Syntheses of Vinylidene-bridged A-Frame Palladium Complexes containing Ph$_2$PCH$_2$PPh$_2$ or Ph$_2$PCHMePPh$_2$: Protonation to Give Carbyne-bridged Complexes

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Treatment of benzene solutions of [Pd(dba)$_2$] (dba = dibenzylideneacetone) or [Pd(PPh$_3$)$_4$] with Ph$_2$PCH$_2$PPh$_2$ (dppm) and X$_2$C=CH$_2$ (X = Cl or Br) gave the 'A-frame' vinylidene-bridged complexes of type [XPd(μ-dppm)$_2$(μ-C=CH$_2$)PdX] [X = Cl (**1a**) or Br (**1b**)] in high yield. Treatment of (**1a**) with LiBr, NaI, or KSCN in acetone gave [XPd(μ-dppm)$_2$(μ-C=CH$_2$)PdX] [X = Br (**1b**), I (**1c**), or NCS (**1d**)], respectively. Complex (**1a**) with TlO$_2$CMe gave [(MeCO$_2$)Pd(μ-dppm)$_2$(μ-C=CH$_2$)Pd(O$_2$CMe)] (**1e**) and with LiC≡CC$_6$H$_4$Me-4 the diacetylide complex [(*p*-MeC$_6$H$_4$C≡C)Pd(μ-dppm)$_2$(μ-C=CH$_2$)Pd(C≡CC$_6$H$_4$Me-*p*)] (**2a**) was obtained in low yield. Better yields of the diacetylides of type [(RC≡C)Pd(μ-dppm)$_2$(μ-C=CH$_2$)Pd(C≡CR)] were obtained by treating (**1a**) with HC≡CR, TlPF$_6$, and NEt$_3$ in dichloromethane; *e.g.* with R = C$_6$H$_4$Me-4 (**2a**), Ph (**2b**), or CMe$_2$(OH) (**2c**). Treatment of (**1a**) with *p*-MeC$_6$H$_4$NC and NaBPh$_4$ in ethanol gave [(*p*-MeC$_6$H$_4$NC)Pd(μ-dppm)$_2$(μ-C=CH$_2$)Pd(CNC$_6$H$_4$Me-*p*)][BPh$_4$]$_2$ (**3**). Treatment of [Pd(PPh$_3$)$_4$] with dppm and Cl$_2$C=CCl$_2$ gave a mixture of [ClPd(μ-dppm)$_2$(μ-C=CCl$_2$)PdCl] (**4**) and [ClPd(μ-dppm)$_2$PdCl] but (**4**) was obtained in high yield and purity when a mixture of [Pd(PPh$_3$)$_4$], dppm, and [PdCl(CCl=CCl$_2$)(PPh$_3$)$_2$] was heated. A mixture of [Pd(PPh$_3$)$_4$] and Ph$_2$PCHMePPh$_2$ (mdppm) when treated with Cl$_2$C=CH$_2$ gave the 'A-frame' vinylidene-bridged complex [ClPd(μ-mdppm)$_2$(μ-C=CH$_2$)PdCl] (**5a**) or (**5b**). Treatment of (**1a**) or (**5a**)/(**5b**) with HBF$_4$·Et$_2$O or CF$_3$CO$_2$H gave [ClPd(μ-L–L)$_2$(μ-CMe)PdCl]$^+$ [L–L = dppm (**6**) or mdppm (**7**)], characterized in solution by n.m.r. spectroscopy. Salts of these carbyne cations were not isolated pure. N.m.r. data are given and discussed.

We have described[1] the synthesis of a dinickel complex [ClNi(μ-dppm)(μ-C=CH$_2$)NiCl] containing a bridging vinylidene group by a two-centre, three-fragment oxidative addition of Cl$_2$C=CH$_2$ to [Ni$_2$(dppm)$_3$] (dppm = Ph$_2$PCH$_2$PPh$_2$). We were also able to make similar heterobimetallic A-frames, *e.g.* [ClNi(μ-dppm)$_2$(μ-C=CH$_2$)NiCl].[1] Balch *et al.*[2] have reported the synthesis of dipalladium A-frames [IPd(μ-dppm)$_2$(μ-R)PdI] (R = CH$_2$ or *o*-C$_6$H$_4$) by treating [Pd$_2$(dppm)$_3$] with CH$_2$I$_2$ or *o*-C$_6$H$_4$I$_2$. We now wish to report on the synthesis and reactions of [ClPd(μ-dppm)$_2$(μ-C=CH$_2$)PdCl]; some of this work has been reported in a preliminary communication.[3]

Results and Discussion

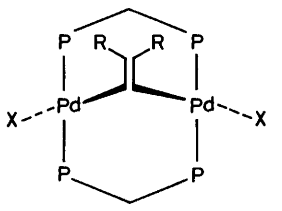
Treatment of a benzene solution of [Pd(PPh$_3$)$_4$] and dppm with vinylidene chloride under reflux gave the yellow complex [ClPd(μ-dppm)$_2$(μ-C=CH$_2$)PdCl] (**1a**), as a benzene solvate in 95% yield; a similar treatment of [Pd(dba)$_2$] (dba = dibenzylideneacetone)[4] with dppm and vinylidene chloride gave (**1a**) in 90% yield. The structure of (**1a**) follows from (*i*) microanalytical data (Table 1), (*ii*) a band at 260 cm^{-1} in the i.r. spectrum, absent from the spectrum of the corresponding iodide and assigned to ν(Pd–Cl), (*iii*) a singlet resonance in the ^{31}P-{^{1}H} n.m.r. spectrum, at 15.6 p.p.m. (Table 2), and of particular value, (*iv*) the ^{1}H and ^{1}H-{^{31}P} n.m.r. spectra which show for the two vinylidene protons a five-line (1:4:6:4:1) pattern due to virtual coupling to all four phosphorus nuclei and a single peak for the phosphorus-decoupled spectrum. The methylene protons of the dppm ligand, which are non-equivalent, gave an AX pattern in the ^{1}H-{^{31}P} n.m.r. spectrum, and each resonance was further split into 1:4:6:4:1 quintets by virtual coupling to the four equivalent phosphorus nuclei in the ^{1}H n.m.r. spectrum [apparent J 5.6 (δ 3.42) and 3.1 Hz (δ 2.56 p.p.m.)]. These spectra are very similar to those reported for [IPd(μ-dppm)$_2$(μ-R)PdI] (R = CH$_2$ or *o*-C$_6$H$_4$)[2] and for [(SCN)Ni(μ-dppm)$_2$(μ-C=CH$_2$)Ni(NCS)], the crystal structure of which we have determined.[1]

Physically or chemically the μ-vinylidene complex (**1a**) is extremely robust, stable to heat (refluxing xylene), light (dichloromethane solutions are unaffected by irradiation, using a fluorescent tube of the 'daylight' type), or oxygen. In this respect it differs from the isomeric complex [ClPd(μ-dppm)$_2$(μ-HC=CH)PdCl] which readily loses acetylene to form [ClPd(μ-dppm)$_2$PdCl] when treated in these ways.[5] When treated with LiBr, NaI, or KSCN in acetone, the chloro-complex (**1a**) gave the corresponding complexes of type [XPd(μ-dppm)$_2$(μ-C=CH$_2$)PdX] with X = Br (**1b**), I (**1c**), or NCS (**1d**), respectively. The i.r. spectrum of (**1d**) showed ν(SCN) at 2 090 cm^{-1}, indicating that the thiocyanate group is *N*-bonded; a similar value (2 095 cm^{-1}) was found for the *N*-bonded thiocyanate in [(SCN)Ni(μ-dppm)$_2$(μ-C=CH$_2$)Ni(NCS)].[1] The dichloro-complex (**1a**) did not react with sodium acetate but reacted with thallium(I) acetate to give [(MeCO$_2$)Pd(μ-dppm)$_2$(μ-C=CH$_2$)Pd(O$_2$CMe)] (**1e**). The structures of complexes (**1b**)—(**1e**) follow from microanalytical and i.r. data (Table 1) and from n.m.r. data (Table 2). The μ-vinylidene complex (**1a**) did not react with CO or with MeO$_2$CC≡CCO$_2$Me. We hoped that the vinylidene group in (**1a**) would be sufficiently polarized to undergo Michael-type additions when treated with nucleophilic reagents, but this was not so. Decomposition occurred when (**1a**) was treated with methyllithium or *p*-tolyl-lithium, as did treatment with the hydrides, NaBH$_4$ or NaBHEt$_3$, or with NaBHEt$_3$ and CO. Complex (**1a**) reacted slowly with *p*-MeC$_6$H$_4$C≡CLi at 0 °C in tetrahydrofuran (thf) to give [(*p*-MeC$_6$H$_4$C≡C)Pd(μ-dppm)$_2$(μ-C=CH$_2$)Pd(C≡CC$_6$H$_4$Me-*p*)] (**2a**) and other products, which were dark and were not identified. With *p*-tolyl isocyanide (**1a**) reacted to give the dication [(*p*-MeC$_6$H$_4$NC)Pd(μ-dppm)$_2$(μ-

Table 1. Analytical (%) and i.r. data (cm^{-1})

Complex	Analysis[a] C	H	X	Colour	I.r.	
$(\mathbf{1a})\cdot1.5C_6H_6$	59.6 (59.5)	4.6 (4.5)	5.85 (5.8)	Yellow	260s	ν(Pd–Cl)
(1b)	53.4 (53.5)	4.0 (4.0)	14.0 (13.7)	Yellow		
$(\mathbf{1c})\cdot1.0C_6H_5Me$	52.1 (52.4)	3.9 (4.0)	18.5 (18.8)	Deep yellow		
(1d)	57.45 (57.7)	4.05 (4.1)	2.4 (2.5)[b]	Cream	2 090vs	ν(NCS)
(1e)	60.0 (59.75)	4.3 (4.5)		Orange		
(2a)	67.5 (67.9)	4.9 (4.9)		Orange	2 100m	ν(C≡C)
$(\mathbf{2b})\cdot0.5CH_2Cl_2$	65.3 (65.7)	4.45 (4.6)	n.d.	Orange	2 080m	ν(C≡C)
(2c)	62.8 (63.4)	4.5 (5.1)		Orange	2 100m	ν(C≡C)
(3)	74.1 (74.2)	5.3 (5.4)	1.35 (1.5)[b]	Pale yellow	2 200m	ν(C≡N)
(4)	56.4, 56.6 (54.4)	4.5, 4.5 (3.9)	11.4 (12.4)[c]	White		
(5)	58.0 (58.6)	4.5 (4.6)	6.7 (6.4)	Deep yellow		

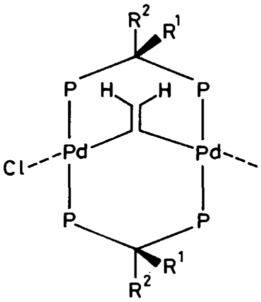
[a] Calculated values in parentheses; n.d. = not determined. The presence of solvent of crystallization was confirmed by ^1H n.m.r. spectroscopy. [b] %N. [c] ^1H N.m.r. spectroscopy indicated that an unknown component was present which had presumably originated from the light petroleum (b.p. 100—120 °C) used in the recrystallization.



	R	X
(1a)	H	Cl
(1b)	H	Br
(1c)	H	I
(1d)	H	NCS
(1e)	H	O_2CMe
(2a)	H	$C{\equiv}CC_6H_4Me$-*p*
(2b)	H	$C{\equiv}CPh$
(2c)	H	$C{\equiv}CCMe_2(OH)$
(3)	H	$C{\equiv}NC_6H_4Me$-*p* (BPh_4^- salt)
(4)	Cl	Cl

$C{=}CH_2)Pd(CNC_6H_4Me$-*p*$)]^{2+}$, isolated as the tetraphenylborate salt (**3**). The diacetylides of type (**2**) were better synthesized by treating the dichloro-complex (**1a**) with two equivalents of thallium(I) hexafluorophosphate in the presence of an excess of the acetylene in dichloromethane–acetone, followed by addition of an excess of triethylamine, to take up the HCl. In this way diacetylide complexes of the type $[(RC{\equiv}C)Pd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)Pd(C{\equiv}CR)]$ were prepared with R = *p*-MeC_6H_4 (**2a**), Ph (**2b**), or $CMe_2(OH)$ (**2c**).

We attempted to synthesize analogues of (**1a**) with other bridging alkylidene groups. Treatment of a benzene solution of $[Pd(PPh_3)_4]$ and dppm with $Cl_2C{=}CCl_2$ gave a mixture of $[ClPd(\mu\text{-dppm})_2PdCl]$ and another component characterized by a singlet resonance at δ 11.2 p.p.m. in its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum. However, by treating $[Pd(PPh_3)_4]$ with dppm and *trans*-$[PdCl(CCl{=}CCl_2)(PPh_3)_2]$ in hot benzene, the required complex $[ClPd(\mu\text{-dppm})_2(\mu\text{-}C{=}CCl_2)PdCl]$ (**4**) was obtained in good yield; this complex showed a singlet at δ 11.2 p.p.m. in its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum and was uncontaminated by impurities; clearly we had prepared this complex in an impure form by the other method described above. On reacting $Cl_2C{=}CMeH$, $[Pd(PPh_3)_4]$, and dppm together, a mixture of $[ClPd(\mu\text{-dppm})_2PdCl]$ and a dark orange material was isolated. This was very air-sensitive and was not characterized further, except to show that it exhibited a resonance centred at −21.0 p.p.m. in its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum. When a mixture of $[Pd(PPh_3)_4]$ and dppm was treated with $Cl_2C{=}CMe_2$,[6] only $[ClPd(\mu\text{-dppm})_2PdCl]$ was obtained and in high yield (based on Pd); a similar treatment with *o*-$(BrCH_2)_2C_6H_4$ gave only $[BrPd(\mu\text{-dppm})_2PdBr]$.



(**5a**) R^1 = H, R^2 = Me
(**5b**) R^1 = Me, R^2 = H

The methyl derivative of dppm, $Ph_2PCHMePPh_2$ (mdppm), gave analogous dipalladium complexes containing bridging vinylidene groups. A mixture of $[Pd(PPh_3)_4]$, mdppm, and $Cl_2C{=}CH_2$ in benzene gave $[ClPd(\mu\text{-mdppm})_2(\mu\text{-}C{=}CH_2)PdCl]$ (**5**) in good yield. This complex is more soluble than its dppm analogue (**1a**). Its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a singlet resonance and single resonances for both the methyl and methine protons in the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum indicated configuration (**5a**) or (**5b**) of which (**5a**), with *pseudo*-equatorial Me groups, seems the more likely. We were somewhat surprised that (**5a**) or (**5b**) formed so readily, since it has been shown that mdppm is not as good a bridging ligand as dppm and has a much greater tendency to chelate than to bridge.[7]

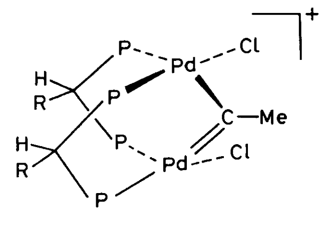
Treatment of a mixture of $[Pd(PPh_3)_4]$ and $Me_3SiCH(PPh_2)_2$ with $Cl_2C{=}CH_2$ gave (**1a**) in good yield; clearly under these conditions C–Si bond cleavage occurred. Attempts to use other diphosphines, *e.g.* $HN(PPh_2)_2$, $MeN(PPh_2)_2$, $Me_2C(PPh_2)_2$, or $CH_2{=}C(PPh_2)_2$ under similar conditions failed, dark intractable oils being obtained and $^{31}P\text{-}\{^1H\}$ n.m.r. investigations showed the presence of Pd^{II} chelates among other products.

Although the vinylidene double bond of (**1a**) does not react with nucleophiles, it protonates in an interesting manner. Treatment of a dichloromethane solution of the μ-vinylidene complex (**1a**) with one mole equivalent of $HBF_4\cdot Et_2O$ caused an immediate colour change to dark orange followed by a slower change to deep yellow (over *ca.* 1 min). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this yellow solution showed that, at first, two

Table 2. N.m.r. spectroscopic data

Compound	^{31}P-{^{1}H}[a]		^{1}H and ^{1}H-{^{31}P}[b]
(1a)	15.6		5.14 [2 H, C=CH$_2$, *J*(PH) 11.0]
			3.42 and 2.56 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 12.8, *J*(PH) 5.6, 3.1 respectively]
(1b)	15.9		5.28 [2 H, C=CH$_2$, *J*(PH) 11.5]
			3.48 and 2.53 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 12.7, *J*(PH) 5.6, 2.9 respectively]
(1c)	16.6		5.18 [2 H, C=CH$_2$, *J*(PH) 11.8]
			3.52 and 2.52 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 12.9, *J*(PH) 5.4, 2.9 respectively]
(1d)	23.6		4.26 [2 H, C=CH$_2$, *J*(PH) 4.6]
			3.07 and 2.26 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 13.2, *J*(PH) 5.8, 3.6 respectively]
(1e)	16.3		4.78 [2 H, C=CH$_2$, *J*(PH) 10.2]
			3.31 and 2.74 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 13.4, *J*(PH) 5.3, 3.4 respectively]
			1.27 (6 H, MeCO$_2$)
(2a)	21.1		5.24 [2 H, C=CH$_2$, *J*(PH) 11.0]
			3.43 and 2.59 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 12.8, *J*(PH) 5.5, 3.2 respectively]
			1.58 (6 H, *Me*C$_6$H$_4$)
(2b)	21.1		5.48 [2 H, C=CH$_2$, *J*(PH) 9.8]
			3.53 and 2.55 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 12.5, *J*(PH) 6.1, 3.2 respectively]
(2c)	21.3		5.72 [2 H, C=CH$_2$, *J*(PH) 11.3]
			3.58 and 2.65 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 12.9, *J*(PH) 5.9, 3.9 respectively]
			2.05 (2 H, OH)
			1.04 (12 H, CMe$_2$)
(3)	27.0		5.39 [2 H, C=CH$_2$, *J*(PH) 12.7]
			3.49 and 2.90 [4 H, PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 10.6, *J*(PH) 5.9, 3.2 respectively]
			2.30 (6 H, *Me*C$_6$H$_4$)
(4)	11.2		3.39 and 2.89 [PC$H_\mathrm{A}H_\mathrm{X}$P, *J*(H$_\mathrm{A}$H$_\mathrm{X}$) 13.0, *J*(PH) 5.6, 3.4 respectively]
(5)	31.3		5.17 [2 H, C=CH$_2$, *J*(PH) 10.7]
			3.85 [2 H, PC*H*MeP, *J*(CHCH$_3$) 7.1, *J*(PH) 6.8]
			1.04 [6 H, PCH*Me*P, *J*(PH) 5.1]
(6)	35.0 (P^1)	20.4 (P^2)[c]	3.97 [1 H, H^1, *J*(H^{1}H^2) 15.5, *J*(P^{1}H^1) 9.0, *J*(P^{2}H^1) 10.3][d]
	−23.0 (P^3)	−39.4 (P^4)	3.69 [1 H, H^2, *J*(P^{1}H^2) 4.8, *J*(P^{2}H^2) 9.5]
	J(P^{1}P^2) 55,	*J*(P^{1}P^3) 10	3.92 [1 H, H^3, *J*(H^{3}H^4) 15.6, *J*(P^{3}H^3) 9.1, *J*(P^{4}H^3) 10.8]
	J(P^{1}P^4) *ca.*1	*J*(P^{2}P^4) 3	2.97 [1 H, H^4, *J*(P^{1}H^4) 3.7, *J*(P^{3}H^4) 4.9, *J*(P^{4}H^4) 6.3]
	J(P^{3}P^4) 96		1.83 [3 H, Pd$_2$CCH$_3$, *J*(P^{1}H) 24.6, *J*(P^{2}H) 6.7, *J*(P^{3}H) 6.3, *J*(P^{4}H) 7.0]
(7)	39.9 (P^1)	30.8 (P^2)[c]	4.11 [1 H, C*H*Me, *J*(HMe) 7.3, *J*(PH) 6][d]
	−13.9 (P^3)	−25.9 (P^4)	4.36 [1 H, C*H*Me, *J*(HMe) 6.6, *J*(PH) 5]
	J(P^{1}P^2) 64	*J*(P^{1}P^3) 17.3	1.65 [3 H, Pd$_2$CCH$_3$, *J*(P^{1}H) 9.0, *J*(P^{2}H) 8.1, *J*(P^{3}H) 3.0, *J*(P^{4}H) 9.5]
	J(P^{1}P^4) 3	*J*(P^{2}P^3) $\simeq 0$	1.12 [3 H, P^{1}CH*Me*P^2, *J*(HMe) 7.3, *J*(PH) *ca.* 4]
	J(P^{2}P^4) 4	*J*(P^{3}P^4) 93	0.85 [3 H, P^{3}CH*Me*P^4, *J*(HMe) 6.6, *J*(PH) *ca.* 6]

[a] Recorded at 40.3 MHz and 25 °C, in 20% CD$_2$Cl$_2$–CH$_2$Cl$_2$. Chemical shifts (δ) in p.p.m. (±0.1 p.p.m.) relative to 85% H$_3$PO$_4$, with positive shifts to high frequency. Coupling constants (*J*) in Hz (±2 Hz). [b] Recorded at 400 MHz in CD$_2$Cl$_2$ at *ca.* 20 °C. Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to SiMe$_4$. Coupling constants (*J*) in Hz (±0.1 Hz). [c] Recorded at 162 MHz. The solution was generated by adding a small excess of HBF$_4$·Et$_2$O to a solution of (**1a**) or (**5**) in CD$_2$Cl$_2$. P^1, P^2, H^1, and H^2 are in the same dppm ligand, as are P^3, P^4, H^3, and H^4; similarly for mdppm. [d] The solution was generated by adding an excess of CF$_3$CO$_2$H to a solution of (**1a**) or (**5**) in CD$_2$Cl$_2$. The spectra were measured at −20 °C. *J*(PH) values were obtained by selective decoupling of the ^{1}H resonances at each phosphorus resonance frequency in turn (see Figure).



(**6**) R = H
(**7**) R = Me

similar products had been formed but after a few more minutes conversion of one of these to the other occurred and a single product was observed. We have not been able to characterize the dark orange, or the other intermediate product but have characterized the final product by ^{31}P-{^{1}H}, ^{1}H, and ^{1}H-{^{31}P} n.m.r. spectroscopy (including selective decoupling). The ^{31}P-{^{1}H} n.m.r. spectrum at 162 MHz was first order and showed four non-equivalent P nuclei, spin–spin coupled to each other but with no *J*(PP) value greater than 100 Hz. A similar result was obtained using CF$_3$CO$_2$H as the proton source, in CD$_2$Cl$_2$ solution and in this case the ^{1}H-{^{31}P} n.m.r. spectrum showed that the vinylidene resonance had disappeared and a new singlet (intensity 3 H) had formed at δ 1.83 p.p.m. The AX pattern for the PCH$_2$P protons in (**1a**) had become a pair of AX patterns of equal intensity (total 4 H), see Figure. We assign the resonance at 1.83 p.p.m. to the methyl group of a bridging carbyne ligand. Selective decoupling experiments, *i.e.* ^{1}H-{^{31}P(selective)}, showed that this methyl group was spin–spin coupled to all four P nuclei, see Figure. The four non-equivalent methylene protons of the dppm ligands are each coupled to two P nuclei only and selective ^{1}H-{^{31}P} n.m.r. experiments established the chemical shifts of the two P nuclei involved. Clearly, the two P nuclei to which this methylene hydrogen is coupled are in the same dppm ligand. The data are in Table 2; thus P^1, P^2, H^1, and H^2 are in the same dppm ligand, as are P^3, P^4, H^3, and H^4. Interestingly, the largest values of *J*(PP) are ^2J(P^{1}P^2) (55 Hz) and ^2J(P^{3}P^4) (96 Hz) (Table 2), *i.e.* values of ^2J(PP) across the palladium atom are remarkably small (< 10 Hz). Since values of ^2J(PP) for *trans* P–Pd$^{\mathrm{II}}$–P arrangements are usually very large (*ca.* 400 Hz)[8] we suggest that the P–Pd–P angles in the protonated complex are very much less than 180° and might even approach 90°, *i.e.* a mutually *cis* arrangement. Since the chemical shifts of the two P nuclei of one dppm ligand (35.0 and 20.4 p.p.m.) are very different from the chemical shifts of the

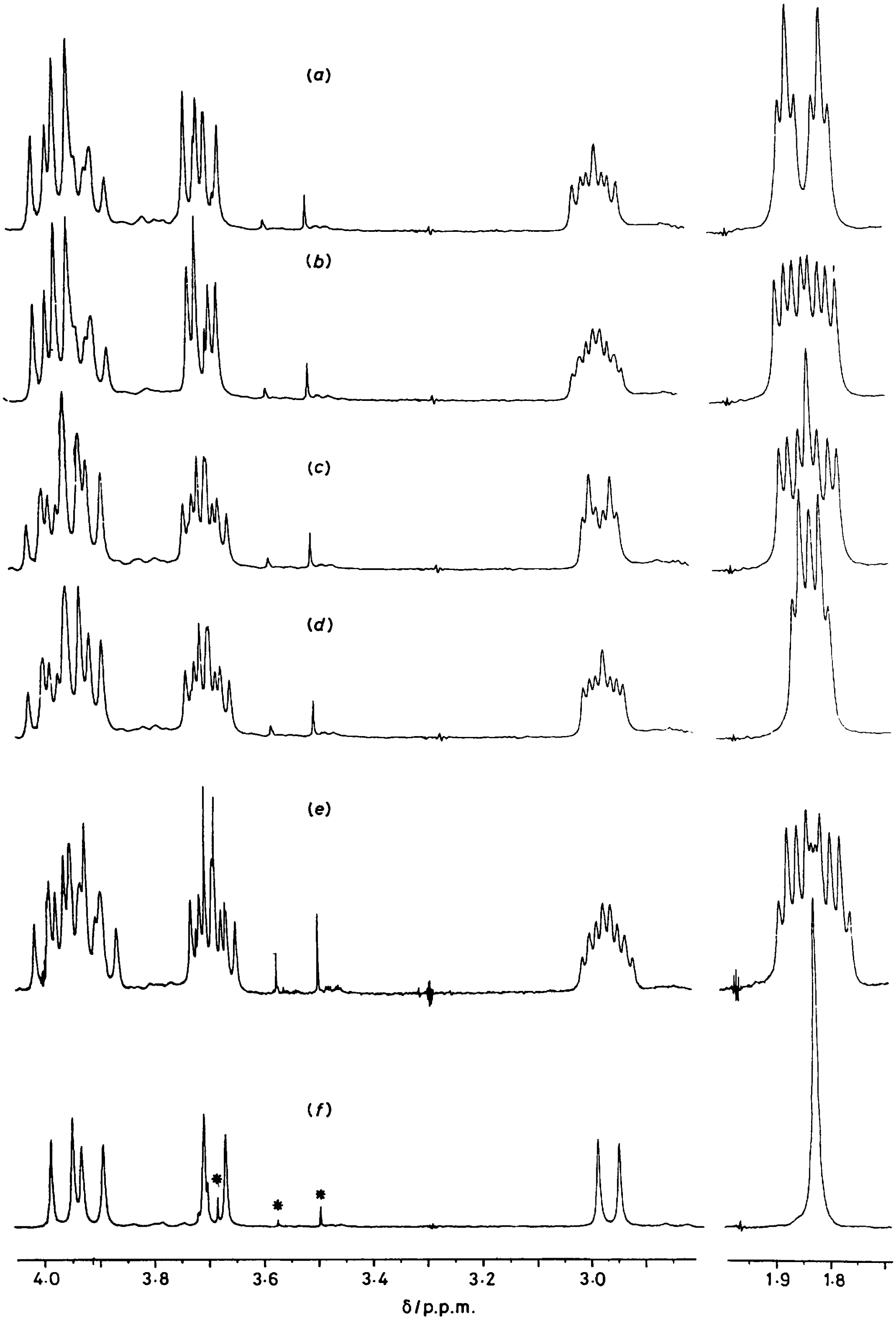


Figure. 400-MHz ^{1}H n.m.r. spectra, in the ligand methylene and carbyne methyl regions of a solution of $[ClPd(\mu\text{-}dppm)_2(\mu\text{-}CMe)PdCl]^+$ (**6**), generated *in situ* by adding a 10-fold excess of CF_3CO_2H to a solution of (**1a**) in CD_2Cl_2. Spectra recorded at −25 °C. With spectra (*a*)—(*d*) there was selective decoupling of phosphorus at the following frequencies: (*a*) +34.9 (P^1), (*b*) +20.4 (P^2), (*c*) −23.0 (P^3), (*d*) −39.6 p.p.m. (P^4). Spectrum (*e*) is undecoupled and spectrum (*f*) is the $^1H\text{-}\{^{31}P\}$, *i.e.* the completely decoupled spectrum; * indicates impurity

other (−23.0 and −39.4 p.p.m.) this clearly indicates a high degree of asymmetry in the protonated (carbyne) complex $[ClPd(\mu\text{-}dppm)_2(\mu\text{-}CMe)PdCl]^+$; a *cis* arrangement of dppm ligands would explain this, *i.e.* both P nuclei of one dppm ligand are *trans* to chlorine and the two P nuclei of the other dppm ligand are *trans* to the carbyne ligand. It is possible that our compound has some similarity to the complex ion $[(MeNC)\text{-}Ni(\mu\text{-}dppm)_2(\mu\text{-}CNMeH)Ni(CNMe)][PF_6]$, the crystal structure of which shows two bridging *cis*-dppm ligands and a bridging methylaminocarbyne ligand.[9,10] A possible structure for the carbyne complex cation $[ClPd(\mu\text{-dppm})_2(\mu\text{-CMe})PdCl]^+$ is as shown, see (**6**); because all four P nuclei are non-equivalent the molecule must not be fluxional, which is surprising. Previously, we had studied the protonation of (**1a**) at room temperature, using CPh_3PF_6 as the source of acid. Whilst this gave satisfactory $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, the ^1H spectra were complicated by overlapping resonances (impurities) and we incorrectly formulated the complex as containing a $\mu,\sigma\text{-}C{=}CH_2$ group.[3]

When an excess of CF_3CO_2D was added to a solution of (**1a**) in CD_2Cl_2 the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum was virtually identical to that of the carbyne complex as was the ^1H n.m.r. spectrum in the methylene region, but the resonance of the methyl of the carbyne group was missing. We suggest that this was due to exchange between methyl hydrogens and the deuterions of the acid. Attempts to isolate (**6**) as its salt with, for example BF_4^-, failed. In one experiment addition of propan-2-ol to a solution, prepared by treating a dichloromethane solution of (**1a**) with $HBF_4{\cdot}Et_2O$, gave a deep yellow solid, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of which suggested that it was mainly (*ca.* 70%) the required salt but that this was contaminated with *ca.* 30% of (**1a**). Treatment of a previously generated solution of (**6**) in dichloromethane with NEt_3 gave a complex mixture.

Treatment of dichloromethane solutions of (**1b**), (**1c**), or (**1d**) with $HBF_4{\cdot}Et_2O$ gave solutions whose n.m.r. spectra suggested the presence of analogues of (**6**) but these were very unstable and reliable n.m.r. data were not obtained. Treatment of a solution of (**6**) with $NBu^n{}_4I$ gave a mixture of products, the major one being $[IPd(\mu\text{-dppm})_2PdI]$.

Treatment of $[ClPd(\mu\text{-mdppm})_2(\mu\text{-}C{=}CH_2)PdCl]$ (**5**) with $HBF_4{\cdot}Et_2O$ or CF_3CO_2H in dichloromethane solution gave a dark orange solution which turned deep yellow in *ca.* 5 min. This solution was studied by $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ n.m.r. spectroscopy, which showed that it contained the hoped for carbyne complex ion $[ClPd(\mu\text{-mdppm})_2(\mu\text{-CMe})PdCl]^+$ (**7**), data in Table 2.

In view of these results, it was of interest to try to synthesise analogous vinylidene-bridged diplatinum and platinum–palladium complexes. We therefore attempted to effect three-fragment two-centre oxidative-addition reactions on platinum(0)–dppm complexes. Treatment of a mixture of $[Pt_2(C_8H_{12}OMe)_2(OMe)_2]$,[11] a useful precursor for platinum(0)–phosphine complexes, and dppm in benzene with $Cl_2C{=}CH_2$ gave a complex mixture of products, none of which was binuclear. When $Br_2C{=}CH_2$ was used instead of $Cl_2C{=}CH_2$, the major product was $[BrPt(\mu\text{-dppm})_2PtBr]$,[12] along with $[PtBr_2(\text{dppm-}PP')]$. $[BrPt(\mu\text{-dppm})_2PtBr]$ was also obtained by treating $[Pt_2(dppm)_3]$[13] with $Br_2C{=}CH_2$ in benzene solution, although $[BrPd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)PdBr]$ (**1b**) was formed in good yield by treating $[Pd(PPh_3)_4]$ with dppm and $Br_2C{=}CH_2$ (see Experimental section). Treatment of $[Pd_2(dppm)_3]$ with CH_2I_2 has been shown to give the methylene-bridged complex $[IPd(\mu\text{-dppm})_2(\mu\text{-}CH_2)PdI]$[2] but we found that treatment of $[Pt_2(dppm)_3]$ with CH_2I_2 gave $[IPt(\mu\text{-dppm})_2PtI]$ and that treatment with $[MCl(CCl{=}CCl_2)(PPh_3)_2]$ (M = Pd[14] or Pt[15]) under various conditions failed to yield any diplatinum or dipalladium complexes.

Experimental

The general methods were as recently reported from this laboratory.[16] The compounds $[Pd(dba)_2]$,[4] $Me_2C{=}CCl_2$,[6] and $[MCl(CCl{=}CCl_2)(PPh_3)_2]$ (M = Pd[14] or Pt[15]) were prepared by literature methods.

Preparations.—$[ClPd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)PdCl]$ (**1a**). (*i*) *From* $[Pd(dba)_2]$. A suspension of $[Pd(dba)_2]$ (1.97 g, 3.2 mmol) in dry benzene (70 cm^3) was treated with dppm (2.63 g, 6.4 mmol) and the mixture stirred until a solution formed. Vinylidene chloride (1.3 g, 13.4 mmol) was then added and the resultant mixture refluxed for 20 min, over which time the required product precipitated. This was filtered off, washed with benzene, and recrystallized from dichloromethane–methanol. Yield: 1.55 g, 90%.

(*ii*) *From* $[Pd(PPh_3)_4]$. A mixture of $[Pd(PPh_3)_4]$ (8.0 g, 7.32 mmol) and dppm (3.46 g, 9 mmol) in benzene (100 cm^3) was stirred for 10 min, vinylidene chloride (1.8 cm^3, 22 mmol) was added and the resultant mixture refluxed for 20 min. The resultant suspension was set aside for 2 h and the required product filtered off, washed with benzene, and recrystallized as above. Yield: 3.88 g, 95%.

$[BrPd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)PdBr]$ (**1b**). Vinylidene bromide (50 μl) was added to a stirred mixture of $[Pd(PPh_3)_4]$ (0.5 g, 0.43 mmol) and dppm (0.25 g, 0.65 mmol) in dry benzene (15 cm^3). After 16 h the resultant yellow precipitate was isolated and recrystallized from dichloromethane–ethanol. Yield: 0.21 g, 83%.

$[IPd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)PdI]$ (**1c**). A suspension of the dichloro-complex (**1a**) (0.20 g, 0.20 mmol) in a solution of sodium iodide (0.3 g, 2.0 mmol) in acetone (20 cm^3) was heated under reflux for 3 h. The resultant solution was evaporated to dryness and the required product extracted into dichloromethane. Microprisms formed from dichloromethane–toluene. Yield: 0.20 g, 80%.

The dibromo-complex (**1b**) was similarly prepared from (**1a**) by treatment with lithium bromide in acetone. Yield: 82%.

$[(SCN)Pd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)Pd(NCS)]$ (**1d**). This was similarly prepared from the dichloro-complex by treatment with potassium thiocyanate in acetone. Microprisms formed from acetone. Yield: 71%.

$[(MeCO_2)Pd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)Pd(O_2CMe)]$ (**1e**). A solution of thallium(I) acetate (0.137 g, 0.52 mmol) in methanol (15 cm^3) was added to a solution of the dichloro-complex (**1a**) (0.25 g, 0.24 mmol) in dichloromethane (25 cm^3) and the resultant mixture stirred in the dark for 2 h. Thallium(I) chloride was filtered off, the filtrate evaporated to dryness, and the required product precipitated by trituration with diethyl ether. Yield: 0.21 g, 78%. Microcrystals formed from acetone–diethyl ether.

$[(PhC{\equiv}C)Pd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)Pd(C{\equiv}CPh)]$ (**2b**). A solution of the dichloro-complex (**1a**) (0.25 g, 0.24 mmol) in dichloromethane (15 cm^3) was treated successively with phenylacetylene (0.2 cm^3), a solution of thallium(I) hexafluorophosphate (0.182 g, 0.52 mmol) in methanol (5 cm^3), and then triethylamine (0.2 cm^3). After 5 min the thallium(I) chloride was filtered off and the volume of the mother-liquor reduced *in vacuo*. This gave the required product as orange microcrystals. Yield: 0.21 g, 76%.

$[(p\text{-}MeC_6H_4C{\equiv}C)Pd(\mu\text{-dppm})_2Pd(C{\equiv}CC_6H_4Me\text{-}p)]$ (**2a**). (*i*) Complex (**2a**) was prepared in a completely analogous fashion to the phenylacetylide complex (**2b**) (above). Yield: 71%.

(*ii*) A solution of *p*-tolyl-lithium in thf–hexane (5 cm^3 containing 1.9 mmol) was added at 0 °C to a stirred suspension of the dichloro-complex (**1a**) (0.21 g, 0.2 mmol) in thf (1 cm^3). A solution formed in 5 min. Methanol (5 cm^3) was then added, the volatiles removed *in vacuo*, and the required product isolated with benzene. Orange microcrystals formed from benzene–cyclohexane. Yield: 0.74 g, 30%.

$[\{(HO)Me_2CC{\equiv}C\}Pd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)Pd\{C{\equiv}CCMe_2(OH)\}]$ (**2c**). This complex was made by treating the dichloro-complex (**1a**) with $TlPF_6$ and $HC{\equiv}CCMe_2(OH)$, as above for (**1a**). Yield: 41%.

$[(p\text{-}MeC_6H_4NC)Pd(\mu\text{-dppm})_2(\mu\text{-}C{=}CH_2)Pd(CNC_6H_4Me\text{-}p)][BPh_4]_2$ (**3**). *p*-Tolyl isocyanide (0.043 g, 65 μl, 0.42 mmol) was added to a stirred suspension of the dichloro-complex (**1a**) (0.20 g, 0.19 mmol) in ethanol (20 cm^3). The resultant mixture was stirred for 30 min after which a solution of sodium tetraphenylborate (0.15 g, 0.45 mmol) in ethanol (10 cm^3) was added and the volume of the solution reduced to *ca.* 5 cm^3 *in vacuo*. The required product was filtered off and recrystallized from dichloromethane–methanol. Yield: 0.29 g, 76%.

[ClPd(μ-dppm)$_2$(μ-C=CCl$_2$)PdCl] (**4**). [PdCl(CCl=CCl$_2$)(PPh$_3$)$_2$] (0.67 g, 0.84 mmol) was added to a solution of [Pd(PPh$_3$)$_4$] (0.95 g, 0.87 mmol) and dppm (0.69 g, 1.74 mmol) in benzene (30 cm^3). The resultant mixture was heated under reflux for 2 h, cooled, and the precipitate of the required product isolated. Microcrystals formed from dichloromethane–methylcyclohexane. Yield: 0.29 g, 60%.

[ClPd(μ-mdppm)$_2$(μ-C=CH$_2$)PdCl] (**5**). A solution of [Pd(PPh$_3$)$_4$] (6.0 g, 5.5 mmol) and mdppm (3.3 g, 8.3 mmol) in benzene (120 cm^3) was stirred for 10 min. Vinylidene chloride (2.9 g, 30 mmol) was then added and the resultant mixture refluxed for 1 h. The resultant orange solution was evaporated to dryness under reduced pressure and the residue triturated with diethyl ether. This gave the required product which formed microcrystals from dichloromethane–methanol. Yield: 1.17 g, 38%.

Attempted Isolation of the Bridging Carbyne Complex (**6**) *as the* BF_4^- *Salt.*—A solution of the dichloro-complex (**1a**) (0.20 g, 0.19 mmol) in dichloromethane (15 cm^3) was treated with $HBF_4 \cdot Et_2O$ until $^{31}P-\{^1H\}$ n.m.r. spectroscopy showed that all (**1a**) had reacted. The solvent was then removed under reduced pressure and the glassy residue triturated with diethyl ether, the resultant solid filtered off, and dried (see text).

Attempted Preparation of [ClPt(μ-dppm)$_2$(μ-C=CH$_2$)PtCl].—A mixture of [Pt$_2$(C$_8$H$_{12}$OMe)$_2$(OMe)$_2$] (0.37 g, 0.5 mmol) and dppm (0.29 g, 0.75 mmol) was refluxed for 20 min, after which $Cl_2C=CH_2$ (0.5 mmol) was added and the resultant mixture stirred at 20 °C for 16 h. The solvent was removed under reduced pressure and the residue examined by $^{31}P-\{^1H\}$ n.m.r. spectroscopy (see text).

Attempted Preparation of [BrPt(μ-dppm)$_2$(μ-C=CH$_2$)PtBr].—Vinylidene bromide (0.185 g, 1.0 mmol) was added to a solution of [Pt$_2$(dppm)$_3$] (0.14 g, 0.093 mmol) in benzene (15 cm^3) and the resultant mixture stirred for 4 h. The solvent was removed under reduced pressure and the residue triturated with diethyl ether. The resultant yellow solid was identified as [BrPt(μ-dppm)$_2$PtBr] by $^{31}P-\{^1H\}$ n.m.r. spectroscopy (see text).

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References

1 X. L. R. Fontaine, S. J. Higgins, B. L. Shaw, M. Thornton-Pett, and W. Yichang, *J. Chem. Soc., Dalton Trans.*, 1987, 1501.

2 A. L. Balch, C. T. Hunt, C-L. Lee, M. M. Olmstead, and J. P. Farr, *J. Am. Chem. Soc.*, 1981, **103**, 3764.

3 S. J. Higgins and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1986, 1629.

4 M. F. Rettig and P. M. Maitlis, *Inorg. Synth.*, 1977, **17**, 134.

5 S. J. Higgins and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1988, 457.

6 W. T. Brady and L. Smith, *Synthesis*, 1971, 415.

7 C-L. Lee, Y. P. Yang, S. J. Rettig, B. R. James, D. A. Nelson, and M. A. Lilga, *Organometallics*, 1986, **5**, 2220.

8 P. S. Pregosin and R. Kunz, '^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes,' Springer-Verlag, Berlin, Heidelberg, and New York, 1979.

9 D. L. DeLaet, P. E. Fanwick, and C. P. Kubiak, *Organometallics*, 1986, **5**, 1807.

10 D. L. DeLaet, R. del Rosario, P. E. Fanwick, and C. P. Kubiak, *J. Am. Chem. Soc.*, 1987, **109**, 754.

11 A. Goel, S. Goel, and P. Vanderveer, *Inorg. Chim. Acta*, 1981, **54**, 169.

12 M. C. Grossel, J. R. Batson, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.*, 1986, **304**, 391.

13 L. Manojlovic-Muir, K. W. Muir, M. C. Grossel, M. P. Brown, C. D. Nelson, A. Yavari, E. Kallas, R. P. Moulding, and R. P. Seddon, *J. Chem. Soc., Dalton Trans.*, 1986, 1955.

14 P. Fitton and J. E. McKeon, *Chem. Commun.*, 1968, 4.

15 B. F. G. Johnson, J. Lewis, J. D. Jones, and K. A. Taylor, *J. Chem. Soc., Dalton Trans.*, 1974, 34.

16 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.

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