Acid-catalysed Additions of Acetylenes to [XPd(μ-$Ph_2PCH_2PPh_2$)$_2$PdX] (X = Cl, Br, or I) to give Dimetallated Olefin Complexes of Type [XPd(μ-$Ph_2PCH_2PPh_2$)$_2$(μ-HC=CR)PdX] (R = H, Ph, or C_6H_4Me-*p*)

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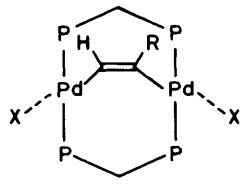
The addition of acetylenes to [XPd(μ-dppm)$_2$PdX] (dppm = $Ph_2PCH_2PPh_2$; X = Cl, Br, or I) is catalysed by traces of acid and (in some cases) methanol, giving [XPd(μ-dppm)$_2$(μ-HC=CR)PdX] (R = H, Ph, or C_6H_4Me-*p*) containing the dipalladated olefin ligand HC=CR. These reactions are readily reversed by heating or by photolysis. Hydrogen-1 and ^{31}P-{^1H} n.m.r. and i.r. spectroscopic data are given and discussed.

The addition of atoms or small molecules across the metal–metal bond of complexes of the types [XM^1(μ-dppm)$_2M^2X$] (M^1, M^2 = Pd or Pt; X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) to give A-frames of type [XM^1(μ-dppm)$_2$(μ-Y)M^2X], with Y = S,[1] SO_2,[1–3] CO,[3,4] N_2R (R = aryl),[5] MeNC,[4] *etc.* is a well established reaction. An alternative route to A-frames of this type is a three-fragment, two-centre oxidative addition to [Pd_2(μ-dppm)$_3$], or related species, which has been used to synthesize complexes of type [XPd(μ-dppm)$_2$(μ-R)PdX] with R = $-CH_2-$[6] or *o*-C_6H_4.[6] We have used such a three-fragment oxidative addition to synthesize [ClPd(μ-dppm)$_2$(μ-C=CH_2)-PdCl], in high (>90%) yield,[7] by treating [$Pd(PPh_3)_4$] with dppm and $Cl_2C=CH_2$ in hot benzene and we wished to compare this μ-vinylidene complex with the isomeric but unknown complex [ClPd(μ-dppm)$_2$(μ-HC=CH)PdCl] (**1a**). However, when we treated [Pd_2(μ-dppm)$_3$] with *cis*-ClCH=CHCl with the intention of forming the μ-acetylene or dipalladated ethylene complex (**1a**), by a three-fragment oxidative addition, none of complex (**1a**) was formed, instead all the products were apparently mononuclear and included [$PdCl_2$(dppm-*PP'*)] (^1H and ^1H-{^{31}P} n.m.r. evidence). It has been reported that, although acetylenes with electron-withdrawing groups such as $RO_2CC{\equiv}CCO_2R$, $RO_2CC{\equiv}CH$ (R = alkyl), or $F_3CC{\equiv}CCF_3$ react with [ClPd(μ-dppm)$_2$PdCl] to give A-frame adducts of type [ClPd(μ-dppm)$_2$(μ-acetylene)PdCl], other acetylenes, such as HC≡CH, PhC≡CH, or PhC≡CPh, do not react.[6] We have found that prolonged treatment of [ClPd(μ-dppm)$_2$PdCl] with acetylene in dichloromethane solution caused gradual darkening of the orange solution to brown and a ^{31}P-{^1H} n.m.r. investigation showed that eventually (after 1 h at 20 °C) all the starting complex had reacted. The major product showed a singlet at δ +9.3 p.p.m. in the ^{31}P-{^1H} n.m.r. spectrum, almost certainly due to complex (**1a**) (see below) but, in addition, significant amounts of [Pd_2(μ-dppm)$_3$] and [$PdCl_2$(dppm-*PP'*)] were present, together with unidentified products. However, acid catalysed the addition of acetylenes to [ClPd(μ-dppm)$_2$PdCl] to a remarkable degree. Thus treatment of a dichloromethane solution of this dipalladium(I) complex with acetylene, in the presence of *ca.* 5 mol % of $HBF_4{\cdot}Et_2O$, caused essentially complete conversion into the A-frame adduct (**1a**) in 5 min at 20 °C. The conversion was monitored by ^{31}P-{^1H} n.m.r. spectroscopy and the single product, subsequently identified as (**1a**), was characterized by a singlet resonance at δ +9.3 p.p.m. The product was readily isolated (see Experimental section) and assigned structure (**1a**) on the following evidence.

(*i*) Elemental analysis (see Experimental section).

(*ii*) The ^1H-{^{31}P} n.m.r. spectrum, which showed a singlet resonance for the HC≡CH protons and an AX pattern for the OCH_2P protons (see Table).



	R	X
(**1a**)	H	Cl
(**1b**)	H	Br
(**1c**)	Ph	Cl
(**1d**)	Ph	Br
(**1e**)	C_6H_4Me-*p*	Cl
(**1f**)	Me	Cl

Table. ^{31}P-{^1H}, ^1H, and ^1H-{^{31}P} n.m.r. spectroscopic data

Compound	^{31}P-{^1H} n.m.r.[a]	^1H and ^1H-{^{31}P}[b]
(**1a**)	9.3 (s)	6.28 [2 H, *HC*=C*H*, *J*(PH) = 15.4[c]], 3.35, 2.90 [PCH_AH_XP, $J(H_AH_X)$ = 12.7, *J*(PH) = 5.4 and 3.6 respectively]
(**1b**)[d]	10.8 (s)	6.30 [2 H, *HC*=C*H*, *J*(PH) = 15.9[c]], 3.37, 2.98 [PCH_AH_XP, $J(H_AH_X)$ = 12.9, *J*(PH) = 5.6 and 3.6 respectively[c]]
(**1c**)	5.3, 11.1 (AA'BB')	5.93 [1 H, *HC*=CPh, t of t, *J*(PH) = 11.3 and 11.5[e]], 3.13, 2.75 [PCH_AH_XP, $J(H_AH_X)$ = 13.0, *J*(PH) = 5.3, 3.7 respectively[c]]
(**1d**)	6.1, 12.4 (AA'BB')	5.99 [1 H, *HC*=CPh, t of t, *J*(PH) = 11.3 and 19.0[e]], 3.18, 2.82 [PCH_AH_XP, $J(H_AH_X)$ = 12.7, *J*(PH) = 5.4, 3.6 respectively[c]]
(**1e**)	4.9, 11.4 (AA'BB')	6.87, 6.21 [4 H, AA'XX', $CH_3C_6H_4$], 5.81 [1 H, *HC*=C$C_6H_4CH_3$, t of t, *J*(PH) = 11.5, 18.6[e]], 3.15, 2.77 [PCH_AH_XP, $J(H_AH_X)$ = 12.8, *J*(PH) = 5.6, 3.7 respectively[c]]

[a] At 40.3 MHz in CH_2Cl_2 or CD_2Cl_2; δ/p.p.m. relative to 85% H_3PO_4. [b] At 100 MHz (unless stated otherwise) in CD_2Cl_2; δ/p.p.m., *J* in Hz. [c] Coupled to all four *P* nuclei giving virtual 1:4:6:4:1 quintets. Values quoted are apparent *J*(PH), *i.e.* separations between adjacent peaks. [d] ^1H and ^1H-{^{31}P} n.m.r. spectra at 162 MHz in CD_2Cl_2. [e] Coupled to two sets of two P nuclei, thus appearing as virtual triplets. Values quoted are apparent *J*(PH).

(*iii*) In the ^1H n.m.r. spectrum the acetylene hydrogens showed a virtual 1:4:6:4:1 quintet pattern due to apparent equal coupling to all four P nuclei, and the pseudo-equatorial and pseudo-axial methylene hydrogens PCH_eH_aP each showed a doublet of 1:4:6:4:1 quintets, again due to virtual coupling to all four *P* nuclei.

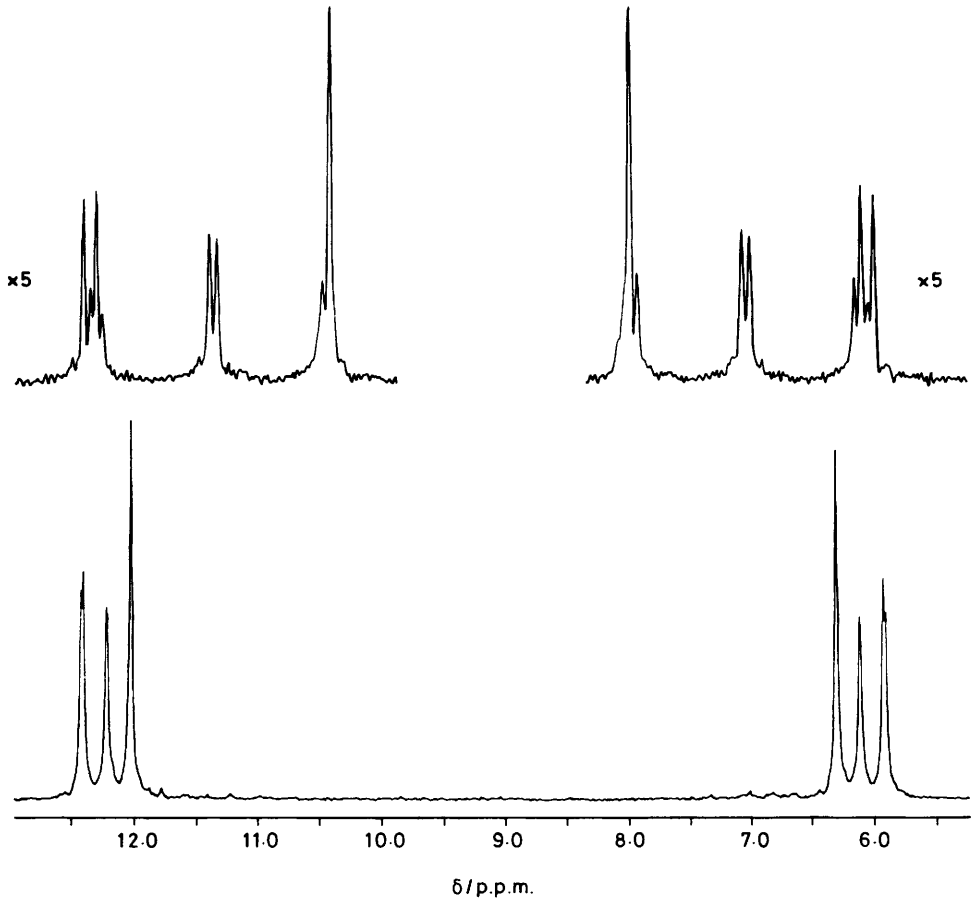


Figure. 162-MHz ^{31}P-$\{^1H\}$ N.m.r. spectrum of $[BrPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdBr]$ (**1d**) in CD_2Cl_2, showing the AA'BB' pattern. The expansions are × 5

(*iv*) The i.r. spectrum showed a band at 274s cm^{-1}, not present in the spectrum of the analogous bromide (see below), and assigned to ν(Pd–Cl). A similar treatment of $[BrPd(\mu\text{-dppm})_2PdBr]$ with acetylene in the presence of $HBF_4{\cdot}Et_2O$ gave the analogous bromide $[BrPd(\mu\text{-dppm})_2(\mu\text{-HC=CH})PdBr]$ (**1b**) in 59% yield; preparative details are in the Experimental section and characterizing spectroscopic data in the Table. Treatment of $[ClPd(\mu\text{-dppm})_2PdCl]$ with a 20-fold excess of PhC≡CH in dichloromethane at 20 °C caused no apparent reaction (^{31}P-$\{^1H\}$ n.m.r. evidence), but in the presence of 5 mol % of $HBF_4{\cdot}Et_2O$ reaction with PhC≡CH was rapid and, after *ca.* 2 min, essentially complete. The product $[ClPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdCl]$ (**1c**) was isolated in 87% yield; characterizing data are in the Experimental section and the Table. We then found that a much weaker protonic acid than $HBF_4{\cdot}Et_2O$, namely methanol, also catalysed the conversion of $[ClPd(\mu\text{-dppm})_2PdCl]$ into (**1c**), albeit slowly. Typically a *ca.* 100-fold excess of methanol catalysed complete addition of PhC≡CH in 20 min; see Experimental section for details. The phenylacetylene adduct (**1c**) showed an AA'BB' ^{31}P-$\{^1H\}$ n.m.r. pattern from which the two ^{31}P chemical shifts were measured (Table) but the patterns were not fully analysed. Similar treatment of $[BrPd(\mu\text{-dppm})_2PdBr]$ with PhC≡CH gave $[BrPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdBr]$ (**1d**) and of $[ClPd(\mu\text{-dppm})_2PdCl]$ with *p*-$MeC_6H_4C{\equiv}CH$ gave $[ClPd(\mu\text{-dppm})_2(\mu\text{-}p\text{-}MeC_6H_4C{=}CH)PdCl]$ (**1e**); preparative and characterizing details are in the Experimental section and the Table. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the phenylacetylene adduct (**1d**) is shown in the Figure. The complex $[IPd(\mu\text{-dppm})_2PdI]$ reacted with PhC≡CH in CD_2Cl_2 solution containing MeOH to give a product with an AA'BB' ^{31}P-$\{^1H\}$ n.m.r. pattern [$\delta(P_A)$ = 7.5, $\delta(P_B)$ = 12.6 p.p.m.] which was almost certainly $[IPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdI]$. When we attempted to isolate this adduct it decomposed and $[IPd(\mu\text{-dppm})_2PdI]$ was recovered. When $[ClPd(\mu\text{-dppm})_2PdCl]$ was treated with MeC≡CH in the presence of a trace of $HBF_4{\cdot}Et_2O$, partial conversion into the adduct $[ClPd(\mu\text{-dppm})_2(\mu\text{-MeC=CH})PdCl]$ seemed to occur; this showed an AA'BB' ^{31}P-$\{^1H\}$ n.m.r. pattern with [$\delta(P_A)$ = 7.1 and $\delta(P_B)$ = 12.0 p.p.m., but on attempted isolation reversion to $[ClPd(\mu\text{-dppm})_2PdCl]$ largely occurred.

The adducts (**1a**), (**1c**), and (**1e**) (and probably the others) were somewhat light- and heat-sensitive. When dichloromethane solutions of these three complexes were exposed to strong light from a fluorescent tube of the daylight type they reverted to $[ClPd(\mu\text{-dppm})_2PdCl]$, essentially quantitatively in 36 [(**1a**)] or 12 h [(**1c**) or (**1e**)]. In similar experiments with the dibromide (**1b**) or (**1d**) reversion to $[BrPd(\mu\text{-dppm})_2PdBr]$ in essentially quantitative yield occurred in *ca.* 6 h. The 'A-frames' (**1a**)—(**1e**) were also heat sensitive and when their solutions in benzene were heated to 80 °C for 2 h the corresponding $[XPd(\mu\text{-dppm})_2PdX]$ complexes were isolated in high yield.

The three adducts (**1a**), (**1c**), and (**1e**) were apparently unaffected by traces of acid (CF_3CO_2H) or base ($KOBu^t$) in dichloromethane solution. However, treatment of the acetylene adduct (**1a**) with 1 mol equivalent of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 caused slow decomposition to dark, unidentified products. This contrasts with the behaviour of the isomeric $[ClPd(\mu\text{-dppm})_2(\mu\text{-C=CH}_2)PdCl]$ which with $HBF_4{\cdot}Et_2O$ or CF_3CO_2H reacts

immediately to give what appears to be $[ClPd(\mu\text{-dppm})_2(\mu\text{-}C\text{–}CH_3)PdCl]^+$.[8] We also find that the acetylene in (**1a**) is not displaced by other potentially bridging groups, *e.g.* CO or $MeO_2CC{\equiv}CCO_2Me$.

It seems possible that, when treated with acid (or methanol), the dipalladium(I) complex $[ClPd(\mu\text{-dppm})_2PdCl]$ is converted, at least in part, into $[ClPd(\mu\text{-dppm})_2(\mu\text{-H})PdCl]^+$. The corresponding diplatinum μ-hydrido complex $[ClPt(\mu\text{-dppm})_2(\mu\text{-H})PtCl]^+$ is well known. Treatment of a dichloromethane solution of $[ClPd(\mu\text{-dppm})_2PdCl]$ with CF_3CO_2H at −70 °C gave new species characterized by a ^{31}P n.m.r. singlet resonance at +11.8 p.p.m. and, in particular, a broad hydride resonance at −14.73 p.p.m. and a singlet methylene resonance at 4.18 p.p.m., in the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum. Unfortunately, below −70 °C material started to come out of solution, at higher temperatures the hydride resonance broadened further. We suggest that the broadening of the hydride resonance was due to some exchange with the CF_3CO_2H protons. When $[ClPd(\mu\text{-dppm})_2PdCl]$ was treated with $HBF_4{\cdot}Et_2O$ (1 mol equivalent) in CH_2Cl_2 and the solvent was removed a blood-red solid was obtained. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this product (dissolved in CD_2Cl_2) showed a singlet resonance at +11.8 p.p.m. together with some smaller peaks, one of which was probably due to $[PdCl_2(dppm\text{-}PP')]$. The i.r. spectrum of the red solid showed a weak peak at 1 905 cm^{-1}, possibly due to ν(Pd–H) but the ^1H and $^1H\text{-}\{^{31}P\}$ n.m.r. spectra showed no hydride resonance, probably due to rapid exchange with acid. Treatment of $[XPd(\mu\text{-dppm})_2PdX]$ (X = Br or I) with $HBF_4{\cdot}Et_2O$ (1 mol equivalent) in CH_2Cl_2 also gave single products ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence) which we suggest are $[XPd(\mu\text{-dppm})_2(\mu\text{-H})PdX]^+$ (X = Br or I), but these could not be isolated pure as the salts with BF_4^-. In one experiment, $[ClPd(\mu\text{-dppm})_2PdCl]$ was treated with 1 mol equivalent of $HBF_4{\cdot}Et_2O$ to generate $[ClPd(\mu\text{-dppm})_2(\mu\text{-H})PdCl]^+$ *in situ*. When PhC≡CH (excess) was added to this solution, conversion into $[ClPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdCl]$ was immediate ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence).

When we treated dichloromethane solutions of either $[ClPt(\mu\text{-dppm})_2PtCl]$ or $[ClPd(\mu\text{-dppm})_2PtCl]$ with HC≡CH or PhC≡CH in the presence of small amounts of $HBF_4{\cdot}Et_2O$ or CF_3CO_2H dimetallated-olefin A-frames analogous to (**1a**) or (**1c**) were not formed and could not be isolated. For example, such treatment of $[ClPd(\mu\text{-dppm})_2PtCl]$ gave mixtures containing $[PdCl_2(dppm\text{-}PP')]$, $[PtCl_2(dppm\text{-}PP')]$ and other, unidentified, products.

Experimental

General methods and instrumentation used were as described in recent publications from this laboratory.[9] The complexes $[XPd(\mu\text{-dppm})_2PdX]$ (X = Cl, Br, or I),[3] $[ClPt(\mu\text{-dppm})_2PtCl]$,[10] $[ClPd(\mu\text{-dppm})_2PtCl]$,[3] $[ClPt(\mu\text{-dppm})_2(\mu\text{-H})PtCl]Cl$,[10] and $[Pt_2(\mu\text{-dppm})_3]$[11] were prepared by literature methods.

$[ClPd(\mu\text{-dppm})_2(\mu\text{-HC=CH})PdCl]$ (**1a**).—Acetylene was bubbled into a solution of $[ClPd(\mu\text{-dppm})_2PdCl]$ (0.20 g, 0.19 mmol) in dry dichloromethane (5 cm^3). The adduct $HBF_4{\cdot}Et_2O$ (*ca.* 1 μl) was then added and the solution stirred for 2 min during which its colour changed from deep orange to pale yellow. Benzene (5 cm^3) was then added and the volume of the mixture was slowly reduced *in vacuo*. The required product separated as yellow microcrystals which were filtered off and dried. Yield 0.103 g, 51% (Found: C, 57.9; H, 4.4; Cl, 6.2. $C_{52}H_{46}Cl_2P_4Pd_2$ requires C, 58.2; H, 4.3; Cl, 6.6%); ν(Pd–Cl) (Nujol) 274 cm^{-1}.

$[BrPd(\mu\text{-dppm})_2(\mu\text{-HC=CH})PdBr]$ (**1b**).—Acetylene was bubbled through a solution of $[BrPd(\mu\text{-dppm})_2PdBr]$ (0.20 g, 0.175 mmol) in dry dichloromethane (17 cm^3) for 5 min. The adduct $HBF_4{\cdot}Et_2O$ (*ca.* 1 μl) was then added and the passage of acetylene continued for a further 5 min. Methanol (1 cm^3) was then added and the volume of the reaction mixture reduced *in vacuo*, giving the required product as yellow microcrystals. Yield 0.12 g, 59% (Found: C, 53.1; H, 3.9; Br, 13.9. $C_{52}H_{46}Br_2P_4Pd_2$ requires C, 53.5; H, 4.0; Br, 13.7%).

$[ClPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdCl]$ (**1c**).—*Method* (*i*) *using methanol as catalyst.* A solution of $[ClPd(\mu\text{-dppm})_2PdCl]$ (0.053 g, 0.05 mmol) in dichloromethane (1.5 cm^3) was treated with PhC≡CH (50 μl, 0.46 mmol) then methanol (150 μl) and the reaction monitored by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. After 20 min complete conversion into (**1c**) had occurred. The solvent was then removed *in vacuo* and the residue treated with methanol (1 cm^3). This gave the required product as yellow microcrystals. Yield 0.051 g, 88% (Found: C, 60.8; H, 4.4; Cl, 6.0. $C_{58}H_{50}Cl_2P_4Pd_2$ requires C, 60.3; H, 4.4; Cl, 6.1%); ν(Pd–Cl) 280m cm^{-1}.

Method (*ii*) *using* $HBF_4{\cdot}Et_2O$ *as catalyst.* Phenylacetylene (0.186 g, 4.8 mmol) and then $HBF_4{\cdot}Et_2O$ (*ca.* 1 μl) were added to a solution of $[ClPd(\mu\text{-dppm})_2PdCl]$ (0.20 g, 0.19 mmol) in dry dichloromethane (6 cm^3). The mixture was then stirred for 2 min during which its colour changed from orange to pale yellow. Diethyl ether (15 cm^3) was slowly added and the mixture was put aside at 0 °C for 2 h. This gave the required product (0.19 g, 87%).

$[BrPd(\mu\text{-dppm})_2(\mu\text{-PhC=CH})PdBr]$ (**1d**).—Phenylacetylene (0.35 cm^3, 3.2 mmol) and then $HBF_4{\cdot}Et_2O$ (10 μl) were added to a solution of $[BrPd(\mu\text{-dppm})_2PdBr]$ (0.20 g, 0.175 mmol) in dry dichloromethane (10 cm^3). The colour of the solution paled to red in <1 min. The solvent was then removed *in vacuo* and the residue was titrated with methanol (3 cm^3). This gave the required product. Yield 0.18 g, 83% (Found: C, 54.0; H, 4.0; Br, 12.4. $C_{58}H_{50}Br_2P_4Pd_2{\cdot}H_2O$ requires C, 55.2; H, 4.2; Br, 12.7%).

$[ClPd(\mu\text{-dppm})_2(\mu\text{-}p\text{-}MeC_6H_4C=CH)PdCl]$ (**1e**).—This was prepared in an analogous manner to (**1d**), method (*ii*), and formed yellow microcrystals. Yield 95% (Found: C, 60.2; H, 4.5; Cl, 6.0. $C_{59}H_{52}Cl_2P_4Pd$ requires C, 60.0; H, 4.5; Cl, 6.1%).

Action of MeC≡CH *on* $[ClPd(\mu\text{-dppm})_2PdCl]$.—Gaseous MeC≡CH (40 cm^3, *ca.* 1.7 mmol) and then $HBF_4{\cdot}Et_2O$ (2 μl) were added to a solution of $[ClPd(\mu\text{-dppm})_2PdCl]$ (0.25 g, 0.24 mmol) in dry dichloromethane (8 cm^3). The solution turned pale yellow. The solvent was removed *in vacuo* and the orange residue examined by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.

$[ClPd(\mu\text{-dppm})_2(\mu\text{-H})PdCl]BF_4$ (**2a**).—The adduct $HBF_4{\cdot}Et_2O$ (26 μl, 0.19 mmol) was added to a solution of $[ClPd(\mu\text{-dppm})_2PdCl]$ (0.20 g, 0.19 mmol) in dry dichloromethane (10 cm^3). The resultant red solution was evaporated to *ca.* 1 cm^3 *in vacuo* and dry diethyl ether (5 cm^3) was added. This gave the required product contaminated with some $[PdCl_2(dppm\text{-}PP')]$. Yield 0.17 g (Found: C, 51.8, 51.9; H, 3.9, 4.0; Cl, 6.5, 6.7. $C_{50}H_{45}BCl_2F_4P_4Pd_2$ requires C, 52.7; H, 4.0; Cl, 6.2%). Infrared spectrum (Nujol): ν(Pd–Cl) 270s, ν(Pd–H) 1 905vs, and ν(B–F) 1 060vs cm^{-1}.

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