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Complexes of $Ph_2PCH{=}CH_2$ with PtX_2 (X = Cl, Br, I or Me) or PdX_2 (X = Cl, Br or I)

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Abstract

Treatment of $Ph_2PCH{=}CH_2$ with $[PtCl_2(NCPh)_2]$ or with $[PtCl_2(COD)]$, gives *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$, which on treatment with LiBr gives the corresponding dibromide, or with NaI, the corresponding di-iodide. In dichloromethane solution, *cis*-$[PtI_2(PPh_2CH{=}CH_2)_2]$ partially isomerizes to give a *cis/trans*-mixture. Treatment of $[PtMe_2(COD)]$ with $Ph_2PCH{=}CH_2$ gives *cis*-$[PtMe_2(PPh_2CH{=}CH_2)_2]$. Treatment of $[PdCl_2(NCPh)_2]$ with $Ph_2PCH{=}CH_2$ gives a mixture of *cis*- and *trans*-$[PdCl_2(PPh_2CH{=}CH_2)_2]$, which with LiBr gives a similar mixture of the corresponding dibromides, while reaction with NaI gives *trans*-$[PdI_2(PPh_2CH{=}CH_2)_2]$. $^{31}P\{^1H\}$ NMR and ^1H- and $^1H\{^{31}P\}$ NMR, and IR spectroscopic data are given.

We have shown previously that, on complexation to a metal centre the vinylidene double bond of the diphosphine ligand $(Ph_2P)_2C{=}CH_2$ (vdpp) becomes activated towards Michael or conjugate addition [1–4]. For example, complexes of the type $[M(CO)_4(\text{vdpp-}P,P')]$ (M = Cr, Mo, or W) undergo addition of a range of amines, hydrazines, or carbon nucleophiles, to give functionalized phosphine complexes [2,3], whereas the free ligand is inactive towards these amines, hydrazines, etc. Complexation to platinum(II), platinum(IV) or palladium(II) induces very high activation of vdpp towards Michael addition [3,4], much more than does complexation to a Group VI metal centre, and clearly the electron-withdrawing power of the coordinated metal has an important activating effect. We have made use of this ability of coordinated vdpp to undergo conjugate additions in synthesizing a new range of functionalized, coordinated diphosphine ligands in relatively simple ways [1–4]. We have chosen to try to extend this work to the synthesis of coordinated, functionalized mono-phosphines using $Ph_2PCH{=}CH_2$, vinylbisdiphenylphosphine, activated by complexation. We expected that $Ph_2PCH{=}CH_2$ would be less activated by complexation than vdpp since (i) the vinyldene double bond of vdpp is activated by the two, adjacent, coordinated P-atoms whereas $Ph_2PCH{=}CH_2$ is only activated

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by one coordinated P, and (ii) conjugate or Michael addition to coordinated vdpp relieves some strain in the 4-membered chelate ring, since the central carbon atom, on Michael addition changes from sp^2- to sp^3-hydridization and a more-favoured internal bond angle; this effect would not be present with coordinated $Ph_2PCH{=}CH_2$. However, the vinyl double bond of $Ph_2PCH{=}CH_2$ has been shown to undergo addition when treated with very powerful nucleophiles. Both n-butyl- and t-butyl-lithium add to give the α-lithiated products $Ph_2PCLiHCH_2R$ [5] and the very powerful nucleophile $PPh_2H + KO^tBu$ has been added to $[Mo(CO)_5(PPh_2CH{=}CH_2)]$ to give $[Mo(CO)_5(PPh_2CH_2CH_2PPh_2)]$ [6,7]. We have used disubstituted derivatives, $[M(CO)_4(PPh_2CH{=}CH_2)_2]$, as intermediates in the syntheses of 10-membered ring complexes, $[(OC)_4M(\mu\text{-dppe})_2M'(CO)_4]$ (M, M' = Cr, Mo or W) [8]. Some complexes of Ag^I with $Ph_2PCH{=}CH_2$ have been described [9] but complexes of $Ph_2PCH{=}CH_2$ with platinum(II) or palladium(II) have not been described. However, since platinum(II) and palladium(II) have been shown to be very effective in activating the vinylidene phosphine vdpp towards Michael additions. we thought that these two metals might be sufficiently effective in promoting additions to the vinylphosphine, $Ph_2PCH{=}CH_2$ and therefore set out to prepare and characterize complexes of this ligand with these two metals. These complexes are described in this paper.

Results and discussion

A convenient method of preparing complexes of tertiary phosphines with $PtCl_2$ is by displacing benzonitrile from $[PtCl_2(PhCN)_2]$ with the tertiary phosphine. When we treated $[PtCl_2(PhCN)_2]$ with two molar equivalents of $Ph_2PCH{=}CH_2$ we readily obtained *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ as white crystals in 85% yield. Details of this preparation are given in the Experimental section, relevant elemental analytical data are in Table 1, $^{31}P\{^1H\}$ NMR and IR data in Table 2, and ^1H NMR data in Table 3. In particular, the far IR spectrum showed two strong bands, at 318 and 295 cm^{-1} due to $\nu(Pt-Cl)$ and characteristic of a *cis*-geometry. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at 3.9 ppm, with satellites due to platinum-195 coupling, the value of $^1J(Pt-P)$ 3633 Hz being typical for a tertiary phosphine coordinated to platinum(II) and in *trans*-position to chlorine [10]. In the $^1H\{^{31}P\}$ and ^1H NMR spectra, the resonances of the three vinyl hydrogens were sufficiently

Table 1

Microanalytical data for complexes of $Ph_2PCH{=}CH_2$

Complex	Analyses (Found (calcd.) (%))		
	C	H	Halogen
cis-$[PtCl_2(PPh_2CH{=}CH_2)_2]\cdot\frac{1}{2}CH_2Cl_2$ [a]	51.2(51.05)	4.0(3.9)	9.75(9.7)
cis-$[PtBr_2(PPh_2CH{=}CH_2)_2]$	43.15(43.15)	3.4(3.35)	20.75(20.5)
$[PtI_2(PPh_2CH{=}CH_2)_2]$	38.25(38.5)	2.95(3.0)	29.15(29.1)
$[PtMe_2(PPh_2CH{=}CH_2)_2]$	55.7(55.45)	4.95(4.95)	
$[PdCl_2(PPh_2CH{=}CH_2)_2]$	55.75(55.9)	4.3(4.35)	11.85(11.8)
$[PtBr_2(PPh_2CH{=}CH_2)_2]\cdot\frac{2}{3}CH_2Cl_2$ [a]	45.8(46.1)	3.7(3.7)	
trans-$[PdI_2(PPh_2CH{=}CH_2)_2]$	42.5(42.85)	3.25(3.35)	32.0(32.35)

[a] The presence of solvent of crystallisation confirmed by ^1H NMR spectroscopy.

Table 2

$^{31}P\{^{1}H\}$ NMR [a] and infrared [b] data for complexes of $Ph_2PCH{=}CH_2$

Complex	$^{31}P\{^{1}H\}$ NMR		Infrared
	$\delta(P)$	$^{1}J(PtP)$	
cis-$[PtCl_2(PPh_2CH{=}CH_2)_2]$	3.9	3633	$\nu(Pt{-}Cl)$ 318s, 295s
cis-$[PtBr_2(PPh_2CH{=}CH_2)_2]$	3.5	3591	
cis-$[PtI_2(PPh_2CH{=}CH_2)_2]$	1.0	3445	
trans-$[PtI_2(PPh_2CH{=}CH_2)_2]$	1.6	2449	
$[PtMe_2(PPh_2CH{=}CH_2)_2]$	18.0	1877	
$[PdCl_2(PPh_2CH{=}CH_2)_2]$ [c]	22.7 14.2		$\nu(Pd{-}Cl)$ 358s, 310s
$[PtBr_2(PPh_2CH{=}CH_2)_2]$ [c]	20.3 12.2		
trans-$[PdI_2(PPh_2CH{=}CH_2)_2]$	4.8		

[a] Recorded at 40.25 MHz and 21°C in CD_2Cl_2. Chemical shifts (δ) in ppm, coupling constants (J) in Hz. [b] Recorded as Nujol mulls, frequencies in cm^{-1}, s = strong, m = medium. [c] Exists as mixture of *cis* and *trans* isomers in solution.

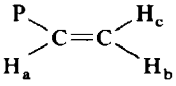
well-separated at 400 MHz to give essentially first order patterns. The assignments of the three hydrogens, H_a (*geminal* to P), H_b (*trans* to P) and H_c (*cis* to P) follow from the values of coupling constants. Thus H_b shows the largest coupling to P (41.7 Hz) (i.e. *vicinal-trans*) and a very small (1.1 Hz, *geminal* coupling) to H_c. The *vicinal-trans* coupling between H_a and H_b, 17.9 Hz, is greater than the *vicinal-cis* coupling of 12.0 Hz between H_b and H_c, as expected [11]. Other coupling constant and chemical shift data are given in Table 3. We also made *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ (in 97% yield) by treating $[PtCl_2(\text{cyclooctadiene})]$ with two equivalents of $PPh_2CH{=}CH_2$ (see Experimental section for details). By treating this dichloro-complex with lithium bromide in a mixture of acetone and dichloromethane, we obtained the corresponding dibromo-complex *cis*-$[PtBr_2(PPh_2CH{=}CH_2)_2]$; preparative details are given in the Experimental section and characterization data in Tables 1–3. The corresponding di-iodide *cis*-$[PtI_2(PPh_2CH{=}CH_2)_2]$ was similarly made (from sodium iodide) and characterized. A freshly prepared solution of this *cis*-di-iodo complex showed a $^{31}P\{^{1}H\}$ resonance at δ 1.0 ppm with $^{1}J(Pt{-}P)$ 3445 Hz but after 1 h a second resonance at δ 1.6 ppm with $^{1}J(Pt{-}P)$ 2449 Hz had formed. We attribute this to the presence of some of the *trans*-isomer, *trans*-$[PtI_2(PPh_2CH{=}CH_2)_2]$; it is well known that the equilibrium ratio of *cis*/*trans*-isomers of compounds of the type $[PtX_2(\text{tertiary phosphine})_2]$ falls on going from X = Cl to I [10].

The dimethyl complex *cis*-$[PtMe_2(PPh_2CH{=}CH_2)_2]$ was made by displacing cycloocta-1,5-diene from $[PtMe_2(COD)]$ by treating it with $PPh_2CH{=}CH_2$ in benzene. This dimethyl complex was characterized by elemental analysis and by IR and NMR spectroscopy (see Tables 1–3).

We attempted to prepare the analogous palladium complexes by similar methods. Treatment of $[PdCl_2(PhCN)_2]$ with two mole equivalents of $PPh_2CH{=}CH_2$ in benzene gave a product, the elemental analytical data of which were in agreement with $[PdCl_2(PPh_2CH{=}CH_2)_2]$. The $^{31}P\{^{1}H\}$ NMR pattern of this product showed two singlets, at 22.7 and 14.2 ppm in the approximate integration ratios of 7/5, which we attribute to the presence of *cis*- and *trans*-isomers. The IR spectrum of

Table 3

^1H NMR data [a] for diphenylvinylphosphine complexes



Complex	$\delta(H_a)$	$^2J(PH_a)$	$^3J(PtH_a)$	$\delta(H_c)$	$^3J(PH_c)$	$^4J(PtH_c)$	$\delta(H_b)$	$^3J(PH_b)$	$^3J(H_aH_c)$	$^3J(H_aH_b)$	$^2J(H_cH_b)$
$PPh_2CH{=}CH_2$	6.80	11.7		5.7	14.1		6.04	31.7	18.0	11.8	2.3
cis-$[PtCl_2(PPh_2CH{=}CH_2)_2]$	6.41	22.4	12.2	5.2	20.7	9.8	5.78	41.7	17.9	12.0	1.1
cis-$[PtBr_2(PPh_2CH{=}CH_2)_2]$	6.45	22.4	13.6	5.2	20.5	10.0	5.77	41.7	18.0	12.0	1.0
cis-$[PtI_2(PPh_2CH{=}CH_2)_2]$	6.48	22.2	15.1	5.2	20.2	9.8	5.74	41.2	17.9	12.0	0.9
cis-$[PtMe_2(PPh_2CH{=}CH_2)_2]$ [b]	6.26	17.8	11.7	5.4	17.5	5.3	5.66	26.3	17.5	12.1	1.9
cis-$[PdCl_2(PPh_2CH{=}CH_2)_2]$	6.46	23.7		5.1	20.6		5.83	41.3	17.8	12.0	0.7
trans-$[PdCl_2(PPh_2CH{=}CH_2)_2]$	7.12	24.7		5.4 [c]	18.3		6.17 [c]	38.0	18.3	12.0	1.2
trans-$[PdI_2(PPh_2CH{=}CH_2)_2]$	7.5 [d]	[d]		5.2 [e]	19.1		5.96 [c]	38.5	18.0	11.9	1.2

[a] Recorded at 400 MHz in CD_2Cl_2 at 24° C unless otherwise stated. Chemical shifts (δ) in ppm, coupling constants (J) in Hz. Proton assignments depicted in Fig. 1. [b] $\delta(CH_3)$ 0.47 ppm, $^2J(PtCH_3)$ 69.3 Hz. ^1H NMR spectrum exhibits $AA'X_3X'_3$ deceptively simple quartet pattern. [c] Pair of virtual triplets also observed due to $J(P_{trans}H)$. [d] Obscured by phenyl resonances, unable to measure coupling constants.

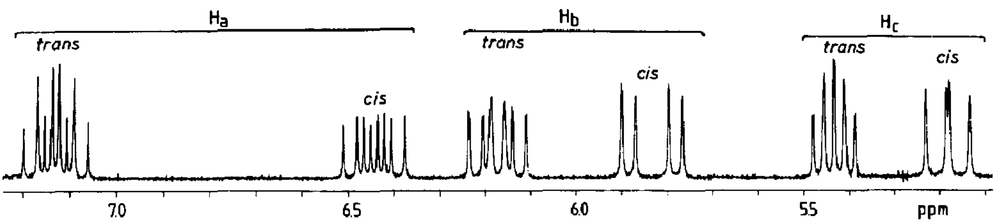


Fig. 1. ^1H NMR spectrum of $[PdCl_2(PPh_2CH{=}CH_2)_2]$ (mixture of *cis*- and *trans* isomers) in the vinyl region. Recorded at 400 MHz in CD_2Cl_2 at 24°C.

this mixture showed a band at 350 cm^{-1}, attributed to *trans*-$[PdCl_2(PPh_2CH{=}CH_2)_2]$ and a band at 310 cm^{-1}, attributed to *cis*-$[PdCl_2(PPh_2CH{=}CH_2)_2]$, we suggest that the other band expected for the *cis*-isomer is either obscured or is too weak to be observed. The ^1H and $^1H\{^{31}P\}$ NMR spectra of $[PdCl_2(PPh_2CH{=}CH_2)_2]$ at 400 MHz show two sets of well resolved vinyl hydrogen resonances. In the ^1H NMR spectrum the patterns of the three vinyl hydrogens of the *cis*-complex are first order, those of H_b and H_c being doublets of doublets, as shown in Fig. 1, the *geminal* coupling $^2J(H_bH_c)$ being essentially zero, whilst the pattern for H_a is a double doublets. In contrast, the patterns for the vinyl hydrogens of the *trans*-complex are second order, showing the phenomenon of virtual coupling to the second phosphorus (see Fig. 1). It is well established that in tertiary phosphine complexes of the types *trans*-$[PdCl_2(PR_3)_2]$, $^2J(PP)$ (*trans*) is very large (frequently several hundred Hz) and the phenomenon of virtual coupling is observed in the ^1H NMR spectrum, whilst with the corresponding *cis*-complexes, *cis*-$[PdCl_2(PR_3)_2]$, $^2J(PP)$ (*cis*) is very much smaller and the phenomenon of virtual coupling is not observed [12]. The corresponding dibromide-complex mixture, *cis*-$[Pbr_2(PPh_2CH{=}CH_2)_2]$/ *trans*-$[PtBr_2(PPh_2CH{=}CH_2)_2]$ was prepared by treating the dichloride mixture with lithium bromide. It was characterized as a *cis*/*trans*-mixture by elemental analysis (Table 1) and by IR and NMR spectroscopy (Tables 2 and 3). Treatment of the *cis*/*trans*-mixture, $[PdCl_2(PPh_2CH{=}CH_2)_2]$, with NaI gave a single product, established by its ^1H and $^1H\{^{31}H\}$ NMR spectrum to be *trans*-$[PdI_2(PPh_2CH{=}CH_2)_2]$ (see the Experimental section for preparative details and the Tables for characterization data).

Experimental

The general techniques and apparatus used were the same as those described in recent papers from this laboratory [13]. Operations involving free phosphines were carried out under dry nitrogen.

Preparation of cis-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ from $[PtCl_2(NCPh)_2]$

The phosphine (0.2 g, 0.94 mmol) was added to a stirred suspension of $[PtCl_2(NCPh)_2]$ (0.217 g, 0.46 mmol) in dry benzene (10 cm^3). The suspension cleared immediately to give a pale yellow solution, which after 1 h was filtered and cooled to ca. 5°C. The product gradually crystallized out and was collected and dried. It was obtained as white prisms. Yield 0.27 g, 85%.

The palladium analogue was prepared similarly from $[PdCl_2(NCPh)_2]$ in 84% yield. The NMR data suggested that it was a mixture of *cis*- and *trans*-isomers.

Preparation of cis-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ *from* $[PtCl_2(COD)]$

$PPh_2CH{=}CH_2$ (90.58 g, 2.74 mmol) was added to a warm suspension of $[PtCl_2(COD)]$ (0.5 g, 1.34 mmol) in dry degassed benzene (40 cm^3). The mixture was refluxed for 10 min to give a colourless solution containing the required product as a suspension of large white prisms. Most of the solvent was evaporated under reduced pressure to give more product. The product was filtered off, washed with diethyl ether, and dried. Yield 0.90 g, 97%.

Preparation of cis-$[PtBr_2(PPh_2CH{=}CH_2)_2]$

A mixture of *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ (0.2 g, 0.29 mmol), LiBr (0.1 g, 1.15 mmol), acetone (10 cm^3) and dichloromethane (10 cm^3) was stirred for 1 h. The resulting pale yellow solution was evaporated to dryness under reduced pressure and the residue extracted with dichloromethane. The extract was filtered and evaporated to low bulk and pentane was added, to give the product as cream microcrystals. Yield 0.194 g, 86%.

cis-$[PtI_2(PPh_2CH{=}CH_2)_2]$ was prepared similarly by treating the dichloro-complex with NaI. Yield 87%.

$[PtBr_2(PPh_2CH{=}CH_2)_2]$ was prepared in an analogous manner to that used for the platinum complex and was obtained as a mixture of *cis*- and *trans*-isomers (see Discussion).

trans-$[PdI_2(PPh_2CH{=}CH_2)_2]$ was prepared similarly by treating the dichloro-complex with NaI. It formed orange microcrystals from dichloromethane/n-pentane. Yield 95%.

Preparation of cis-$[PtMe_2(PPh_2CH{=}CH_2)_2]$

The phosphine (0.60 g, 2.83 mmol) was added to a solution of $[PtMe_2(COD)]$ (0.471 g, 1.41 mmol) in benzene (10 cm^3). The mixture was then heated under reflux for 3 h, filtered, and evaporated to dryness in vacuo. The residual yellow oil was dissolved in a minimum of dichloromethane and methanol added, to give the product as white microcrystals. Yield 0.76 g, 83%.

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