Interaction of Allylic Alcohols with Halogeno-bridged Platinum(II) Complexes $[Pt_2X_4(PR_3)_2]$ (X = Cl or Br) and $[NBu^n_4]_2[Pt_2Cl_6]$: Crystal Structure of $[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ †‡

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A series of complexes of type *cis*-$[PtCl_2(PR_3)Q]$ (PR_3 = PMe_3, PEt_3, PPr^n_3, or PMe_2Ph; Q = prop-2-en-1-ol, but-1-en-3-ol, or 3-methylbut-1-en-3-ol) have been prepared. The crystal structure of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ is described: no intramolecular hydrogen bond is present. Crystal data: space group $P2_1/n$, a = 12.540(3), b = 10.668(7), c = 10.929(2) Å, β = 97.02(2)°, and Z = 4. The complexes *cis*-$[PtCl_2(PR_3)Q]$ have been studied by variable-temperature ^1H and ^{31}P n.m.r. spectroscopy. There is no evidence for rotamers, as found with other olefin complexes. At room temperature slow dissociation to give the bridged complex $[Pt_2Cl_4(PR_3)_2]$ and the free allyl alcohol occurs. The complex *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ does not exchange rapidly with free allyl alcohol and separate resonances due to free and complexed allyl alcohol could be observed: in contrast $[NBu^n_4][PtCl_3(CH_2{=}CHCH_2OH)]$ exchanges rapidly with free allyl alcohol on the n.m.r. time scale. N.m.r. studies of the interaction between chloro-bridged complexes of the type $[Pt_2Cl_4(PR_3)_2]$ {and also $[Pt_2Br_4(PMe_2Ph)_2]$} and allylic alcohols show that at low temperatures the bridged species is rapidly and reversibly converted into *trans*-$[PtCl_2(PR_3)(CH_2{=}CHCR^1R^2OH)]$ together with some of the *O*-bonded species, *trans*-$[\overline{PtCl_2(PR_3)(CH_2{=}CHCR^1R^2O}H)]$. Above *ca.* 260 K the resonances start to broaden due to exchange with the bridged complex and have also become much less intense due to reversion back to the bridged complex: *cis*-$[PtCl_2(PR_3)(CH_2{=}CHCR^1R^2OH)]$ is also gradually formed above *ca.* 260 K. A $[Pt_2Br_4(PMe_2Ph)_2]$–$CH_2{=}CHCH_2OH$ system also shows the presence of *trans*-$[PtBr_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ and in this case the *cis* isomer forms to a detectable extent even at 213 K. The bridged complex $[Pt_2Cl_4(PPr^nBu^t_2)_2]$ containing the bulky phosphine shows the presence of rotamers at 243 K and with allyl alcohol two rotamers *trans*-$[PtCl_2(PPr^nBu^t_2)(CH_2{=}CHCH_2OH)]$ form at 213 K. The ^1H and ^{31}P n.m.r. and i.r. data are given and discussed.

THIS paper is mainly concerned with a study of interactions between allylic alcohols and chloro-bridged complexes of platinum(II) of the type $[Pt_2Cl_4L_2]$, L = tertiary phosphine. There were several reasons why we began this study. It was shown in 1964 that $[Pt_2Cl_4(PEt_3)_2]$ reacted with allyl alcohol over a period of a few hours at room temperature to give the olefin complex *cis*-$[PtCl_2(PEt_3)(CH_2{=}CHCH_2OH)]$.[1] Since it has been suggested [2] that the hydroxyl group of an allyl alcohol ligand interacts intramolecularly with the platinum or chlorine, we hoped to make an accurate crystal-structure determination of a typical allyl alcohol complex of type *cis*-$[PtCl_2(PR_3)(C_3H_5OH)]$ and look for OH ··· Pt or OH ··· Cl interactions together with other structural features of interest.

The suggestion has also been made that π-bonding ligands such as carbon monoxide (and by inference olefins) would substitute $[Pt_2Cl_4(PR_3)_2]$ rapidly in the *trans* position but that *trans*-$[PtCl_2(PR_3)Q]$ (Q = CO or olefin) would be unstable relative to $[Pt_2Cl_4(PR_3)_2]$. In fact a transient species, presumably *trans*-$[PtCl_2(PR_3)(CO)]$, was observed when bridged complexes of this type were treated with carbon monoxide, but only the *cis*-carbonyl complexes were isolated and no details of the transient *trans* species were given.[3]

One would expect from considerations of entropy that the stability of a mononuclear complex *trans*-$[PtCl_2(PR_3)(olefin)]$, relative to a chloro-bridged complex $[Pt_2Cl_4(PR_3)_2]$, would increase as the temperature is lowered. We set out to demonstrate this by n.m.r. spectroscopy. There have been extensive studies, using variable-temperature n.m.r., of olefin rotation and olefin exchange in metal–olefin complexes including complexes of type *cis*-$[PtCl_2(PR_3)(olefin)]$.[4-8] Analogous studies with allylic alcohol complexes do not appear to have been made, however. We have therefore looked for olefin rotation and olefin exchange in allyl alcohol–platinum complexes.

RESULTS AND DISCUSSION

In the course of this work we prepared a series of complexes of type *cis*-$[PtCl_2(PR_3)Q]$ with PR_3 = PMe_3, PEt_3, PPr^n_3, or PMe_2Ph and Q = prop-2-en-1-ol (allyl alcohol), but-1-en-3-ol, and 3-methylbut-1-en-3-ol § by treating the chloro-bridged complex with the allylic alcohol. Characterizing microanalytical, molecular-weight, and i.r. data are given in Table 1 and preparative details are in the Experimental section. Crystals of *cis*-$[PtCl_2(PMe_2Ph)(C_3H_5OH)]$ suitable for a structural study by *X*-ray diffraction were formed from allyl alcohol as solvent and the structure of this complex is described first.

The molecular structure and atom numbering are shown in Figure 1, and some bond lengths and angles are given in Table 2. The molecule is seen to have the CH_2OH group of the allyl alcohol *anti* to the phosphine ligand, which adopts a conformation with its methyl groups to either side of the *cis*-chloro-ligand. The two Pt–C bond distances differ by 5σ, so that their differences from the mean of 2.151 Å are probably significant. The bending away from the platinum of the four atoms attached to the olefinic carbons is evident in the Figure.

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† No reprints available.

‡ Dichloro(dimethylphenylphosphine)(prop-2-en-1-ol)platinum(II).

§ Recommended names for the last two alcohols are but-3-en-2-ol and 2-methylbut-3-en-2-ol.

From a plane through C(9) and C(10), which is perpendicular to the Pt–C(9)–C(10) plane, the displacements of C(11), H(91), H(92), and H(10) are respectively 0.327, 0.17, 0.16, and 0.18 Å. The values for the three hydrogen atoms are in very close agreement with the 0.17 Å found from neutron-diffraction work [9] on Zeise's salt, $K[PtCl_3(C_2H_4)]$. The olefinic C–C bond length of 1.375(7) Å and the Pt–Cl bond length *trans* to it [2.329(1) Å] are also in close agreement with those in Zeise's salt. The suggested internal O–H ⋯ Cl hydrogen bond is not present in the crystal, but there is a very weak intermolecular O–H ⋯ Cl bond of length 3.20 Å, with an O–H ⋯ Cl angle of 159(3)°.

TABLE 1

Analytical (%: calculated values in parentheses) and i.r. (cm^{-1}) data

Complex	Analyses C	Analyses H	Analyses Cl	Decomp. point (θ_c/°C)	Nujol mull ν(O–H)	Nujol mull ν(Pt–Cl)
cis-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ [a]	28.2 (28.6)	3.6 (3.7)	15.4 (15.15)	105	3 445 [b]	317s, 289s
cis-$[PtCl_2(PMe_3)(CH_2{=}CHCH_2OH)]$	18.2 (18.0)	3.9 (3.8)	17.75 (17.7)	110	3 375	326s, 271s
cis-$[PtCl_2(PEt_3)(CH_2{=}CHCH_2OH)]$	24.35 (24.45)	4.8 (4.8)	16.15 (16.05)	115	3 450	327s, 277s
cis-$[PtCl_2(PPr^n_3)(CH_2{=}CHCH_2OH)]$	30.0 (29.75)	5.5 (5.6)	14.75 (14.65)	115	3 370	327s, 278s
$[NBu^n_4][PtCl_3(CH_2{=}CHCH_2OH)]$ [c]	38.05 (37.9)	6.95 (7.05)		87—93 [d]	3 410	311m, 325s, 338m
cis-$[PtCl_2(PMe_2Ph)\{CH_2{=}CHCH(Me)OH\}]$ [e]	30.5 (30.3)	4.0 (4.0)	14.8 (14.9)	105	3 480	320s, 284s
cis-$[PtCl_2(PPr^n_3)\{CH_2{=}CHCH(Me)OH\}]$	31.2 (31.35)	5.75 (5.85)	14.4 (14.25)	130	3 425	325s, 297s
cis-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCMe_2OH)]$	31.95 (31.85)	4.25 (4.3)	14.8 (14.45)	110	3 405	321s, 280s

[a] Molecular weight, 477(462). [b] 3 400 cm^{-1} in CH_2Cl_2 solution. [c] N, 2.1 (2.35%). [d] Melting point. [e] Molecular weight, 486(476).

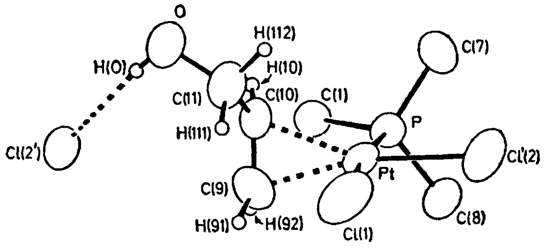


FIGURE 1 The molecular structure and atom numbering of $[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$. The phenyl carbon atoms C(2)—C(6) and their attached hydrogens have been omitted for clarity

N.M.R. Studies.—The ^{31}P-{^1H} spectra of *cis*-$[PtCl_2L(CH_2{=}CHCH_2OH)]$ (L = PMe_3, PEt_3, PPr^n_3, or PMe_2Ph) in $CDCl_3$ showed only a single sharp resonance, flanked by ^{195}Pt satellites, over the temperature range 213—296 K (data in Table 3). We presume that this species has the configuration (1; $R^1 = R^2 = H$) (looking along the olefin–platinum bond) as found in the crystal. The other possible configuration (2) is, for some reason which we do not understand, insufficiently stable to be present in a detectable amount. Similar behaviour was noted for the *cis*-butene complexes *cis*-$[PtCl_2L(C_4H_8)]$ (L = $AsEt_3$ or $AsPh_3$).[8] An alternative explanation, that rotation about the platinum–olefin bond is fast even at 213 K, seems highly unlikely in view of the relatively high barriers to rotation found in propene complexes of the type *cis*-$[PtCl_2L(CH_2{=}CHCH_3)]$.[3,8]

The ^1H n.m.r. spectrum of *cis*-$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ was unchanged over the range 243—296 K. For this complex and the analogous complexes with other phosphines, the olefinic resonances span a much smaller range than in the free ligand and the resonances of the diastereotopic methylene group fall in the middle of this range. These two features combine to give an appreciably 'second-order' appearance to the spectrum. With the aid of ^{31}P decoupling and the addition of D_2O we were able to analyse the spectrum of *cis*-$[PtCl_2(PPr^n_3)(CH_2{=}CHCH_2OH)]$ on the basis of an ABMNX spin system (^1H n.m.r. parameters in Table 4). We have not analysed the ^1H spectra of the equivalent complexes with PMe_3, PEt_3, and PMe_2Ph but note that the hydroxyl proton always showed well resolved coupling to both methylene protons and its chemical shift varied by only 0.14 p.p.m. over the four complexes.

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pt–Cl(1)	2.356(1)	Cl(1)–Pt–Cl(2)	88.9(1)
Pt–Cl(2)	2.329(1)	Cl(1)–Pt–P	173.8(1)
Pt–P	2.255(1)	Cl(2)–Pt–P	86.5(1)
Pt–C(9)	2.141(4)	Cl(2)–Pt–C(9)	166.5(1)
Pt–C(10)	2.161(4)	Cl(2)–Pt–C(10)	156.1(1)
P–C(1)	1.820(4)	Pt–P–C(1)	116.6(1)
P–C(7)	1.806(5)	Pt–P–C(7)	113.3(1)
P–C(8)	1.815(5)	Pt–P–C(8)	110.7(1)
C–C(phenyl)	1.375—1.398(7), average = 1.382		
C(9)–C(10)	1.375(7)	C(9)–C(10)–C(11)	124.4(3)
C(10)–C(11)	1.517(6)	C(10)–C(11)–O	108.6(3)
C(11)–O	1.416(5)		
O ⋯ Cl(2′)	3.202(3)		
C–H	0.81—1.12(5)		
O–H(O)	0.76(5)	O–H(O) ⋯ Cl(2′)	3.202(3)
H(O) ⋯ Cl(2′)	2.49(5)	O–H(O)–Cl(2′)	159(3)

Cl(2′) is related to Cl(2) by the transformation $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$.

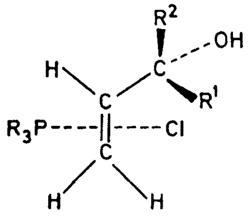
TABLE 3

Phosphorus-31 n.m.r. parameters of *cis*-$[PtCl_2(PR_3)(CH_2{=}CHCR^1R^2OH)]$ [a]

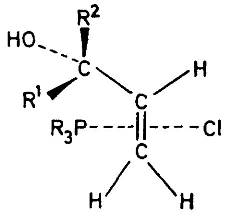
Complex	δ_P [b]	^1J(PtP)/Hz
$[PtCl_2(PMe_3)(CH_2{=}CHCH_2OH)]$	−15.4	3 125
$[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$	−8.4	3 147
$[PtCl_2(PEt_3)(CH_2{=}CHCH_2OH)]$ [c]	−10.2	3 098
$[PtCl_2(PPr^n_3)(CH_2{=}CHCH_2OH)]$	5.8	3 082
$[PtCl_2(PMe_2Ph)\{CH_2{=}CHCH(Me)OH\}]$ [c]	−8.2 −9.0	3 130 3 157
$[PtCl_2(PPr^n_3)\{CH_2{=}CHCH(Me)OH\}]$	5.5 5.9	3 087 3 064
$[PtCl_2(PMe_2Ph)(CH_2{=}CHCMe_2OH)]$	−9.1	3 162

[a] In $CDCl_3$ except for [c] CH_2Cl_2–$CDCl_3$. [b] In p.p.m. to high frequency of H_3PO_4.

The problems of spectral analysis were much less severe for *cis*-[PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHCMe$_2$OH)] enabling a full analysis from ^{1}H and ^{1}H-{^{31}P} studies to be made. Interestingly, only one of the two C–Me groups showed resolved coupling to ^{195}Pt and the hydroxyl proton (Table 4). We also studied the salt [NBu$^n_4$][PtCl$_3$(CH$_2$=CHCH$_2$OH)]. The ^{1}H n.m.r. spectrum of the anion resembles that of free allyl alcohol much more closely than do the complexes with phosphines and again a full analysis was possible.



(1)



(2)

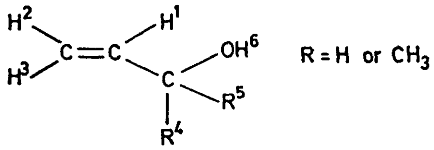
The allyl alcohol ligand in (1) forms a chiral centre. Thus the complex *cis*-[PtCl$_2$(PMe$_2$Ph){CH$_2$=CHCH(Me)-OH}], formed from a *dl* mixture of the alcohol, gave a mixture of two pairs of enantiomers (ratio 2 : 1) (1; R^1 = H, R^2 = Me) and (1; R^1 = Me, R^2 = H) and their mirror images. The analogous complex with PPr$^n_3$ behaved similarly (^{31}P n.m.r. data in Table 2).

We found that solutions of complexes of type *cis*-[PtCl$_2$(PR$_3$)(CH$_2$=CHCR^{1}R^{2}OH)], initially colourless, developed a yellow colouration on long standing at room temperature. The ^{31}P and ^{1}H n.m.r. spectra showed that this was due to partial dissociation to give the bridged complex [Pt$_2$Cl$_4$(PR$_3$)$_2$] and the allylic alcohol. For the complexes of allyl alcohol itself the rate of dissociation was slow, *e.g.* 25% in 4 d for the PMe$_2$Ph derivative, but was substantially faster for *cis*-[PtCl$_2$(PMe$_2$Ph)-(CH$_2$=CHCMe$_2$OH)]. The ^{1}H n.m.r. spectra showed sharp peaks due to free and complexed allylic alcohol even at 333 K, showing that exchange is not rapid. These observations contrast with [NBu$^n_4$][PtCl$_3$(CH$_2$=CHCH$_2$OH)] which showed no tendency to dissociate into [Pt$_2$Cl$_6$]$^{2-}$ and allyl alcohol even after several weeks in solution, but which exchanged rapidly on addition of the free ligand {*cf.*[5] K[PtCl$_3$(C$_2$H$_4$)]}.

As explained previously we hoped to detect the intermediate *trans*-[PtCl$_2$(PR$_3$)(CH$_2$=CHCH$_2$OH)] in the reaction of [Pt$_2$Cl$_4$(PR$_3$)$_2$] with allyl alcohol by ^{31}P n.m.r. studies. Figure 2 shows the ^{31}P-{^{1}H} n.m.r. spectrum of a *ca.* 0.1 mol dm^{-3} solution of [Pt$_2$Cl$_4$(PPr$^n_3$)$_2$] in CH$_2$Cl$_2$–CD$_2$Cl$_2$ following the addition of allyl alcohol (1 mol per platinum atom) at 183 K and the effect of gradually increasing the temperature. At 183 K the bridged complex was largely replaced by a new species having δ_P 6.4 p.p.m. and ^1J(PtP) 3 323 Hz. The absence of any features apart from the 1 : 4 : 1 triplet establishes that the new complex is monomeric and therefore almost certainly *trans*-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)] (3; R^1 = R^2 = H, R = Pr^n). As anticipated the ratio of *trans* to bridged complex decreased on raising the temperature (see Figure 2) and above 263 K the resonances started to broaden due to exchange. This broadening was accompanied by the emergence of some *cis*-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)], identified from its ^{31}P n.m.r. parameters. The proportion of *cis* isomer steadily increased with time and on raising the temperature, and its resonances remained sharp at 296 K (at which temperature little of the *trans* isomer appeared to be present). Incidentally, the ^{195}Pt–^{31}P coupling constants of [Pt$_2$Cl$_4$(PPr$^n_3$)$_2$] and *trans*-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)] increased linearly with temperature at the rates of 0.98 and 0.85 Hz K^{-1} respectively whereas *cis*-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)] showed a much smaller, non-linear variation of ^1J(PtP) with temperature.

TABLE 4

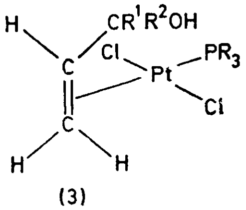
Hydrogen-1 n.m.r. parameters[a]



Complex	Chemical shifts/p.p.m.						Coupling constants[b] (*J*/Hz)											
	H^1	H^2	H^3	H^4	H^5	H^6	H^{1}H^2	H^{1}H^3	H^{1}H^4	H^{1}H^5	H^{4}H^5	H^{4}H^6	H^{5}H^6	PtH^1	PtH^2	PtH^3	PtH^4	PtH^5
cis-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)]	4.75	3.94	4.30	4.33	4.15	3.47	7.5	13.9	6[c]	2[c]	15	6[d]	9[d]	60	68	64	[e]	[e]
cis-[PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHCMe$_2$OH)][f]	3.53	4.48	4.49	1.18	1.57	4.19	3.2[c]	4.9[c]	0	0	0	1.0	0	67.7	61.3	60.8	8.2	*ca.* 0
[NBu$^n_4$][PtCl$_3$(CH$_2$=CHCH$_2$OH)]	5.40	4.38	4.53	4.10		[g]	8.0	13.5	4.0			6.8		68.5	69	61		43

[a] In CDCl$_3$; phosphine resonances omitted. [b] ^{1}H–^{1}H coupling constants not included are *ca.* 0 Hz for all complexes. [c] Same sign for both values. [d] Uncertain as to which value corresponds to which coupling constant. [e] Coupling not identified in spectrum. [f] *J*(PH^1) 1.4, *J*(PH^3) 1, *J*(PH^3) 3 Hz. [g] Obscured by cation resonance.

The low-temperature spectra showed a small amount of an additional species having δ_P = −2.8 p.p.m. and ^1J(PtP) 3 907 Hz (at 183 K). The lack of fine structure to the central peak rules out a bridged complex and in view of the high value of ^1J(PtP) we suggest that it is the oxygen-bonded complex *trans*-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)]. Corroborating this is



(3)

the observation that $[Pt_2Cl_4(PPr^n_3)_2]$, when treated with a large excess of methanol in $CDCl_3$, is substantially converted into a new, monomeric species, presumably *trans*-$[PtCl_2(PPr^n_3)(HOMe)]$, which has δ_P 1.1 p.p.m. and $^1J(PtP)$ 3 927 Hz at 243 K and exchanges with $[Pt_2Cl_4(PPr^n_3)_2]$ at room temperature.

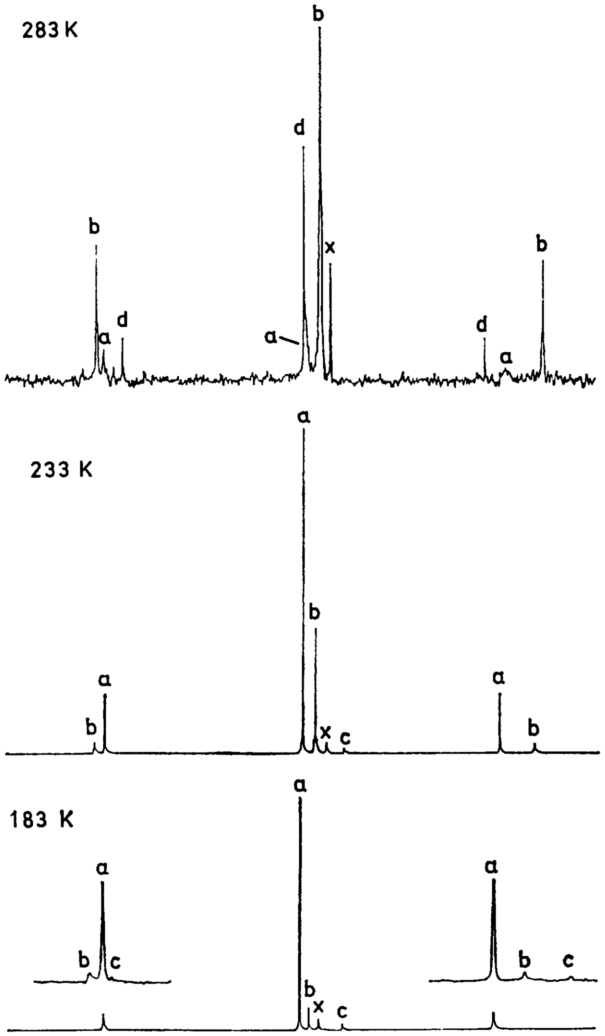
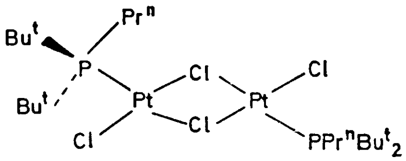


FIGURE 2 Variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Pt_2Cl_4(PPr^n_3)_2]$ in $CH_2Cl_2-CD_2Cl_2$ following the addition of allyl alcohol at 183 K. The labelled resonances are due to following (a) *trans*-$[PtCl_2(PPr^n_3)(CH_2=CHCH_2OH)]$, (b) $[Pt_2Cl_4(PPr^n_3)_2]$, (c) *trans*-$[PtCl_2(PPr^n_3)(CH_2=CHCH_2OH)]$, (d) *cis*-$[PtCl_2(PPr^n_3)(CH_2=CHCH_2OH)]$, and (x) impurity present in $[Pt_2Cl_4(PPr^n_3)_2]$ with no ^{195}Pt satellites. The ordinate of the 283 K spectrum has been recorded on an expanded scale and peak (b) truncated

The addition of allyl alcohol to $[Pt_2Cl_4(PMe_2Ph)_2]$ in $CH_2Cl_2-CD_2Cl_2$ gave qualitatively similar results to those above except that low-temperature studies were less satisfactory owing to the much lower solubility of this complex. At 213 K, *trans*-$[PtCl_2(PMe_2Ph)(CH_2=CHCH_2OH)]$ had δ_P -10.1 p.p.m. and $^1J(PtP)$ 3 441 Hz with a temperature coefficient of 0.93 Hz K^{-1}.

We also studied the action of allyl alcohol on the bromo-bridged complex, $[Pt_2Br_4(PMe_2Ph)_2]$, as a *ca.* 0.025 mol dm^{-3} solution in $CH_2Cl_2-CD_2Cl_2$. At 183 K *ca.* 10% of the bridged species was converted into *trans*-$[PtBr_2(PMe_2Ph)(CH_2=CHCH_2OH)]$ [$\delta_P = -12.7$ p.p.m., $^1J(PtP)$ 3 284 Hz]. The proportion of *trans* complex decreased with increasing temperature and was undetectable by 273 K. Interestingly, *cis*-$[PtBr_2(PMe_2Ph)(CH_2=CHCH_2OH)]$ began to form even at 213 K and was the major component at 273 K. With the corresponding chloro-complex appreciable amounts of *cis*-$[PtCl_2(PMe_2Ph)(CH_2=CHCH_2OH)]$ were not detected below 273 K. This is probably a consequence of the smaller *trans* effect of chloride relative to bromide. The identity of *cis*-$[PtBr_2(PMe_2Ph)(CH_2=CHCH_2OH)]$ was established from the n.m.r. parameters [$\delta_P = -7.4$ p.p.m. and $^1J(PtP)$ 3 049 Hz at 273 K] since we were unable to isolate this complex from the solution.

We also investigated the interaction of allyl alcohol with $[Pt_2Cl_4(PPr^nBu^t_2)_2]$. As expected the very bulky phosphine prevented isolation of *cis*-$[PtCl_2(PPr^nBu^t_2)(CH_2=CHCH_2OH)]$ although ^{31}P n.m.r. spectra showed formation of the *trans* isomer. A feature of $PPr^nBu^t_2$ as a ligand is that there is a high energy barrier to rotation of a t-butyl group past a chloride ligand in the *cis* position and at low temperatures rotational isomers can be detected by n.m.r. spectroscopy.[10] Thus in $CDCl_3$ the $^{31}P-\{^1H\}$ spectrum of $[Pt_2Cl_4(PPr^nBu^t_2)_2]$ showed a



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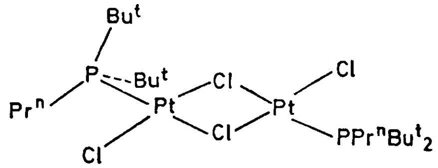
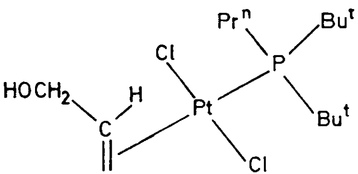
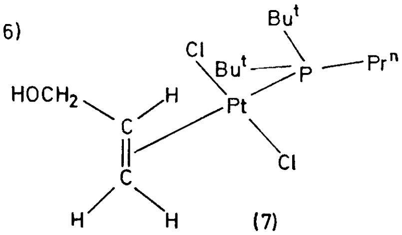


(5)



(6)



(7)

single phosphorus environment at 296 K but four at 243 K. The two t-butyl groups can be *gauche* with respect to the terminal chlorine as in (4) or the bridging chlorine as in (5). The other phosphine would behave similarly giving a total of three rotational isomers. The conformer containing chemically inequivalent phosphines had δ_P 33.5 and 33.7 p.p.m. with ^1J(PtP) 3 904 and 3 922 Hz respectively [^4J(PP) <1 Hz], while the two conformers containing equivalent phosphines had δ_P 34.3 and 34.9 p.p.m. with ^1J(PtP) 3 895 and 3 911 Hz respectively, and ^3J(PtP) *ca.* 23 Hz in all cases. On adding allyl alcohol to this solution (1 mol per platinum atom) at 213 K, equal amounts of two new species were produced [δ_P 35.4, ^1J(PtP) 3 450 Hz; and δ_P 34.9, ^1J(PtP) 3 447 Hz] which we suggest are due to the conformers (6) and (7) [or (7) and (6)]. On raising the temperature the peaks due to these species broadened and coalesced (at 243 K) at which temperature the peaks due to the various rotamers of [$Pt_2Cl_4(PPr^nBu^t_2)_2$] were still sharp. The coalescence could be due to rotation of either the allyl alcohol or the $PPr^nBu^t_2$ ligand (or both) although the former explanation seems more compatible with the behaviour of the bridged complex.

On adding allyl alcohol (1 mol per platinum atom) to a solution of *cis*-[$PtCl_2(PMe_2Ph)\{CH_2$=CHCH(Me)OH$\}$] in CH_2Cl_2–$CDCl_3$ at 213 K, *cis*-[$PtCl_2(PMe_2Ph)(CH_2$=$CHCH_2OH)$] was produced in slightly greater amount than the sum of the two isomers of *cis*-[$PtCl_2(PMe_2Ph)$-$\{CH_2$=CHCH(Me)OH$\}$]. Thus exchange occurs between these two complexes even at low temperatures but this is not rapid since sharp peaks due to both species were observed in the ^{31}P-$\{^1H\}$ and ^1H-$\{^{31}P\}$ n.m.r. spectra at 296 K. Similar behaviour was noted when allyl alcohol was added to *trans*-[$PtCl_2(PPr^n_3)\{CH_2$=CHCH(Me)OH$\}$] {prepared *in situ* from [$Pt_2Cl_4(PPr^n_3)_2$] and but-1-en-3-ol at 213 K} except that broadening of the ^{31}P resonances occurred above 263 K owing to exchange with [Pt_2Cl_4-$(PPr^n_3)_2$].

EXPERIMENTAL

The ^1H, ^1H-$\{^{31}P\}$, and ^{31}P-$\{^1H\}$ n.m.r. spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock. Except where otherwise stated, measurements were made at ambient magnet temperature (*ca.* 296 K). Coupling constants from ^1H spectra are accurate to ± 0.2 Hz and values of ^1J(PtP) to ± 2 Hz or better.

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Analyses, decomposition points (melting point in one case), and i.r. data are in Table 1.

cis-*Dichloro(dimethylphenylphosphine)(prop-2-en-1-ol)-platinum*(II).—A mixture of di-μ-chloro-dichlorobis(dimethylphenylphosphine)diplatinum(II) (0.135 g) and prop-2-en-1-ol (0.4 cm^3) was heated to *ca.* 60 °C for a few minutes until the solid had dissolved. The resulting yellow solution was put aside for 16 h at 20 °C when it had become colourless. The solution was then cooled to *ca.* −30 °C to give the required product (0.145 g, 71%) as white prisms. It could be recrystallized from dichloromethane–diethyl ether containing a drop of prop-2-en-1-ol. cis-*Dichloro(prop-2-en-1-ol)(trimethylphosphine)platinum*(II) (70%) and cis-*dichloro(prop-2-en-1-ol)(tri-n-propylphosphine)platinum*(II) (62%) were prepared similarly.

cis-*(But-1-en-3-ol)dichloro(tri-n-propylphosphine)platinum*(II).—The bridged compound (0.21 g) was dissolved in a mixture of dichloromethane (2 cm^3) and but-1-en-3-ol (1 cm^3). The mixture was put aside at room temperature for 16 h during which the required product separated. It formed white prisms from dichloromethane–light petroleum (b.p. 60—80 °C). Yield 0.157 g (64%). cis-*(But-1-en-3-ol)-dichloro(dimethylphenylphosphine)platinum*(II) was made similarly. Yield 77%.

Tetra-n-butylammonium Trichloro(prop-2-en-1-ol)platinate(II).—Tetra-n-butylammonium di-μ-chloro-tetrachlorodiplatinate(II) (0.113 g) and prop-2-en-1-ol (1 cm^3) were mixed and warmed until the solid dissolved. The solution was then cooled to −30 °C when it gave the required product as yellow microcrystals (0.091 g, 73%).

Crystal Data.—$C_{11}H_{17}Cl_2OPPt$, $M = 462.2$, Monoclinic, $a = 12.540(3)$, $b = 10.668(7)$, $c = 10.929(2)$ Å, $\beta = 97.02(2)°$, $U = 1\,451(1)$ Å^3, $D_m = 2.10$, $Z = 4$, $D_c = 2.116$ g cm^{-3}, $F(000) = 872$, space group $P2_1/n$, Mo-K_α radiation, graphite monochromatized, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 102.3 cm^{-1}.

Structure Determination.—All measurements were made on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections with $35 < 2\theta < 40°$. Intensities of all independent reflections with $2\theta < 45°$ were determined in the ω—2θ scan mode using scan speeds from 0.49° min^{-1} for the weaker reflections to 29.3° min^{-1} for the most intense reflections. Lorentz, polarization, and absorption (*X*-RAY program, $A^* = 2.61$—5.11) corrections were calculated, and the 1 720 reflections having $I > 3\sigma(I)$ [with $\sigma(I)$ calculated from counting statistics] were used in the subsequent structure analysis; another 195 reflections below this threshold were excluded as 'unobserved.' Solution of the structure from Patterson and difference syntheses was followed by isotropic refinement of non-hydrogen atoms to $R = 0.127$, and introduction of anisotropic temperature factors for Pt, P, and Cl then reduced R to 0.054. At this stage the absorption corrections were introduced and further refinement lowered R to 0.029. The carbon and oxygen atoms were then allowed anisotropic vibrations with a consequent reduction of R to 0.026. A difference synthesis now revealed the following features >0.3 e Å^{-3}: (*a*) all hydrogen atoms, with peak heights of 0.30—0.65 e Å^{-3}; (*b*) peaks close to those atoms bearing hydrogens, having heights up to 0.6 e Å^{-3}, and reflecting the previous errors in these heavy-atom positions due to their attempts to compensate for the missing hydrogens; (*c*) peaks of 0.89, 0.85, and 0.82 e Å^{-3} at the midpoints of the Pt–P and Pt–Cl bonds; and (*d*) peaks of 0.31—0.35 e Å^{-3} close to the Cl atoms. Inclusion of the hydrogen atoms as fixed contributions with further refinement of the non-hydrogen atoms gave $R = 0.020$, and finally refinement of all atoms (with isotropic temperature factors for H) converged smoothly to $R = 0.019$. In the final stages when the hydrogen atoms were being refined, block-diagonal refinement with shift factors of 0.5 was used. The hydrogen atoms have positional standard deviations of 0.04—0.05 Å (by inversion of the block-diagonal least-squares matrix) while their temperature factors of 0.05—0.09 Å^3 are physically reasonable when compared with those of the atoms to which they are attached. The refinement employed weights $w = 1/\sigma^2(F)$ with $\sigma(F)$ derived from counting statistics, and the atomic scattering factors were calculated using the analytical approximations and coefficients given in ref. 11, those for hydrogen being the ' bonded-atom ' values.[12] The atomic co-ordinates and their estimated standard deviations are listed in Table 5, and the anisotropic temperature factors with a listing of observed and calculated structure factors are in Supplementary Publication No. SUP 22630 (14 pp.).*

TABLE 5

Atomic co-ordinates and estimated standard deviations

Atom	x	y	z
Pt(1)	0.158 43(1)	0.227 91(2)	0.231 89(1)
Cl(1)	0.044 91(14)	0.225 79(17)	0.388 50(14)
Cl(2)	0.300 62(11)	0.168 60(15)	0.377 63(12)
P(1)	0.280 39(9)	0.239 79(11)	0.096 86(10)
C(1)	0.229 4(4)	0.280 6(4)	−0.061 2(4)
C(2)	0.213 3(4)	0.403 9(5)	−0.095 8(4)
C(3)	0.172 8(4)	0.433 2(5)	−0.217 2(5)
C(4)	0.148 9(4)	0.341 4(6)	−0.303 0(4)
C(5)	0.164 8(4)	0.218 3(6)	−0.270 0(4)
C(6)	0.203 8(4)	0.187 7(4)	−0.148 4(4)
C(7)	0.354 4(4)	0.096 0(5)	0.085 0(5)
C(8)	0.380 2(4)	0.359 1(5)	0.144 0(5)
C(9)	0.034 6(4)	0.324 9(5)	0.117 0(5)
C(10)	0.027 3(4)	0.199 8(5)	0.086 9(4)
C(11)	−0.058 3(4)	0.111 8(5)	0.123 9(5)
O(1)	−0.126 0(3)	0.075 7(3)	0.016 5(3)
H(2)	0.238(3)	0.466(4)	−0.036(3)
H(3)	0.162(3)	0.517(5)	−0.241(4)
H(4)	0.118(4)	0.365(5)	−0.390(4)
H(5)	0.154(4)	0.139(5)	−0.329(4)
H(6)	0.211(3)	0.100(4)	−0.128(4)
H(71)	0.302(4)	0.024(5)	0.060(4)
H(72)	0.389(4)	0.082(4)	0.152(4)
H(73)	0.405(3)	0.111(5)	0.027(4)
H(81)	0.412(4)	0.330(5)	0.207(4)
H(82)	0.435(4)	0.347(5)	0.071(4)
H(83)	0.350(3)	0.429(4)	0.162(4)
H(91)	−0.017(3)	0.363(5)	0.172(4)
H(92)	0.067(3)	0.385(5)	0.069(4)
H(10)	0.053(3)	0.168(4)	0.015(3)
H(111)	−0.097(3)	0.165(4)	0.193(4)
H(112)	−0.026(3)	0.030(4)	0.161(3)
H(O)	−0.158(3)	0.133(5)	−0.006(4)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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