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THE INTERACTION OF VINYL ACETATE AND ALLYL ACETATE WITH CHLORO-BRIDGED PLATINUM(II) COMPLEXES $[Pt_2Cl_4(PR_3)_2]$: CRYSTAL STRUCTURE OF *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ *

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Summary

Five complexes of type *cis*-$[PtCl_2(PR_3)Q]$ (PR_3 = PMe_3, PMe_2Ph, PEt_3; Q = $CH_2{=}CHOCOCH_3$ or $CH_2{=}CHCH_2OCOCH_3$) have been prepared. The crystal structure of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ is described. Crystals of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ are triclinic, with a 8.441(4), b 13.660(5), c 7.697(3) Å, α 101.61(3)°, β 111.85(3)°, γ 95.22(3)°, $P\bar{1}$, $Z = 2$. The structure was determined from 2011 reflections with $I > 3\sigma(I)$ and refined to $R = 0.037$. The CH_3COO grouping is *syn* to the *cis*-PMe_2Ph ligand, with bond lengths of Pt—Cl (*trans* to P) 2.367(3), Pt—Cl (*trans* to olefin) 2.314(3), Pt—P 2.264(2), and Pt—C of 2.147(12) and 2.168(11) Å. The complexes *cis*-$[PtCl_2(PR_3)Q]$ were studied by variable temperature ^1H and ^{31}P NMR spectroscopy. Spectra of the vinyl acetate complexes were temperature dependent as a result of rotation about the platinum—olefin bond. The rotation was "frozen out" at ca. 240 K; for *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ $\Delta G^\ddagger$ (rotation) 15.0 ± 0.2 kcal mol^{-1}. NMR parameters for the rotamers are reported. NMR studies of the interaction between chloro-bridged complexes of type $[Pt_2Cl_2(PR_3)_2]$ (PR_3 = P-n-Pr_3 or PMe_2Ph) and vinyl acetate shows that even at low temperatures (213 K) equilibrium favours the bridged complex and the proportion of *trans*-$[PtCl_2(PR_3)(CH_2{=}CHOCOCH_3)]$ is very small e.g. 2%. The allyl acetate complexes *cis*-$[PtCl_2(PR_3)(CH_2{=}CHCH_2OCOCH_3)]$ showed only one rotamer over the range 333—213 K. Reversible dissociation of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OCOCH_3)]$ to $[Pt_2Cl_4(PMe_2Ph)_2]$ + allyl acetate was studied at ambient temperature. At low temperatures e.g. 213—190 K addition of allyl acetate to a $CDCl_3$ solution of $[Pt_2Cl_2(P\text{-n-}Pr_3)_2]$ reversibly gave some olefin complex *trans*-$[PtCl_2(P\text{-n-}Pr_3)(CH_2{=}CHCH_2OCOCH_3)]$ and some *O*-bonded complex *trans*-$[PtCl_2(P\text{-n-}Pr_3)(CH_2{=}CHCH_2OCOCH_3)]$.

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* Dedicated to Joseph Chatt on the occasion of his 65th birthday.

TABLE 1

ANALYTICAL, MOLECULAR WEIGHT, AND IR (Nujol mull, cm^{-1}) DATA

Complex	Mol. wt. (Found (calcd.))	Analyses (Found (calcd.) (%))			Decomp. point θ_c (°C)	$\nu(C{=}O)$	$\nu(Pt{-}Cl)$
		C	H	Cl			
cis-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$	444 (428)	29.3 (29.4)	3.45 (3.5)		105	1769	328s, 288s
cis-$[PtCl_2(PMe_3)(CH_2{=}CHOCOCH_3)]$		19.9 (19.6)	3.5 (3.5)	16.3 (16.6)	110	1770	330s, 285s
cis-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OCOCH_3)]$		31.1 (31.0)	3.7 (3.8)	14.25 (14.1)	100	1727	309s, 285s
cis-$[PtCl_2(PMe_3)(CH_2{=}CHCH_2OCOCH_3)]$	450 (442)	21.85 (21.8)	3.95 (3.9)	15.9 (16.0)	100	1725	327s, 285s
cis-$[PtCl_2(PEt_3)(CH_2{=}CHCH_2OCOCH_3)]$	471 (484)	27.0 (27.3)	4.55 (4.8)	14.5 (14.6)	105	$\left\{\begin{array}{l}1729^{a}\\1745\end{array}\right.$	327s, 274s

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[a] Single band at 1735 cm^{-1} in $CHCl_3$ solution.

In a previous paper [1] we described a preparative and NMR study of the products formed by interacting allylic alcohols with halo-bridged platinum(II) complexes of the types $[Pt_2X_4(PR_3)_2]$ (X = Cl or Br) and $[N\text{-}n\text{-}Bu_4]_2[Pt_2Cl_6]$: the crystal structure of *cis*-$[PtCl_2(CH_2{=}CHCH_2OH)(PMe_2Ph)]$ was also described. We now describe a study with two other functionalized olefins viz. vinyl acetate and allyl acetate, both of which are important commercially. These two olefins are potentially very useful starting materials for other reactions catalysed by transition metal complexes such as hydro-formylation, -allylation or -vinylation. Vinyl acetate and allyl acetate have been hydroformylated using cobalt carbonyl [2], *N*-methylpyrrolidinerhodium/water [3], and triphenylphosphinerhodium [4,5]. A mixture of products is generally formed and the factors affecting terminal and non-terminal addition of the HCHO i.e. the regioselectivity, are not understood.

There have also been many studies on palladium(II) catalysed vinyl ester and allyl ester exchanges [6] and also on the remarkably facile allylation reaction catalysed by palladium(0)—triphenylphosphine complexes [7,8]. Relatively little is known about how these simple functionalized olefins interact with metal complexes. We have chosen first to study interaction with bridged chloroplatinum(II) complexes of the type $[Pt_2Cl_4(PR_3)_2]$, but hope later to study rhodium and palladium systems, relevant to catalytic systems. We anticipated that platinum(II) would give stable olefin complexes for structure determination by crystallography and also the presence of the platinum-195 isotope would greatly assist in the identification of labile species formed in solution using nuclear magnetic resonance spectroscopy at variable temperature.

We find that both vinyl acetate and allyl acetate, over a period of several hours, slowly and reversibly react with bridged chloroplatinum(II) complexes of type $[Pt_2Cl_4(PR_3)_2]$ ($PR_3 = PMe_3$, PMe_2Ph or PEt_3) to give colourless complexes of the type *cis*-$[PtCl_2(\text{olefin})(PR_3)]$. By using a large excess of the olefin the reaction was driven essentially to completion. Characterising microanalytical and IR data are given in Table 1: the NMR data are discussed later along with other NMR studies. Crystals of the vinyl acetate complex *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ suitable for a structural study by X-ray diffraction were formed from dichloromethane—vinyl acetate and the structure of this complex is described first.

The molecular structure and atom numbering are shown in Fig. 1 and bond lengths and angles are given in Table 2. In contrast to our results for the analogous allyl alcohol complex [1] we find here that the group is *syn* to the *cis*-phosphine ligand, which has its phenyl group orientated roughly parallel to the vinyl acetate ligand, in which the carbon and oxygen atoms are nearly in a plane. There are intramolecular non-bonding contacts of 3.34(2) Å between C(2) of the phenyl group and C(12) of the vinyl acetate, and of 3.32 and 3.29(2) Å, respectively, from the methyl carbon C(7) to C(9) and O(11) of the vinyl acetate; these values are close to the sums of Van der Waals radii. The Pt—Cl bond lengths differ by 0.053 Å because of the differing *trans*-influences of phosphine and olefin; in the allyl alcohol complex we found a smaller difference of 0.027 Å [1].

NMR studies. The ^1H and ^{31}P NMR spectra of the two vinyl acetate complexes *cis*-$[PtCl_2(PMe_3)(CH_2{=}CHOCOCH_3)]$ and *cis*-$[PtCl_2(PMe_2Ph)$-

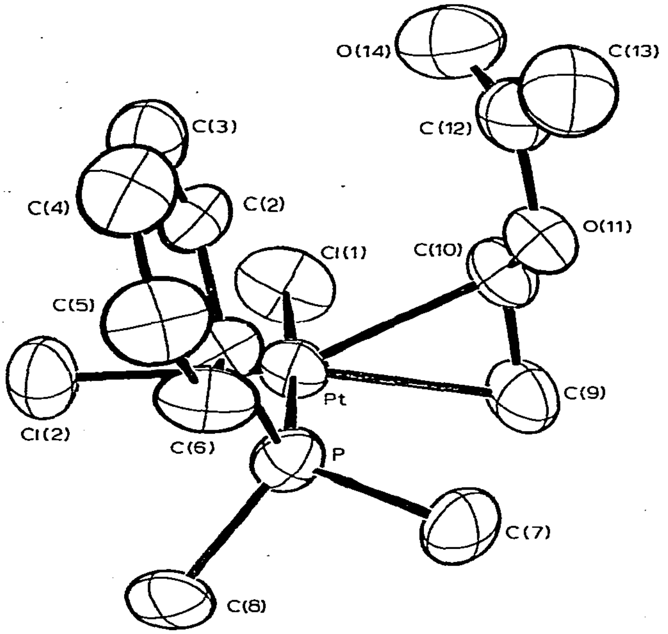


Fig. 1. ORTEP drawing of the molecular structure of *cis*-[$PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)$] showing atom numbering.

($CH_2{=}CHOCOCH_3$)] were temperature-dependent as a result of rotation about the platinum—olefin bond. The rotation was "frozen-out" at ca. 243 K for *cis*-[$PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)$] and at a few degrees lower for the trimethylphosphine analogue: in both cases well-resolved spectra of the two possible rotational isomers were obtained. Both complexes gradually dissociated in solution to give the bridged species [$Pt_2Cl_4L_2$] (L = PMe_2Ph or PMe_3) and free vinyl acetate. The rate of dissociation was much greater than for the equivalent com-

TABLE 2

SELECTED BOND LENGTHS AND ANGLES WITH e.s.d.'s IN PARENTHESES

Pt—Cl(1)	2.367(3) Å	Cl(1)—Pt—Cl(2)	88.7(1)°
Pt—Cl(2)	2.314(3)	Cl(1)—Pt—P	175.5(1)
Pt—P	2.264(2)	Cl(1)—Pt—C(9)	88.2(3)
Pt—C(9)	2.147(12)	Cl(1)—Pt—C(10)	86.7(3)
Pt—C(10)	2.168(11)	Cl(2)—Pt—P	87.9(2)
P—C(1)	1.814(9)	Cl(2)—Pt—C(9)	167.8(3)
P—C(7)	1.855(13)	Cl(2)—Pt—C(10)	154.6(3)
P—C(8)	1.798(9)	P—Pt—C(9)	94.5(3)
C(9)—C(10)	1.362(13)	P—Pt—C(10)	97.6(3)
C(10)—O(11)	1.377(13)	Pt—P—C(1)	113.8(3)
O(11)—C(12)	1.366(11)	Pt—P—C(7)	117.4(3)
C(12)—C(13)	1.476(21)	Pt—P—C(8)	110.1(3)
C(12)—O(14)	1.221(16)	C(9)—C(10)—O(11)	120.2(8)
C—C(phenyl)	1.381—1.442(17)	C(10)—O(11)—C(12)	118.2(8)
		O(11)—C(12)—C(13)	112.3(9)
		O(11)—C(12)—O(14)	118.9(10)
		C(13)—C(12)—O(14)	128.8(9)

plexes with the allyl alcohol [1], with some dissociation being observed even after 1 h at 243 K; the complexes also slowly decomposed in the solid state. The ^1H resonances of the free ligand remained sharp at room temperature showing that as with the allyl alcohol complexes, exchange between free and coordinated vinyl acetate is slow on the NMR time scale.

The ratio of rotational isomers at low temperature was ca. 3/1 for *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ and 5/1 for the analogous trimethylphosphine derivative (both in CD_2Cl_2). These ratios were unchanged over the temperature range 253—213 K which implies that the enthalpy difference between the two configurations is small. For *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ the isomer ratio is solvent dependent, it being 1.4/1 in $CDCl_3$. Lewis and his co-workers have derived values of the free energy of activation of olefin rotation for a wide range of platinum(II)-olefin complexes from NMR coalescence temperatures using an approximate equation [9,10]. The $^{31}P\{^1H\}$ NMR spectra (Table 3) of the vinyl acetate complexes are particularly suitable for this treatment since the coalescing peaks are singlets and their chemical-shift separation greatly exceeds the linewidth [11]. We have determined the coalescence temperature, T_c, of the two central peaks in the $^{31}P\{^1H\}$ spectrum of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ in $CDCl_3$, as 288 ± 2 K. The chemical-shift separation of these peaks is 58.6 ± 0.6 Hz at 243 K yielding a value for $\Delta G^{\ddagger}(T_c)$ of 15.0 ± 0.2 kcal mol^{-1}. This may be compared with the values of 13.5 and 12.3 kcal mol^{-1} reported for *cis*-$[PtCl_2(PMe_2Ph)L]$ ($L = CH_2{=}CHCH_3$ and C_2H_4 respectively). [10].

At low temperature, the ^1H NMR spectra of the vinyl acetate complexes showed separate P-methyl resonances for each rotamer. In the case of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ each rotamer gave rise to two distinct resonances since the P-methyl groups are diastereotopic. Without ^{31}P decoupling these resonances appeared as doublets $[^2J(PH)]$ flanked by ^{195}Pt satellites. The vinylic protons appeared as two weakly-coupled ABX-patterns with further coupling to ^{31}P and ^{195}Pt. With the aid of ^{31}P-decoupled spectra we were able to obtain most of the NMR parameters and the results are presented in Table 4. The parameters of the PMe_2Ph derivative were not markedly different in $CDCl_3$ solution. The ^1H chemical shifts of the olefinic protons are clearly very sensitive to the orientation of the ligand, the reversal of the order of $\delta(H(2))$ and $\delta(H(3))$ being particularly notable. Unusually, the geminal coupling between

TABLE 3

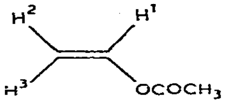
PHOSPHORUS-31 NMR PARAMETERS FOR THE *cis*-COMPLEXES

Complex	Major isomer		Minor isomer	
	$\delta(P)$ [a]	$^1J(PtP)$ (Hz)	$\delta(P)$	$^1J(PtP)$ (Hz)
$[PtCl_2(PMe_3)(CH_2{=}CHOCOCH_3)]$ [b]	—12.0	3234 ± 1	—13.8	3031 ± 1
$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ [b]	—6.1	3383 ± 1	—7.0	3043 ± 1
$[PtCl_2(PMe_3)(CH_2{=}CHCH_2OCOCH_3)]$ [c]	—16.2	3029 ± 2		
$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OCOCH_3)]$ [c]	—8.1	3055 ± 2		
$[PtCl_2(PEt_3)(CH_2{=}CHCH_2OCOCH_3)]$ [c]	14.9	3009 ± 1		

[a] In ppm to high frequency of H_3PO_4. [b] In CD_2Cl_2 or CH_2Cl_2/CD_2Cl_2. [c] In $CDCl_3$.

TABLE 4

HYDROGEN-1 NMR PARAMETERS OF *cis*-[$PtCl_2L(CH_2{=}CHOCOCH_3)$] (L = PMe_3 or PMe_2Ph) [a]



	L = PMe_3 [b]		L = PMe_2Ph [c]	
	major isomer	minor isomer	major isomer	minor isomer
$\delta(CH_3)$	2.24 [d]	2.16	1.43	2.16
$\delta(H_1)$	7.56	6.70	7.69	6.12
$\delta(H_2)$	4.09	3.67	4.25	3.15
$\delta(H_3)$	3.79	4.48	3.91	4.39
$^3J(H_1H_2)$	4.9	4.4	4.9	4.5
$^3J(H_1H_3)$	10.9	11.0	10.9	11.0
$^2J(H_2H_3)$	2.1	2.2	2.0	1.9
$J(PtH_1)$	76.8	64	78	62.8
$J(PtH_2)$	74.9	[e]	73.8	68.4
$J(PtH_3)$	48.0	[e]	48.3	49
$J(PH_1)$	<0.2	[e]	<0.2	4.3
$J(PH_2)$	0.7	[e]	0.7	2.2
$J(PH_3)$	5.6	[e]	5.3	<1

[a] Coupling constants ±0.1 Hz; phosphine resonances have been omitted. [b] At 238 K in CD_2Cl_2. [c] At 243 K in CD_2Cl_2. [d] $J(PtH)$ ca. 2 Hz. This was the only methyl resonance to show coupling to ^{195}Pt. [e] Coupling not identified in spectrum.

them exceeds that in vinyl acetate itself (1.6 Hz at 243 K). In a large number of related complexes, the geminal coupling constant was found to be vanishingly small [1,10,12]. For *cis*-[$PtCl_2(PMe_3)(CH_2{=}CHOCOCH_3)$] the ^1H chemical shift of the methyl(acetate) group is similar in both isomers to the value of 2.18 ppm observed for free vinyl acetate at the same temperature. This is also true of the less abundant rotamer in the PMe_2Ph analogue, but for the preferred rotamer the shift is markedly lower, 1.43 ppm (Table 4). If this greater shielding is caused by the magnetic anisotropy of the phenyl group then it would imply that the acetate is *syn* to the phosphine, i.e. similar to the configuration found in the crystal.

Proton NMR data for complexes of the type *trans*-[$PtCl_2(Q)$(4-methylpyridine oxide)] (Q = vinyl butyrate or vinyl benzoate) have been reported by Kaplan and Orchin [13]. They found that the geminal coupling constant $J(H(2)H(3))$ was small (ca. 1 Hz) and that $J(PtH(1)) > J(PtH(2))$ or $J(PtH(3))$. The complex [$PtCl(acac)(CH_2{=}CHOCOCH_3)$] has been described, although ^1H NMR data for the vinyl acetate ligand were not reported [14].

In our earlier paper [1], we showed by ^{31}P NMR spectroscopy that chloro-bridged complexes of the type [$Pt_2Cl_4(PR_3)_2$] interact with allylic alcohols at low temperatures to give *trans*-[$PtCl_2(PR_3)Q$] (Q = olefin), which is in equilibrium with the bridged complex. In a similar manner we have studied the interaction of vinyl acetate with [$Pt_2Cl_4(P\text{-}n\text{-}Pr_3)_2$] in $CDCl_3$ and with [$Pt_2Cl_4(PMe_2Ph)_2$] in CH_2Cl_2/CD_2Cl_2. In both cases the equilibrium lies much more in favour of the bridged complex than was the case with allyl alcohol. At 213 K with ca. 1.0 *M* vinyl acetate and ca. 0.1 *M* bridged complex the proportion of *trans*-complex was only ca. 2% in each case; no other species were detected. The ^{31}P NMR parameters at 213 K were $\delta(P)$ 6.0 ppm and $^1J(PtP)$ 3428 Hz for *trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)(CH_2{=}CHOCOCH_3)]$ and $\delta(P)$ —9.4 ppm and $^1J(PtP)$ 3544 Hz for the analogous dimethylphenylphosphine complex. On raising the temperature the proportion of the *trans*-complex decreased and the lines gradually broadened due to exchange with $[Pt_2Cl_4(PR_3)_2]$. *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHOCOCH_3)]$ slowly formed at 296 K.

The allyl acetate complexes *cis*-$[PtCl_2L(CH_2{=}CHCH_2OCOCH_3)]$ (L = PMe_3, PMe_2Ph or PEt_3) showed only one species in their $^{31}P\{^1H\}$ NMR spectra over the range 333—213 K (^{31}P NMR parameters in Table 3). The rate of dissociation in solution was intermediate between the equivalent vinyl acetate and allyl alcohol complexes. For the PEt_3 and PMe_3 derivatives the decomposition proceeded to completion and in the latter case was accompanied by the precipitation of $[Pt_2Cl_4(PMe_3)_2]$ from the solution. In contrast, the PMe_2Ph system eventually reached an equilibrium in which the ratio of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OCOCH_3)]$ to $[Pt_2Cl_4(PMe_2Ph)_2]$ was ca. 1/4. The position of equilibrium could be shifted in favour of the former by adding allyl acetate to the solution. Addition of a large excess (fifteen fold or greater) of allyl acetate caused the peaks of the two species to broaden and coalesce especially on raising the temperature to 333 K, owing to exchange.

The ^1H NMR spectra of all the allyl acetate derivatives were very complex as the result of a near-superimposition of several of the chemical shifts and consequently were not easily analysed. The ^1H chemical shift of the acetate group was 2.12, 2.05, and 2.10 ppm for the complexes with PMe_3, PMe_2Ph and PEt_3, respectively, compared to 2.09 ppm in the free ligand. By analogy with the ^1H methyl shifts in the vinyl acetate complexes these values could be taken as suggesting that the CH_2OCOCH_3 moiety is *anti* to the phosphine (as is the CH_2OH group in solid *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$) [1] but such a comparison may not be justified.

On adding allyl acetate (1 mol per platinum atom) to a ca. 0.1 *M* solution of $[Pt_2Cl_4(P\text{-}n\text{-}Pr_3)_2]$ in $CDCl_3$ at 213 K, ca. 5% of the bridged complex was converted to *trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)(CH_2{=}CHCH_2OCOCH_3)]$ ($\delta(P)$ 6.8 ppm, $^1J(PtP)$ 3375 Hz). Some *trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)(CH_2{=}CHCH_2OH)]$ was also detected owing to a trace (ca. 0.4%) of allyl alcohol in the allyl acetate, on the basis of ability to rupture $[Pt_2Cl_4(P\text{-}n\text{-}Pr_3)_2]$ the complexing ability of allyl alcohol is about 100 times that of allyl acetate. On adding a tenfold excess of allyl acetate to the solution, a small amount of an additional species became visible in the $^{31}P\{^1H\}$ spectrum and on cooling to 190 K with CH_2Cl_2/CD_2Cl_2 as solvent the amount had increased sufficiently for its ^{195}Pt satellites to be detected. The NMR parameters ($\delta(P)$ —4.5 ppm and $^1J(PtP)$, 3941 Hz) under these conditions are not far removed from those of a similar species observed in the reaction of allyl alcohol or methanol with $[Pt_2Cl_4(P\text{-}n\text{-}Pr_3)_2]$ which was surmised to be the *O*-bonded form, *trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)(CH_2{=}CHCH_2OH)]$ [1]. Consequently we suggest that the additional species described above is *trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)(CH_2{=}CHCH_2OCOCH_3)]$. The amount of the latter species relative to the π-bonded form was also similar to that observed in the allyl alcohol reaction. We have found that methyl acetate reacts with $[Pt_2Cl_4(P\text{-}n\text{-}Pr_3)_2]$ at 233 K to give a species with δ(P) −5.0 ppm, ${}^1J$(PtP) 3992 Hz, which we suggest is an *O*-bonded *trans*-complex *trans*-[PtCl$_2$(P-n-Pr$_3$)(CH$_3$COOCH$_3$)] [15].

Experimental

The ^{1}H, ^{1}H{^{31}P} and ^{31}P{^{1}H} NMR spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock. Except where otherwise stated, measurements were made at ambient temperature (ca. 296 K). Concentrations were ca. 0.1 mol dm^{-3} for the complexes with allyl acetate and saturated for those with vinyl acetate. It was important to examine the vinyl acetate complexes as soon as possible after dissolution to avoid decomposition.

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Analytical, decomposition points and IR data are in Table 1.

cis-Dichloro(dimethylphenylphosphine)(vinyl acetate)platinum(II).

μ-Dichloro-dichlorobis(dimethylphenylphosphine)diplatinum(II) (0.310 g) was dissolved in a mixture of dichloromethane (5 cm^3) and vinyl acetate (4 cm^3) with warming. This solution was left for 16 h at ca. 0°C to give the required product (0.321 g, 86%) as white prisms. It could be recrystallized from dichloromethane/diethyl ether containing a small amount of vinyl acetate to suppress dissociation.

cis-Dichloro(trimethylphosphine)(vinyl acetate)platinum(II) (77%) was prepared similarly.

cis-(Allyl acetate)dichloro(dimethylphenylphosphine)platinum(II). μ-Dichlorodichloribis(dimethylphenylphosphine)diplatinum(II) (0.182 g) was dissolved in a mixture of dichloromethane (4 cm^3) and allyl acetate (1 cm^3) with warming. The solution was left for 15 h to give the required product as white prisms (0.176 g, 78%), which could be recrystallized from dichloromethane/diethyl ether.

cis-(Allyl acetate)dichloro(trimethylphosphine)platinum(II) (71%) and *cis*-(allyl acetate)dichloro(triethylphosphine)platinum(II) (74%) were prepared similarly.

Crystal data. *cis*-[PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHOCOCH$_3$)], C$_{12}$H$_{17}$Cl$_2$O$_2$PPt, mol. wt. 490.2, triclinic, space group $P\bar{1}$, a 8.441(4), b 13.660(5), c 7.697(3) Å, α 101.61(3)°, β 111.85(3)°, γ 95.22(3)°, V 793.4(5) Å^3, Z = 2, D_x 2.052 g cm^{-3}, μ(Mo-K_α) 93.66 cm^{-1}.

Structure determination. Measurements were made on a SYNTEX P2$_1$ diffractometer using graphite monochromatized Mo-K_α radiation (λ 0.71069 Å). Cell dimensions and their standard deviations were determined by least-squares treatment of the setting angles for 15 reflections with $35° < 2\theta < 40°$. The intensities of the 2090 independent reflections in the range $4° < 2\theta < 45°$ were measured by ω—2θ scans, with scans running from 0.8° below $K_{\alpha1}$ to 0.8° above $K_{\alpha2}$ and with scan speeds from 0.49° min^{-1} for the weaker reflections to 29.30° min^{-1} for the most intense reflections. The structure analysis used the 2011 reflections having $I > 3\sigma(I)$, and these were corrected for Lorentz, polarization and transmission factors (A^* = 2.35—4.51), and for the ca. 30% decline of intensity shown by a control reflection during the course of data collection. Solution of the structure from Patterson and electron density syntheses was followed by least-squares refinement, initially full-matrix, but in the final stage

TABLE 5

ATOMIC COORDINATES AND e.s.d.'s

	X	*Y*	*Z*
Pt	0.01267(4)	0.16182(2)	0.05469(4)
Cl(1)	0.3023(3)	0.1473(2)	0.2329(4)
Cl(2)	0.1036(3)	0.2183(2)	−0.1627(4)
P	−0.2614(3)	0.1706(2)	−0.1371(3)
C(1)	−0.3009(11)	0.2994(6)	−0.1293(13)
C(2)	−0.1688(13)	0.3850(7)	0.0024(14)
C(3)	−0.2069(15)	0.4817(8)	0.0020(16)
C(4)	−0.3672(17)	0.4951(8)	−0.1243(19)
C(5)	−0.4965(15)	0.4118(9)	−0.2531(19)
C(6)	−0.4620(13)	0.3150(8)	−0.2521(15)
C(7)	−0.4413(13)	0.1060(8)	−0.0940(15)
C(8)	−0.3088(13)	0.1088(7)	−0.3849(12)
C(9)	−0.0662(14)	0.0782(7)	0.2262(13)
C(10)	−0.0227(13)	0.1783(7)	0.3243(12)
O(11)	−0.1499(9)	0.2325(5)	0.3346(9)
C(12)	−0.1009(17)	0.3334(7)	0.4248(13)
C(13)	−0.2491(18)	0.3802(9)	0.4386(19)
O(14)	0.0510(13)	0.3734(6)	0.4862(12)

with anisotropic temperature factors using the 9 × 9 block-diagonal approximation. With Pt, P, and Cl anisotropic, C and O isotropic *R* was 0,054, reduced to 0.039 on inclusion of the absorption corrections, and allowance for anisotropic vibrations for C and O gave a final *R* of 0.037. A difference map now revealed all of the hydrogen atoms, but some of them were not very well placed and hydrogen atoms were therefore not introduced into the structure.

The final atomic coordinates and vibration parameters are listed in Table 5, and bond lengths and angles are given in Table 2; the molecular structure is shown in Fig. 1.

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References

1 J.R. Briggs, C. Crocker, W.S. McDonald and B.L. Shaw, J. Chem. Soc. Dalton, in press.
2 H. Adkins and G. Krsek, J. Amer. Chem. Soc., 71 (1949) 3051.
3 B. Fell and M. Barl, J. Mol. Catal., 2 (1977) 301.
4 C.K. Brown and G. Wilkinson, J. Chem. Soc. A, (1970) 2753.
5 R.L. Pruett, Advan. Organometal. Chem., 17 (1979) 1.
6 P.M. Henry, Accounts Chem. Res., (1973) 16.
7 K.E. Atkins, W.E. Walker and R.M. Maniyik, Tetrahedron Lett., 43 (1970) 3821.
8 B.M. Trost and J.P. Genet, J. Amer. Chem. Soc., 98 (1976) 8516, and ref. therein.
9 J. Ashley-Smith, I. Douek, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1972) 1776.
10 J. Ashley-Smith, Z. Douek, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1974) 128.
11 D. Kost, E.H. Carlson and M. Raban, J. Chem. Soc. Chem. Commun., (1971) 656.
12 C.E. Holiday, G. Hulley, B.F.G, Johnson and J. Lewis, J. Chem. Soc. Dalton, (1970) 1653.
13 P.D. Kaplan and M. Orchin, Inorg. Chem., 6 (1967) 1096.
14 A.C. Jesse, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 32 (1979) 87.
15 J.R. Briggs, C. Crocker and B.L. Shaw, unpublished results.