2$ (**2**) with iodobenzene probably proceeds via **3** and **4** (Scheme 1), although these compounds could not be detected. The isolated product **5** can be formed from **4** by well-established processes of β-hydride elimination from a σ-bonded alkyl group and hydride addition to a metal-bound olefin (Scheme 2). Thus, β-hydride elimination from **4** could give the hydrido-palladium(II) complex **12**, in which the double bonds may be close to the metal atom, if not actually coordinated to it. The hydride ligand can then add to the adjacent vinyl group of VP to give **5**. In principle, this addition could occur in two ways, forming either the observed five-membered ring product Pd{*o*-$CH(CH_3)C_6H_4PPh_2$} or a six-membered ring product Pd{*o*-$CH_2CH_2C_6H_4PPh_2$}. The former is clearly favoured, as is true also for the additions of platinum(II) hydrido-halide complexes to VP [26].

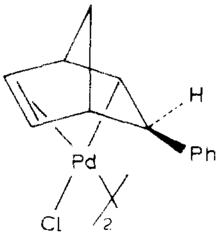
A somewhat similar reaction sequence has been invoked to account for the formation of $PtI(CH_3)$\{*o*-$Ph_2PC_6H_4C(CH_3)$=CH_2\} from the reaction of methyl iodide with $Pt(CH_3)_2(VP)$ [27]. It comprises (1) oxidative addition of methyl iodide to give a transient methylplatinum(IV) species (2) methyl group migration to the vinyl group of VP (3) β-hydride elimination from the resulting metallacycle to generate coordinated *o*-$Ph_2PC_6H_4C(CH_3)$=CH_2 (4) reductive elimination of methane to give the final product. One difference is that the methyl group migrates to the α-carbon atom of the vinyl group, whereas in the present work the phenyl group moves to the β-carbon atom.

Our failure to detect the intermediate phenylpalladium(II) complex **3** is reminiscent of the formation of the *endo*-phenylnorbornenyl complex **13** by treatment of



(**12**)

Scheme 2



(**13**)

$PdCl_2(nbd)$ (nbd = norbornadiene) with $(C_6H_5)_2Hg$ [28,29]. In this case, too, the presumed intermediate $PdCl(C_6H_5)(nbd)$ could not be detected, although its platinum(II) analogue could be isolated and underwent no further reaction.

Although other organic halides readily add to **2**, the σ-bonded organic groups (methyl, allyl, benzyl) are apparently less ready than phenyl to transfer to one of the adjacent vinyl centres.

Experimental

Reactions were carried out and worked up under nitrogen with use of standard Schlenk techniques, although the solid products were fairly stable to air. Solvents and organic halides were dried and distilled by standard procedures. Elemental analyses and molecular weight determinations by vapour pressure osmometry (CH_2Cl_2, 37 °C) were performed in the Microanalytical Laboratory of this School.

Instruments. Bruker CXP200 (^1H NMR at 200 MHz, ^{31}P NMR at 80.38 MHz MHz), Bruker HFX270 (^1H NMR at 270 MHz); Perkin–Elmer 683 (IR). Chemical shifts (δ) are in ppm relative to internal Me_4Si (^1H) or external 85% H_3PO_4 (^{31}P), high frequency being taken as positive.

Starting materials. The complex $Pd(VP)_2$ (**2**) was made by the reaction of $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ with VP in a mol ratio of exactly 1/2; the complexes $M(VP)_2$ (M = Ni, Pt) were made from $M(1,5\text{-}COD)_2$ and two mol equivs of SP. These preparations will be described elsewhere [10].

Reactions of bis{(2-vinylphenyl)diphenylphosphine}palladium(0), Pd(VP)₂ ($\mathit{2}$*) with organic halides*

(1) Iodobenzene. To a solution of **2** (0.56 g, 0.82 mmol) in benzene (10 ml) was added an excess of iodobenzene (2.5 ml). After the mixture had been stirred for 6 h at room temperature, the original orange-yellow colour had not changed, so the solution was heated under reflux for 16 h. Solvent was evaporated under reduced pressure to give an orange-yellow oil which solidified on addition of hexane (50 ml). After being washed with hexane (3 × 20 ml), the solid was dissolved in dichloromethane (10 ml) and the solution was filtered through Celite. Solvent was removed under reduced pressure to give a yellow, spongy solid which, on washing with ether (3 × 10 ml), gave yellow, crystalline $PdI\{o\text{-}CH(CH_3)C_6H_4PPh_2\}\{(E)\text{-}o\text{-}Ph_2PC_6H_4CH{=}CHC_6H_5\}$ (**5**) (0.48 g, 66%). An analytically pure sample, m.p. 138–140 °C, was obtained by recrystallization from dichloromethane/ether and drying in vacuo overnight. (Found: C, 62.38; H, 4.90; I, 14.03; mol. wt., 853;

$C_{46}H_{39}IP_2Pd$ calc: C, 62.29; H, 4.43; I, 14.31%; mol. wt., 887). Infrared (KBr) 1620 cm^{-1} [ν(C=C)]. ^{1}H NMR: $\delta(CD_2Cl_2)$ 1.04 (approx. 1/3/3/1 q, $CHCH_3$) ($\{^{31}P\} \Rightarrow$ d, J(HH) 7 Hz), 3.73 (m, $CHCH_3$) ($\{^{31}P\} \Rightarrow$ q, J(HH) 7 Hz), 6.7–8.3 (m, C_6H_5, C_6H_4, CH=CH); peaks due to residual ether observed at δ 1.16(t), 3.43(q) (J(HH) 7 Hz); in $CDCl_3$, peak due to residual CH_2Cl_2 observed at δ 5.3. $^{31}P\{^1H\}$ NMR: $\delta(CD_2Cl_2)$ 20.0, 45.7 (ABq, J 383 Hz).

Complex **5** (0.20 g, 0.23 mmol) dissolved in dichloromethane (5 ml) was treated with a solution of $AgPF_6$ (0.057 g, 0.23 mmol) in acetone and the mixture was stirred for 18 h. The precipitated AgI was removed by filtration through paper and washed with dichloromethane (2 × 25 ml). Evaporation of the combined filtrate and washings to dryness gave a yellow spongy solid which crystallized on washing with ether (10 ml). The yield of $[\mathrm{Pd}\{\overline{o\text{-}\mathrm{CH(CH_3)C_6H_4P}}\mathrm{Ph_2}\}\{(E)\text{-}o\text{-}\mathrm{Ph_2PC_6H_4CH{=}CHC_6H_5}\}]\mathrm{PF_6}$ (**6**) was 0.17 g (85%). An analytically pure sample of the CH_2Cl_2 solvate, m.p. 148–152°C (dec.), was obtained by recrystallization from dichloromethane/ether. (Found: C, 59.21; H, 4.44; F, 12.12. $C_{46}H_{39}F_6P_3Pd \cdot 0.5CH_2Cl_2$ calc: C, 58.94; H, 4.25; F, 12.03%). Infrared (KBr) 840 cm^{-1} (s, br, PF_6). ^{1}H NMR: $\delta(CD_2Cl_2)$ 1.24 (approx. 1 : 3 : 3 : 1 q, $CHCH_3$) ($\{^{31}P\} \Rightarrow$ d, J(HH) 7 Hz), 3.89 (approx. q of d, $CHCH_3$) ($\{^{31}P\} \Rightarrow$ q, J(HH) 7 Hz), 6.3–8.0 (m, C_6H_5, C_6H_4, CH=CH); peaks due to residual ether at δ 1.16(t), 3.43(q) (J(HH) 7 Hz). $^{31}P\{^1H\}$ NMR: $\delta(CD_2Cl_2)$ 27.9, 42.0 (ABq, J 331 Hz).

(2) Bromobenzene. A mixture of **2** (0.47 g, 0.68 mmol) and bromobenzene (2 ml) in benzene (10 ml) was stirred at room temperature for 3 h and heated under reflux for 13 h. Work-up as described for (1) gave 0.46 g of yellow solid which, in contrast to **5**, was soluble in ether. Precipitation with hexane from a dichloromethane/ether solution gave a yellow solid, m.p. 138–141°C, which analysed satisfactorily for $\mathrm{PdBr}\{\overline{o\text{-}\mathrm{CH(CH_3)C_6H_4)P}}\mathrm{Ph_2}\}\{(E)\text{-}o\text{-}\mathrm{Ph_2PC_6H_4CH{=}CHC_6H_5}\} \cdot 0.5\mathrm{CH_2Cl_2}$ (**6**) (0.26 g, 46%), although NMR spectra indicate the presence of at least one other species. (Found: C, 63.61; H, 4.66; Br, 9.05; mol. wt., 810; $C_{46}H_{39}BrP_2Pd \cdot 0.5CH_2Cl_2$ calc: C, 63.29; H, 4.57; Br, 9.05%; mol. wt., 841). ^{1}H NMR: $\delta(CD_2Cl_2)$ 0.98 (approx. q, $CHCH_3$) ($\{^{31}P\} \Rightarrow$ d; J(HH) 7 Hz), 3.50 (m, $CHCH_3$) ($\{^{31}P\} \Rightarrow$ q, overlapping with another resonance), 6.7–8.3 (m, C_6H_5, C_6H_4, CH=CH); unassigned minor peaks at δ 0.65–0.80 (m), 1.28 (s), 1.78 (s), 2.4 (approx. t, spacing 12 Hz), 2.84 (dd, spacings 12 Hz, 4 Hz), 5.84, 6.04 (each d, spacing 8 Hz). $^{31}P\{^1H\}$ NMR: $\delta(CD_2Cl_2)$ 20.3, 44.6 (ABq, J 385 Hz), 22.1, 41.4 (ABq, J 391 Hz), ratio approx. 7/3.

(3) Methyl iodide. Addition of methyl iodide (0.1 ml) to a solution of **2** (0.40 g, 0.58 mmol) in benzene (10 ml) caused precipitation of a yellow solid within 5 min. After 16 h, the mixture was evaporated to dryness under reduced pressure. The solid was dissolved in warm dichloromethane (20 ml) and the solution was filtered through Celite. On addition of ether (20 ml) and evaporation to ca. half-volume an orange solid precipitated (0.62 g). The NMR spectra (^{1}H, ^{31}P) described in the text suggest that the solid is a mixture of *trans*-$[PdI(CH_3)(VP)_2]$ (**8**), an isomer or isomers of **8** derived by transfer of the methyl group to one of the vinyl groups, and variable amounts of the methiodide of VP. The microanalytical data were in reasonable agreement with those required for **8** (Found: C, 59.11; H, 4.54. $C_{41}H_{37}IP_2Pd$ calc: C, 59.69; H, 4.52%).

(4) Allyl bromide. A solution of **2** (0.40 g, 0.58 mmol) in benzene (10 ml) was treated with allyl bromide (0.05 ml, 0.58 mmol) and the mixture was stirred

overnight at room temperature. Filtration and evaporation to dryness gave a yellow solid which was washed with ether (3 × 10 ml). The yield of $PdBr(\eta^3\text{-}C_3H_5)(o\text{-}Ph_2PC_6H_4CH{=}CH_2)$ (**10**) was 0.23 g (66%). An analytically pure sample, m.p. 153–155 °C, was obtained by recrystallization from dichloromethane/ether/hexane (Found: C, 54.16; H, 4.35; Br, 15.81; P, 6.45; mol. wt., 512; $C_{23}H_{22}BrPPd$ calc: C, 53.57; H, 4.30; Br, 15.49; P, 6.01%; mol. wt., 516). The ^1H NMR spectrum at room temperature is described in the text. At −90 °C in $CDCl_2$, it is as follows, protons being numbered as in **10**: δ 2.93 (approx. d, H^6, J_{68} ca. 10 Hz), 3.3 (d, overlapping q due to residual ether, H^7), 3.56 (dd, H^5, J_{58} 13, $J(PH^5)$ 10 Hz), 4.64 (br. t, H^4, J_{48} ca. 6, $J(PH^4)$ ca. 6 Hz), 5.14 (d, H^2, J_{12} 11 Hz), 5.59 (approx. qnt, H^8), 5.67 (d, H^3, J_{13} 18 Hz), 6.6–7.8 (m, Ar + H^1). $^{31}P\{^1H\}$ NMR: $\delta(CD_2Cl_2)$ 17.5 (s)

(5) Benzyl bromide. A solution of **2** (0.38 q, 0.56 mmol) in benzene (10 ml) was treated with an excess of benzyl bromide, causing a colour change from dark to light yellow. Work-up as described for (4) and recrystallization from dichloromethane/ether gave a yellow solid (0.18 g, 58%) which analysed satisfactorily for $PdBr(CH_2Ph)(o\text{-}Ph_2PC_6H_4CH{=}CH_2) \cdot 0.5CH_2Cl_2$ (**11**) (Found: C, 53.68; H, 4.00; Cl, 5.99; Br, 13.14. $C_{27}H_{24}BrPPd \cdot 0.5CH_2Cl_2$ calc: C, 54.30; H, 4.13; Cl, 5.83; Br, 13.14%). ^1H NMR: $\delta(CD_2Cl_2)$ ca. 2.0, 2.2, 2.7 (each br m), 4.7 (br m), 6.8–7.9 (m, Ar). $^{31}P\{^1H\}$ NMR: $\delta(CD_2Cl_2)$ 53.2 (s), 53.7 (s).

Crystallography

A dark red, thin, plate-like crystal of **5** of approximate dimensions 0.1 × 0.3 × 0.3 mm³ was obtained from dichloromethane/ether. Crystal data were established from precession photographs and measured accurately by means of a Nicolet XRD P3 four-circle diffractometer. The θ–2θ scan technique was used to collect intensities out to a maximum Bragg angle of 18°.

Crystal data. $C_{46}H_{39}IP_2Pd$, M 887.1, triclinic, space group $P\bar{1}$, a 13.404(5), b 13.850(6), c 14.158(7) Å, α 118.39(3), β 92.28(4), γ 95.58(3)°, U 2290 Å^3, D_c 1.29 g cm^{-3} for $Z = 2$, μ(Mo-$K_{\bar{\alpha}}$) 7.87 cm^{-1}; absorption corrections, maximum transmission 0.9324, minimum transmission 0.7192; number of independent reflections measured 3156, number with $I > 2\sigma(I)$ 2139; g 0.0121, R 0.087, R_w 0.049.

Structure determination. The structure was solved by heavy atom vector methods and difference Fourier syntheses. Blocked cascade least-squares refinements (SHELXTL) [30] were employed and the weights $1/[\sigma^2(F) + g(F^2)]$ were applied to reflection data. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Anomalous dispersion coefficients were from ref. 31. In the final states of refinement, all non-hydrogen atoms were assigned anisotropic thermal parameters but the phenyl rings were treated as rigid hexagonal groups with C–C bond lengths of 1.395 Å. The hydrogen atom positions were refined from idealized coordinates calculated geometrically with fixed isotropic temperature factors and C–H bond lengths of 0.96 Å.

Attempts to characterize residual electron density evident in final difference Fourier syntheses were unsuccessful. The highest residual peak was approximately half the height of the peak corresponding to the last carbon atom located by this method. Since solvent incorporation in the crystal was only of minor interest, the final converged model includes only the palladium complex.

Supplementary material which includes thermal parameters for non-hydrogen atoms, atomic coordinates and thermal parameters for hydrogen atoms, and structure factors may be obtained from the authors.

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