CP/MAS NMR and X-ray crystallographic characterization of *trans*-PdX₂(PPh₂vinyl)₂ (X = CI, I); UV and Et₂O·BF₃ reaction studies, including the formation of [Pd(μ -CI)(PPh₂vinyl)₂]₂[BF₄]₂

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Abstract: The complexes $PdCl_2(PPh_2vinyl)_2$ and $PdI_2(PPh_2vinyl)_2$ have been prepared and crystallographically characterized as their *trans* square planar isomers. *Trans*- $PdCl_2(PPh_2vinyl)_2$ exists in a centrosymmetric structure with a planar $PdCl_2P_2$ core whereas *trans*- $PdI_2(PPh_2vinyl)_2$ shows no local Pd-centred symmetry and significant distortion of the PdI_2P_2 core from planarity. Crystallographic data is in accord with the ³¹P{¹H} CP/MAS NMR spectra of the two complexes, which display a single resonance for the chloro-complex and two resonances for the iodo-complex. UV irradiation of CH_2Cl_2 solutions of $PdCl_2(PPh_2vinyl)_2$ followed by re-dissolution in CDCl₃ indicates no permanent chemical change. However, post-irradiation CP/MAS ³¹P{¹H} NMR spectroscopy demonstrates the presence of *trans*- $PdCl_2(PPh_2vinyl)_2$ in two solid state structures, plus *cis*- $PdCl_2(PPh_2vinyl)_2$. $PdI_2(PPh_2vinyl)_2$ exists only in its *trans* form in both solid state and solution. Irradiation results in phosphine displacement and the formation of *sym*- $[PdI_2(PPh_2vinyl)_2$ reacts in the presence of $Et_2O\cdotBF_3$ to afford $[Pd(\mu-Cl)(PPh_2vinyl)_2]_2[BF_4]_2$ whereas $PdI_2(PPh_2vinyl)_2$ is recovered in 95% yield, with the remaining material undergoing phosphine abstraction to form *sym*- $[PdI_2(PPh_2vinyl)]_2$.

Key words: palladium, phosphine, alkene, isomerization, CP/MAS.

Résumé : On a préparé les complexes $PdCl_2(PPh_2vinyl)_2$ et $PdI_2(PPh_2vinyl)_2$ et sur la base de la cristallographie, on a établi qu'il s'agit des isomères plans carrés *trans*. Le *trans*-PdCl_2(PPh_2vinyl)_2 existe dans une structure centrosymétrique comportant une unité centrale $PdCl_2P_2$ plane alors que le *trans*-PdI_2(PPh_2vinyl)_2 est fortement déformé par rapport à la planéité. Les données cristallographiques sont en accord avec le spectre RMN CP/MAS du ³¹P{¹H} des deux complexes qui ne présentent qu'une seule résonance pour le complexe chloré et deux résonances pour le complexe iodé. L'irradiation UV de solutions de CH_2Cl_2 du complexe $PdCl_2(PPh_2vinyl)_2$ suivie d'une redissolution dans le CDCl₃ indique qu'il n'y a pas de changement chimique permanent. Toutefois, la spectroscopie RMN CP/MAS du ³¹P{¹H} démontre la présence de *trans*-PdI_2(PPh_2vinyl)_2 dans deux structures à l'état solide en plus de *cis*-PdI_2(PPh_2vinyl)_2. Le PdI_2(PPh_2vinyl)_2 n'existe que dans sa forme *trans* tant à l'état solide qu'en solution. L'irradiation provoque un déplacement de la phosphine et la formation de *sym*-[PdI_2(PPh_2vinyl)]_2 et de phosphine libre; cette dernière est caractérisée sous la forme de Ph_2P(O)vinyl après une oxydation aérobique. Le *trans*-PdCl_2(PPh_2vinyl)_2 réagit en présence de Et₂O·BF₅ pour conduire à la formation de [Pd(μ -Cl)(PPh_2vinyl)_2]eBF4]_2 alors que le PdI_2(PPh_2vinyl)_2 est récupéré avec un rendement de 95%, le reste du produit subissant une abstraction de phosphine avec formation de la *sym*-[PdI_2(PPh_2vinyl)]_2.

Mots clés : palladium, phosphine, alcène, isomérisation, CP/MAS.

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Introduction

Increasing interest exists in the formation of high molecular weight materials from metal complexes and the incorporation of such complexes into organic polymers. Pendant alkene moieties incorporated into phosphine ligands and their complexes have demonstrated polymerization in the presence of UV radiation and Lewis acids (1, 2). The potential for similar polymerization or alternative metal-centred reaction pathways is assessed in the present work for palladium(II) complexed diphenylvinylphosphine. Palladium(II) readily forms PdX_2P_2 (X = halide, P = tertiary phosphine) complexes with monodentate and bidentate phosphines. These complexes have formed the focus of numerous studies as a vehicle for probing *cis/trans* isomerization (3) and



Fig. 1. Single crystal X-ray diffraction structure of *trans*-PdCl₂(PPh₂vinyl)₂.

ligand/anion exchange processes (4), and as potential stoichiometric and catalytic reagents in synthesis (5). The principal modes of characterization have been solution ³¹P{¹H} NMR spectroscopy and single crystal X-ray diffraction studies. The former technique demonstrates that monodentate phosphine complexes generally exist as cis/trans mixtures in solution, although modification of P and X can lead to the trans isomer being overwhelmingly thermodynamically favored (6). Crystallization generally leads to the isolation of trans complexes; indeed 45 of the 55 reported PdX₂P₂ single crystal X-ray diffraction structures of monodentate phosphine complexes are of the trans isomer.² Solid state distortion from square planar geometries in these crystallographic studies is known but is not universal. In contrast, such distortion is not observed by solution ³¹P{¹H} NMR spectroscopy.

Cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy offers an increasingly available and complementary characterization technique that probes the solid state structure of non-crystalline materials. The study of solid samples by conventional NMR apparatus and experiments yields at best broad signals or a rolling baseline. Two principal factors contribute to this uninformative data; dipole-dipole nucleur interactions and chemical shift anisotropy (CSA). The former is removed in solution by molecular motion, which is sufficiently rapid to afford an averaged molecular orientation and thus zero local field. The effect of CSA, the directional influence of chemical bonds on nucleur shielding, is reduced to zero by the same motion in solution. Both factors vary in magnitude as a function of $3 \cos^2 \theta - 1$, where θ is the orientation to the applied field. Thus, spinning samples at a frequency larger than the CSA linewidth (usually a few kilohertz), and at an angle where the term $3 \cos^2 \theta - 1$ becomes zero (54° 44') allows the observation of sharp solid state spectra. Such 'magic angle spinning' when coupled with the sensitivity enhancement of cross polarization provides effective and informative solid state NMR data. In the present study we have investigated the solid state and solution chemistry of the PdX_2P_2 complexes (X = Cl, I; $P = PPh_2vinyl$) as part of our recent studies of bifunctional phosphine/alkene ligands (7, 8). The reported solution NMR data for these complexes are supplemented here by crystallographic characterization, and by CP/MAS NMR spectroscopy (9). Reactivity initiated by UV irradiation and in the presence of Lewis acids has also been considered.

Results and discussion

Synthesis and characterization of $PdX_2(PPh_2vinyl)_2$ (X = Cl, I)

Synthesis of $PdCl_2P_2$ complexes (P = tertiary phosphine) is well established and readily achieved by the reaction of $PdCl_2(PhCN)_2$ with two equivalents of tertiary phosphine. Iodide complexes may be isolated in high yield by metathesis of the respective chloride with excess aqueous NaI (9). The utilization of such synthetic routes and subsequent recrystallization from diethylether–dichloromethane affords crystalline $PdCl_2(PPh_2vinyl)_2$ and $PdI_2(PPh_2vinyl)_2$ in high yield. Crystals of both $PdCl_2(PPh_2vinyl)_2$ and $PdI_2(PPh_2vi$ $nyl)_2$ proved suitable for single crystal X-ray diffraction studies, with structure elucidation demonstrating the formation of *trans* square planar $PdCl_2(PPh_2vinyl)_2$ and $PdI_2(PPh_2vinyl)_2$ (Figs. 1 and 2, respectively).

Metal-centred bond lengths and angles for $PdCl_2(PPh_2vi-nyl)_2$ indicate a centrosymmetric and therefore planar $PdCl_2P_2$ core, with Cl-Pd-Cl and P-Pd-P vectors being almost orthogonal (Table 1). In contrast, no local Pd-centred





Table 1. Bond lengths and angles for trans-PdCl₂(PPh₂vinyl)₂ and trans-PdI₂(PPh₂vinyl)₂.

Bond lengths (Å)	trans-PdCl ₂ -	trans-PdI ₂ -	[Pd(µ-Cl)(PPh ₂ -	
and angles $(^{\circ})^{a}$	$(PPh_2vinyl)_2$	$(PPh_2vinyl)_2$	$vinyl)_2]_2[BF_4]_2$	
Pd—X(1)	2.2979(5)	2.5938(4)	2.3882(11)	
Pd—X(2)		2.5959(4)	2.3927(10)	
Pd—P(1)	2.3284(5)	2.3336(13)	2.2742(11)	
Pd—P(2)	_	2.3324(13)	2.2599(12)	
C(1)—C(2)	1.303(4)	1.287(8)	1.306(7)	
C(15)—C(16)		1.294(8)	1.303(6)	
X-Pd-X	180.0	169.78(2)	84.27(4)	
P-Pd-P	180.0	175.80(5)	93.02(4)	
X(1)-Pd-P(1)	90.967(19)	88.39(3)	90.79(4)	
X(1)-Pd-P(2)	_	91.75(3)	175.14(4)	
P(1)-C(1)-C(2)	126.0(2)	126.7(5)	125.6(4)	
P(2)-C(15)-C(16)	_	126.6(5)	122.1(4)	
$^{a}X = Cl. I.$				

symmetry is observed for PdI2(PPh2vinyl)2. Moreover, there are significant distortions from planarity for the PdI₂P₂ core and non-equivalence of both iodide and phosphine moieties. The presence and absence of local symmetry between the chloride and iodide complexes may be attributed to the relative ligand field splitting contributions of the respective an- $^{31}P{^{1}H}$ NMR spectroscopy is not Solution ions. representative of either trans solid state structure. For the former complex, this is due to the rapid establishment of cistrans equilibria. Whilst for the latter thermal energy is sufficient to allow rapid exchange on the NMR time-scale between inequivalent phosphines resulting in the observation of a single solution resonance for the two ligands, Table 2. However, CP/MAS ³¹P{¹H} NMR spectroscopy does readily characterize the two solid state structures affording a single resonance for the centrosymmetric trans-PdCl₂(PPh₂vinyl)₂ and two resonances for the asymmetric trans-PdI₂(PPh₂vinyl)₂. In both cases, the observed chemical shifts are similar to those assigned to the solution resonances of the trans $PdX_2(PPh_2vinyl)_2$ complexes, Table 2. ${}^{13}C{}^{1}H{}$ CP/MAS NMR spectroscopy has been successfully employed in the characterization of other palladium(II) phosphines (10). Such spectra were recorded here for both *trans* complexes. However, it is apparent from solution ${}^{13}C{}^{1}H{}$ NMR spectroscopy that phenyl and vinyl ${}^{13}C{}^{1}H{}$ resonances lie within the same region and display significant ${}^{13}C{}^{-31}P$ coupling. This feature, along with the additional complications of solid state line broadening, plus non-equivalence for the phosphine ligands of $PdI_2(PPh_2vinyl)_2$, results in extensively overlaid resonances for which deconvolution and assignment are unreliable.

UV irradiation of $PdX_2(PPh_2vinyl)_2$ (X = Cl, I)

The solution irradiation of $PdX_2(PPh_2vinyl)_2$ complexes offers three principal routes of reactivity. UV absorbance followed by relaxation to the kinetically favored *cis* isomer may occur to afford *trans-cis* isomerization (11). Alternatively, short wavelength UV activation of alkene moieties

trans-PdI₂L₂

trans-PdI₂L₂

Ph₂P(O)vinyl

 $[PdI_2L]_2$

4.2

4.2

22.9

26.9

Complex	Treatment	$\delta^{31}P$ CP/MAS	Assignment ^a	δ ³¹ P CDCl ₃	Assignment ^a		
trans-PdCl ₂ (PPh ₂ vinyl) ₂	Pre-irradiation	14.6	Symmetrical <i>trans</i> -PdCl ₂ L ₂ $P\overline{1}$	13.6	trans-PdCl ₂ L ₂		
				21.8	cis-PdCl ₂ L ₂		
trans-PdCl ₂ (PPh ₂ vinyl) ₂	Post-irradiation	14.5	Symmetrical <i>trans</i> -PdCl ₂ L ₂ $P\overline{1}$	13.6	trans-PdCl ₂ L ₂		
		16.3	Symmetrical trans-PdCl ₂ L ₂				
		24.2. 31.6	Asymmetric <i>cis</i> -PdCl ₂ L ₂	21.8	cis-PdCl ₂ L ₂		

Asymmetric *trans*-PdI₂L₂ $P\overline{1}$

Asymmetric trans-PdI₂L₂ P1

Ph₂P(O)vinyl

Asymmetric [PdI₂L]₂

Table 2. CP/MAS ${}^{31}P{}^{1}H$ NMR data for *trans*-PdCl₂(PPh₂vinyl)₂, and *trans*-PdI₂(PPh₂vinyl)₂ and for the same complexes after UV irradiation.

 $^{a}L = PPh_{2}vinyl$

trans-PdI₂(PPh₂vinyl)₂

trans-PdI₂(PPh₂vinyl)₂

Fig. 3. CP/MAS ³¹P{¹H} NMR spectra of *trans*-PdCl₂(PPh₂vinyl)₂ before and after UV irradiation.

5.4, 7.8

5.4, 7.6

28.1, 30.3

22.9

Pre-irradiation

Post-irradiation



can produce oligomerization or polymerization (1), while homolytic or heterolytic bond cleavage may result in generalized or specific bond cleavage.³ The significance of these various factors can be elucidated by comparison of pre- and post-irradiation solution and solid state NMR data (Table 2).

Irradiation of ca. 10^{-1} M CH₂Cl₂ solutions of PdCl₂(PPh₂vinyl)₂ and PdI₂(PPh₂vinyl)₂ using wavelengths of $\lambda \ge 200$ nm results in the rapid precipitation of palladium containing materials. Precipitation results from the rapid solvent heating associated with the relaxation of excited states through vibrational processes. Where appropriate the formation of *cis*-[PdCl₂P₂] and *sym*-[PdI₂P]₂, which are recognized to be of lower solubility than the corresponding *trans*-[PdX₂P₂], may also be significant (6, 10, 11). Decanting residual solvent after ca. 2 min irradiation followed by drying in vacuo affords a 95% yield (wt/wt) of materials slightly darkened from the respective yellow and red colors of the initial complexes. Consideration of the post-irradiation NMR spectrum of PdCl₂(PPh₂vinyl)₂ affords the following observations. Solution ¹H NMR spectroscopy indicates no change

in the extensively coupled vinylic protons associated with cis and trans PdCl₂(PPh₂vinyl)₂. Moreover, no upfield resonances are observed which might be assigned to polyvinyl moieties. Solution ³¹P{¹H} NMR spectroscopy also displays resonances that can be assigned to cis and trans PdCl₂(PPh₂vinyl)₂, with no additional features (Table 2). Thus, it may be concluded that any new solid state feature observed in the post-irradiation CP/MAS ³¹P{¹H} NMR spectrum of PdCl₂(PPh₂vinyl)₂ corresponds to *cis* and *trans* isomers of this complex (Fig. 3). Three new peaks are observed in the CP/MAS $^{31}P{^{1}H}$ NMR spectrum at 16.3, 24.0, and 31.5 ppm. The former may be assigned to a crystallization of *trans*-PdCl₂(PPh₂vinyl)₂ in an alternative space group to that crystallographically characterized here; a feature which has been observed for other palladium(II) and platinum(II) complexes (12, 13). Consideration of the resonances at 24.0 and 31.5 ppm in isolation is problematic because, in addition to cis-[PdCl₂P₂] complexes, other species such as phosphine oxides afford similar chemical shifts. However, because only *cis* and *trans* PdCl₂(PPh₂vinyl)₂ are

³M. Edge, P. Faulds, D.G. Kelly, A. McMahon, G.C. Ranger, and D. Turner. Eur. Polym. J. manuscript 214/99, in press.





Table 3. ${}^{31}P{}^{1}H$, ${}^{13}C{}^{1}H$, and ${}^{1}H$ NMR data for Ph₂P(O)vinyl.

NMR nucleus	Position ^a	δ (ppm)	Coupling(Hz)
³¹ P{ ¹ H}		23.3	
$^{1}\mathrm{H}$	H _a	6.68	12.5, ^b 18.7, ^c 24.5 ^e
	H _b	6.31	12.5, ^b 1.8, ^c 41.0 ^e
	H_c	6.27	18.7, ^c 1.8, ^d 22.3 ^e
	Ph	7.20-7.55	multiplet
$^{13}C{^{1}H}$	α	131.65	96.5 ^f
	β	135.04	singlet
	i (ipso)	132.80	106.2^{f}
	o (ortho)	131.75	9.7 <i>f</i>
	m (meta)	128.97	12.2 <i>f</i>
	p (para)	132.26	2.5 ^f

 $a H_a Ph_2P > C = C < H_a$

 $d^{3}J_{\rm hc}$.

 $e n J_{\rm PH}$.

 $f^{n}J_{\rm CP}$.

observed on re-dissolution these solid state resonances must be assigned to an unsymmetrical *cis*-PdCl₂(PPh₂vinyl)₂ species. While these solid state chemical shifts lie downfield by as much as 10 ppm from solution values, similar movements have been observed in comparable palladium(II) systems (11). Because conventional concentration and crystallization processes yield *trans*-PdCl₂(PPh₂vinyl)₂, irradiation may be viewed as enhancing the solid-state concentration of *cis*-PdCl₂(PPh₂vinyl)₂.

Irradiation of *trans*-PdI₂(PPh₂vinyl)₂ affords a material for which CP/MAS ³¹P{¹H} resonances at 7.0 and 5.3 ppm are observed which are representative of the original complex. New resonances occur at 23.0, 27.5, and 29.8 ppm (Fig. 4). Unlike the additional post-irradiation resonances of PdCl₂(PPh₂vinyl)₂ these new peaks are not lost on redissolution. Instead, two peaks of approximately equal intensity are recorded at 22.9 and 26.9 ppm in the solution Scheme 1. Reactivity of $PdX_2(PPh_2vinyl)_2$ on irradiation and in the presence of $Et_2O \cdot BF_3$.



³¹P{¹H} NMR spectrum. Formation of *cis*-PdI₂(PPh₂vinyl)₂ is unlikely due to the relative instability of this isomer, which does not form by the solution equilibration of trans-PdI₂(PPh₂vinyl)₂. Moreover, kinetically slow isomerization of such an apparently thermodynamically unstable cis species may also be excluded by the static intensities of ³¹P{¹H} solution NMR resonances over ca. 7 d. Thus, these new resonances may be assigned to reaction, rather than isomerization products. ¹H NMR spectroscopy again excludes polymerization products by the absence of upfield resonances. However, extraction of irradiated material with hexane affords identical ³¹P{¹H} and ¹H NMR data to Ph₂P(O)vinyl samples obtained by direct PPh₂vinyl oxidation (Table 3). Thus, it may be suggested that the relaxation of excited species can result in Pd-P cleavage and the subsequent aerobic oxidation of free phosphine (14). Extraction of Ph₂P(O)vinyl, followed by recrystallization of the remaining material from Et₂O-CH₂Cl₂ results in the preferential precipitation of deep red sym-[PdI₂(PPh₂vinyl)]₂. The latter may be manually separated from traces of the paler trans-PdI₂(PPh₂vinyl)₂. Elemental analysis and comparison with published NMR data confirm the formation of sym- $[PdI_2(PPh_2vinyl)]_2$ (15) (Scheme 1).

Reaction of $PdX_2(PPh_2vinyl)_2$ (X = Cl, I) and $Et_2O \cdot BF_3$

The addition of $Et_2O \cdot BF_3$ to a CH_2Cl_2 solution of $PdCl_2(PPh_2vinyl)_2$ results in an immediate yellow to orange

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 $^{^{}c}{}^{3}J_{ac}$.



Fig. 5. Single crystal X-ray diffraction structure of [Pd(µ-Cl)(PPh₂vinyl)₂]₂[BF₄]₂.

color change. Removal of solvent in vacuo after 12 h and recrystallization from $Et_2O-CH_2Cl_2$ yields the crystallographically characterized [Pd(μ -Cl)(PPh_2vinyl)_2]_2[BF_4]_2, formed by a combination of halide abstraction and exchange (Fig. 5). Solution NMR spectroscopy indicates that this air stable complex is the sole palladium containing product. The complex is stable in CH_2Cl_2, but appears to be reduced to palladium metal in CHCl_3. Whilst reports exist of BF₃ extraction in palladium phosphine systems (16), it is notable that the reaction of PdCl_2(PPh_2vinyl)_2 with AgBF_4 results in palladium reduction to the phosphallyl complex [Pd(η^1 -PPh_2vinyl)(η^3 -PPh_2vinyl)]_2[BF_4]_2 (17) (Scheme 1).

The reactivity of $PdI_2(PPh_2vinyl)_2$ with $Et_2O\cdot BF_3$ differs markedly from that of the chloride analogue. Under identical conditions halide abstraction does not occur. The majority of the complex is recovered unchanged, with the remaining material undergoing phosphine abstraction to *sym*-[PdI_2(PPh_2vinyl)]_2. Abstraction occurs by virtue of the Lewis acid–base interaction with BF₃; a reaction that is confirmed by the observation of a comparable ³¹P{¹H} NMR resonance from binary phosphine–BF₃ mixtures. The latter adduct is air sensitive, being hydrolyzed and oxidized in air to Ph_2P(O)vinyl. Separation and characterization of PdI_2(PPh_2vinyl)_2, Ph_2P(O)vinyl, and *sym*-[PdI_2(PPh_2vinyl)]_2 are thus accomplished by similar methods to those employed in UV initiated reaction studies.

The respective centrosymmetric and distorted square planar structures that have been crystallographically observed for *trans*-PdCl₂(PPh₂vinyl)₂ and *trans*-PdI₂(PPh₂vinyl)₂ have been confirmed using CP/MAS NMR spectroscopy. The latter technique, in conjunction with solution NMR spectroscopy, indicates that UV irradiation of PdCl₂(PPh₂vinyl)₂ affords cis and trans- PdCl₂(PPh₂vinyl)₂. Similar treatment of PdI₂(PPh₂vinyl)₂ results in phosphine dissociation and the formation of sym-[PdI₂(PPh₂vinyl)]₂. PdCl₂(PPh₂vinyl)₂ reacts in the presence of the Lewis acid Et₂O·BF₃ to yield $[Pd(\mu-Cl)(PPh_2vinyl)_2]_2[BF_4]_2$, whilst the corresponding iodide again undergoes phosphine dissociation forming sym-[PdI₂(PPh₂vinyl)]₂. Although UV irradiation and Lewis acids have been reported to initiate vinyl phosphine polymerization, no evidence suggesting such reactivity is recorded in the present study.

Experimental

Crystallographic characterization

Data collection and structure solution for *trans*-PdCl₂(PPh₂vinyl)₂, *trans*-PdI₂(PPh₂vinyl)₂, and [Pd(μ -Cl)(PPh₂vinyl)₂]₂[BF₄]₂ were performed using published methods (18), Table 4.⁴

⁴ Complete X-ray data have been deposited as supplementary material and may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 134114, 134115, and 136137, respectively). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

	trans- PdCl ₂ -(PPh ₂ vinyl) ₂	trans- PdI ₂ -(PPh ₂ vinyl) ₂	$[Pd(\mu-Cl)(PPh_2-vinyl)_2]_2[BF_4]_2$	
Color and habit	yellow block	red block	yellow block	
Size (mm)	$0.30 \times 0.20 \times 0.20$	$0.30 \times 0.20 \times 0.20$	$0.10 \times 0.10 \times 0.05$	
Empirical formula	C ₁₄ H ₁₃ ClPPd	$C_{28}H_{26}I_2P_2Pd$	$C_{29}H_{28}BCl_3F_4P_2Pd$	
Formula weight	300.86	784.63	738.01	
a (Å)	8.0956(2)	9.6628(3)	13.3531(3)	
<i>b</i> (Å)	9.3183(4)	11.8875(5)	13.5800(5)	
<i>c</i> (Å)	10.2254(4)	14.1588(5)	17.4792(5)	
α (°)	67.3560(14)	68.7735(17)		
β (°)	88.185(2)	77.089(2)	103.4594(17)	
γ (°)	68.614(2)	68.184(2)		
V (Å ³)	657.57(4)	1400.02(9)	3082.54(16)	
Mo- K_{α} , λ (nm)	0.71073	0.71073	0.71073	
System	triclinic	triclinic	monoclinic	
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/n$	
Ζ	2	2	4	
Temperature (K)	293(2)	293(2)	150(2)	
Collection	Enraf Nonius KappaCCD	Enraf Nonius KappaCCD	Enraf Nonius KappaCCD	
Total reflections	8104	19234	18038	
Observed data $(I > 2\sigma(I))$	2313	5713	4415	
20	$2.94 < 2\theta < 25.03$	$2.28 < 2\theta < 26.38$	$2.95 < 2\theta < 23.25$	
Absorption correction	SORTAV	SORTAV	SORTAV	
Solution	SHELXS-97	SHELXS-97	SHELXS-97	
Refinement	SHELXL-97 Full matrix F^2	SHELXL-97 Full matrix F^2	SHELXL-97 Full matrix F^2	
Hydrogen atoms	Detected & riding	Riding	Riding	
R	0.0226	0.0409	0.0359	
wR	0.0598	0.1014	0.0830	
Difference (eÅ ⁻³)	0.233, -0.556	0.878, -1.018	1.246, -0.850	

Table 4. Crystal data for trans-PdCl₂(PPh₂vinyl)₂, trans-PdI₂(PPh₂vinyl)₂, and [Pd(µ-Cl)(PPh₂vinyl)₂]₂[BF₄]₂.

Synthesis and spectroscopy

Solvents were dried and distilled under nitrogen by conventional methods (19). Palladium chloride, diphenylvinylphosphine, and Oxone[®] (potassium peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) were obtained from Aldrich and used as received. Pd(PhCN)₂Cl₂ was prepared by published methods (20). Solution NMR were recorded in CDCl₃ at 270.1, 67.9, 81.0 MHz for ¹H, ¹³C{¹H}, and ³¹P{¹H}, respectively, using a JEOL GSX-270 spectrometer. CP/MAS ³¹P{¹H} NMR was recorded using a 7mm bore Varian UNITYplus spectrometer at 121 MHz. Acquisition parameters were; spectral width 100 kHz, relaxation delay 20.0 s, spin-rate 4500 Hz.

 $PdCl_2(PPh_2vinyl)_2$: The complex was prepared on a 5 g scale using published methods; typical yields of 79–88% being obtained. Elemental analysis for C₂₈H₂₆Cl₂P₂Pd, expected: C 55.9, H 4.4; found: C 56.1, H 4.4. ¹H and ³¹P{¹H} NMR spectra were recorded and found to correspond to published data (9).

 $PdI_2(PPh_2vinyl)_2$: The complex was prepared by halide metathesis of PdCl₂(PPh₂vinyl)₂. Thus, PdCl₂(PPh₂vinyl)₂ (4.05 g; 6.8 mmol) was dissolved in CH₂Cl₂ (25 cm³) and stirred with 10 cm³ aqueous saturated NaI. After 0.5 h the aqueous solution was separated. The process was repeated with two further portions of aq. NaI. Finally the organic layer was separated and PdI₂(PPh₂vinyl)₂ precipitated by the addition of Et₂O. Yield (4.85 g, 91%). Elemental analysis for C₂₈H₂₆I₂P₂Pd, expected: C 42.8, H 3.3; found: C 42.8, H 3.3. ¹H and ³¹P{¹H} NMR spectra were recorded and correspond to published data (9).

UV irradiation

The following is typical of the treatment of chloro- and iodo- complexes. $PdCl_2(PPh_2vinyl)_2$ (0.70 g; 1.16 mmol) was dissolved in 10 cm³ of dry CH₂Cl₂. The solution was placed in a ca. 5 cm diameter petri dish, and exposed to UV radiation ($\lambda \ge 200$ nm, 200 W) for 2 min. Remaining solvent was decanted from the precipitated material and the solid dried in vacuo. Yield 0.65 g (93% wt/wt).

BF₃ reactivity

The following is typical of the treatment of chloro- and iodo- complexes. $PdCl_2(PPh_2vinyl)_2$ (0.087 g; 0.14 mmol) was dissolved in $10cm^3$ of dry CH_2Cl_2 under nitrogen. The addition of $100 \ \mu L \ Et_2O \cdot BF_3$ (0.79 mmol) produced no visual change. The solution was stirred for ca. 12 h and concentrated to dryness before further study. Yield 0.67 g (96% wt/wt).

*Ph*₂*P*(*O*)*vinyl*: PPh₂vinyl (1.08 g; 5.1 mmol) was dissolved in CH₂Cl₂ (25 cm³) and slurried with Oxone[®] for 1 d, after which the solution was filtered and concentrated to dryness affording Ph₂P(O)vinyl in quantitative yield. Elemental analysis for C₁₄H₁₃OP, expected: C 64.5, H 5.7; found: C 64.7, H 6.0. NMR (see Table 3). IR (KBr); v(O=P) 1148 cm⁻¹; MS (EI) *m/e* = 228 (100%).

 $[PdI_2(PPh_2vinyl)]_2$: Complex was formed in ca. 5% yield along with Ph₂P(O)vinyl by the irradiation of PdI₂(PPh₂vinyl)₂. A ca. 12% yield, along with F₃B·PPh₂vinyl, was observed from the reaction of PdI₂(PPh₂vinyl)₂ and Et₂O·BF₃. In the latter reaction F₃B·PPh₂vinyl was identified by comparison with ${}^{31}P{}^{1}H{}$ NMR data obtained from binary $Et_2O \cdot BF_3$ and PPh₂vinyl solutions ($\delta = 1.7$ ppm, CDCl₃), and undergoes hydrolysis and oxidation in air to Ph₂P(O)vinyl. *sym*-[PdI₂(PPh₂vinyl)]₂ was readily separated from Ph₂P(O)vinyl by hexane extraction of the latter. The complex was then recrystallized from CH₂Cl₂-Et₂O from which this comparatively insoluble complex preferentially precipitates. Manual separation from traces of the visually distinct PdI₂(PPh₂vinyl)₂ affords spectroscopically and analytically pure sym-[PdI₂(PPh₂vinyl)]₂·Et₂O. Elemental analysis for C₂₈H₂₆I₄P₂Pd₂·Et₂O, expected: C 31.5, H 3.0; found: C 31.4, H 2.7. ¹H (for proton notation see Table 3) $\delta = 5.58$ (H_b dd ${}^{3}J(PH) = 20.7 \text{ Hz}, {}^{3}J(H_{a}H_{c}) = 18.2 \text{ Hz}, 2H, H_{c}), 6.10 (H_{c} \text{ dd})$ ${}^{3}J(PH) = 42.4 \text{ Hz}, \; {}^{3}J(\ddot{H}_{a}H_{b}) = 12.0 \text{ Hz}, \; 2H, \; H_{b}), \; 7.10 \; (H_{a}$ ddd ${}^{2}J(PH) = 24.1 Hz$, ${}^{3}J(H_{a}H_{c}) = 18.2 Hz$, ${}^{3}J(H_{a}H_{b}) =$ 12.0 Hz, 2H, H_a), 7.36–7.75 (m, 20H, Ph). ${}^{31}P{}^{1}H{}\delta = 26.9$.

 $[Pd(\mu-Cl)(PPh_2vinyl)_2]_2[BF_4]_2$: Product formed by the method outlined above was crystallized from dichloromethane– diethylether to afford an orange microcrystalline solid. There is evidence of decomposition in air and over several hours in chloroform to afford palladium metal. However, the complex is sufficiently stable in CDCl₃ to obtain NMR spectra. Elemental analysis for C₂₈H₂₆BClF₄PPd·CH₂Cl₂, expected: C 47.1, H 3.8; found: C 47.3, H 3.6. ¹H (for proton notation see Table 3) δ = 5.70 (H_b t, br), 6.06 (H_c t, br), 6.22 (H_a m, br), 7.38–7.58 (m, 20H, Ph). ³¹P{¹H}-³¹P{¹H} δ = 28.6.

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