Interaction of Allylic Alcohols with Halogeno-bridged Platinum(II) Complexes [Pt₂X₄(PR₃)₂] (X = Cl or Br) and [NBuⁿ₄]₂[Pt₂Cl₆]: Crystal Structure of [PtCl₂(PMe₂Ph)(CH₂=CHCH₂OH)] †‡

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A series of complexes of type cis-[PtCl₂(PR₃)Q] (PR₃ = PMe₃, PEt₃, PPrⁿ₃, or PMe₂Ph; 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-[PtCl₂(PMe₂Ph)-(CH₂=CHCH₂OH)] 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, $\beta = 97.02(2)°$, and $Z = 4$. The complexes cis-[PtCl₂(PR₃)Q] have been studied by variable-temperature ¹H and ³¹P 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 [Pt₂Cl₄-(PR₃)₂] and the free allyl alcohol occurs. The complex cis-[PtCl₂(PMe₂Ph)(CH₂=CHCH₂OH)] does not exchange rapidly with free allyl alcohol and separate resonances due to free and complexed allyl alcohol could be observed: in contrast [NBuⁿ₄][PtCl₃(CH₂=CHCH₂OH)] 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 [Pt₂Cl₄(PR₃)₂] {and also [Pt₂Br₄-(PMe₂Ph)₂]} and allylic alcohols show that at low temperatures the bridged species is rapidly and reversibly converted into trans-[PtCl₂(PR₃)(CH₂=CHCR¹R²OH)] together with some of the O-bonded species, trans-[PtCl₂(PR₃)(CH₂=CHCR¹R²OH)]. 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-[PtCl₂(PR₃)(CH₂=CHCR¹R²OH)] is also gradually formed above ca. 260 K. A [Pt₂Br₄(PMe₂Ph)₂]–CH₂=CHCH₂OH system also shows the presence of trans-[PtBr₂(PMe₂Ph)(CH₂=CHCH₂OH)] and in this case the cis isomer forms to a detectable extent even at 213 K. The bridged complex [Pt₂Cl₄(PPrⁿBuᵗ₂)₂] containing the bulky phosphine shows the presence of rotamers at 243 K and with allyl alcohol two rotamers trans-[PtCl₂(PPrⁿBuᵗ₂)(CH₂=CHCH₂OH)] form at 213 K. The ¹H and ³¹P 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 [Pt₂Cl₄L₂], L = tertiary phosphine. There were several reasons why we began this study. It was shown in 1964 that [Pt₂Cl₄(PEt₃)₂] reacted with allyl alcohol over a period of a few hours at room temperature to give the olefin complex cis-[PtCl₂(PEt₃)(CH₂=CHCH₂OH)].[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-[PtCl₂(PR₃)(C₃H₅OH)] 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 [Pt₂Cl₄(PR₃)₂] rapidly in the trans position but that trans-[PtCl₂(PR₃)Q] (Q = CO or olefin) would be unstable relative to [Pt₂Cl₄(PR₃)₂]. In fact a transient species, presumably trans-[PtCl₂(PR₃)-(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-[PtCl₂-(PR₃)(olefin)], relative to a chloro-bridged complex [Pt₂Cl₄(PR₃)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-[PtCl₂(PR₃)(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-[PtCl₂(PR₃)Q] with PR₃ = PMe₃, PEt₃, PPrⁿ₃, or PMe₂Ph 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-[PtCl₂(PMe₂Ph)(C₃H₅OH)] 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 CH₂OH 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

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

TABLE 1

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

	Analyses			Decomp. point	Nujol mull	
Complex	C	H	Cl	(θ_c/°C)	ν(O–H)	ν(Pt–Cl)
cis-[PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHCH$_2$OH)] [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$_2$OH)]	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$_2$OH)]	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$_2$OH)]	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$_2$OH)] [c]	38.05 (37.9)	6.95 (7.05)		87—93 [d]	3 410	311m, 325s, 338m
cis-[PtCl$_2$(PMe$_2$Ph){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$_2$Ph)(CH$_2$=CHCMe$_2$OH)]	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$_2$Cl$_2$ solution. [c] N, 2.1 (2.35%). [d] Melting point. [e] Molecular weight, 486(476).

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$_2$H$_4$)]. 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)°.

N.M.R. Studies.—The ^{31}P-{^{1}H} spectra of cis-[PtCl$_2$L-(CH$_2$=CHCH$_2$OH)] (L = PMe$_3$, PEt$_3$, PPr$^n_3$, or PMe$_2$Ph)
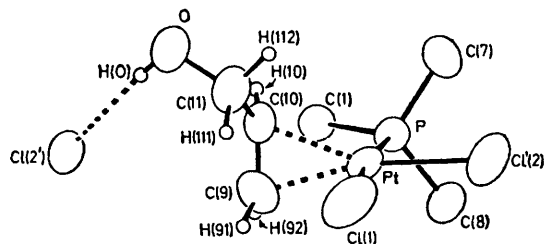

FIGURE 1 The molecular structure and atom numbering of [PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHCH$_2$OH)]. The phenyl carbon atoms C(2)—C(6) and their attached hydrogens have been omitted for clarity

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$_2$L(C$_4$H$_8$)] (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$_2$L(CH$_2$=CHCH$_3$)].[3,8]

The ^{1}H n.m.r. spectrum of cis-[PtCl$_2$(PMe$_2$Ph)-(CH$_2$=CHCH$_2$OH)] was unchanged over the range 243—296 K. For this complex and the analogous complexes

to give an appreciably ' second-order ' appearance to the spectrum. With the aid of ^{31}P decoupling and the

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 $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$.

addition of D$_2$O we were able to analyse the spectrum of cis-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)] on the basis of an ABMNX spin system (^{1}H n.m.r. parameters in Table 4). We have not analysed the ^{1}H spectra of the equivalent
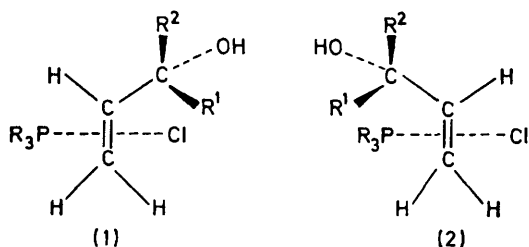
TABLE 3

Phosphorus-31 n.m.r. parameters of cis-[PtCl$_2$(PR$_3$)(CH$_2$=CHCR^{1}R^{2}OH)] [a]

Complex	δ_P [b]	^1J(PtP)/Hz
[PtCl$_2$(PMe$_3$)(CH$_2$=CHCH$_2$OH)]	−15.4	3 125
[PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHCH$_2$OH)]	−8.4	3 147
[PtCl$_2$(PEt$_3$)(CH$_2$=CHCH$_2$OH)] [c]	−10.2	3 098
[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)]	5.8	3 082
[PtCl$_2$(PMe$_2$Ph){CH$_2$=CHCH(Me)OH}] [c]	$\begin{cases} -8.2 \\ -9.0 \end{cases}$	$\begin{matrix} 3\ 130 \\ 3\ 157 \end{matrix}$
[PtCl$_2$(PPr$^n_3$){CH$_2$=CHCH(Me)OH}]	$\begin{cases} 5.5 \\ 5.9 \end{cases}$	$\begin{matrix} 3\ 087 \\ 3\ 064 \end{matrix}$
[PtCl$_2$(PMe$_2$Ph)(CH$_2$=CHCMe$_2$OH)]	−9.1	3 162

[a] In CDCl$_3$ except for [c] CH$_2$Cl$_2$–CDCl$_3$. [b] In p.p.m. to high frequency of H$_3$PO$_4$.

complexes with PMe$_3$, PEt$_3$, and PMe$_2$Ph 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.

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
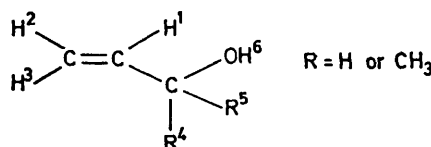
(Table 4). We also studied the salt [NBu$^n_4$][PtCl$_3$-(CH$_2$=CHCH$_2$OH)]. The ^{1}H n.m.r. spectrum of the anion resembles that of free allyl alcohol much more closely than do the complexes with phosphines and again a full analysis was possible.

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;

mediate 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$^n_3$)-

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^1H^2	H^1H^3	H^1H^4	H^2H^3	H^4H^5	H^4H^6	H^5H^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^4) 3 Hz. g Obscured by cation resonance.

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 inter-

(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.

The low-temperature spectra showed a small amount

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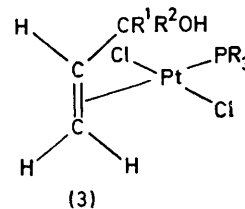
of an additional species having δ_P = −2.8 p.p.m. and ^1J(PtP) 3 907 Hz (at 183 K). The lack of fine structure to the central peak rules out a bridged complex and in view of the high value of ^1J(PtP) we suggest that it is the oxygen-bonded complex trans-[PtCl$_2$(PPr$^n_3$)(CH$_2$=CHCH$_2$OH)]. Corroborating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

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.
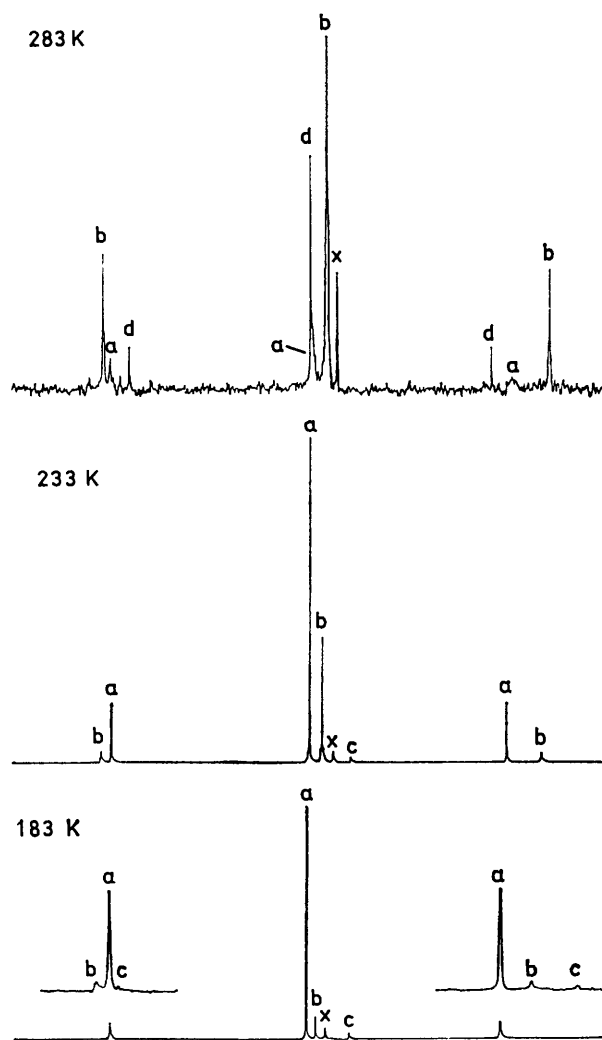

FIGURE 2 Variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Pt_2Cl_4(PPr^n_3)_2]$ in CH_2Cl_2–CD_2Cl_2 following the addition of allyl alcohol at 183 K. The labelled resonances are due to following (a) trans-$[PtCl_2(PPr^n_3)(CH_2=CHCH_2OH)]$, (b) $[Pt_2Cl_4-(PPr^n_3)_2]$, (c) trans-$[PtCl_2(PPr^n_3)(CH_2=CHCH_2OH)]$, (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

and ^1J(PtP) 3 927 Hz at 243 K and exchanges with $[Pt_2Cl_4(PPr^n_3)_2]$ at room temperature.

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-$[PtBr_2-(PMe_2Ph)(CH_2=CHCH_2OH)]$ [δ_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 [δ_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
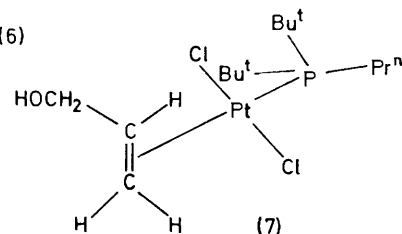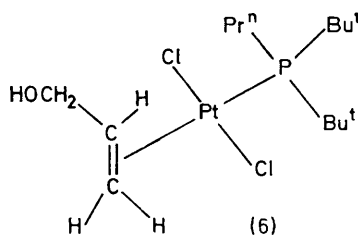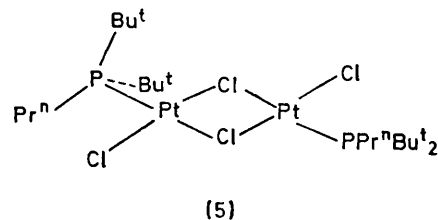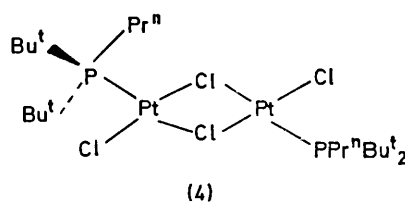
a ligand is that there is a high energy barrier to rotation of a t-butyl group past a chloride ligand in the cis position and at low temperatures rotational isomers can be detected by n.m.r. spectroscopy.[10] Thus in $CDCl_3$ the $^{31}P-\{^1H\}$ spectrum of $[Pt_2Cl_4(PPr^nBu^t_2)_2]$ showed a

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$_2$Cl$_4$(PPr^{n}Bu$^t_2$)$_2$] were still sharp. The coalescence could be due to rotation of either the allyl alcohol or the PPr^{n}Bu$^t_2$ 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$_2$Ph){CH$_2$=CHCH(Me)OH}] in CH$_2$Cl$_2$–CDCl$_3$ at 213 K, *cis*-[PtCl$_2$(PMe$_2$Ph)(CH$_2$= CHCH$_2$OH)] was produced in slightly greater amount than the sum of the two isomers of *cis*-[PtCl$_2$(PMe$_2$Ph)-{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-{^{1}H} and ^{1}H-{^{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$_2$Cl$_4$(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$_2$Cl$_4$-(PPr$^n_3$)$_2$].

EXPERIMENTAL

The ^{1}H, ^{1}H-{^{31}P}, and ^{31}P-{^{1}H} 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 ^{1}H 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 cm³) 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 cm³) and but-1-en-3-ol (1 cm³). 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 cm³) 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$_2$OPPt, M = 462.2, Monoclinic, a = 12.540(3), b = 10.668(7), c = 10.929(2) Å, β = 97.02(2)°, U = 1 451(1) Å³, 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, λ = 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 < 2θ < 40°. Intensities of all independent reflections with 2θ < 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 Å³ are physically reasonable when compared with those of the atoms to which they are attached. The refinement em-

ployed 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

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)

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 aniso-tropic temperature factors with a listing of observed and calculated structure factors are in Supplementary Public-ation No. SUP 22630 (14 pp.).*

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

REFERENCES

[1] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 3269.
[2] J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *J. Chem. Soc.*, 1963, 5170.
[3] J. Ashley-Smith, I. Donek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776.
[4] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.
[5] R. Cramer, *Inorg. Chem.*, 1965, **4**, 445.
[6] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.
[7] C. E. Holloway, G. Halley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (A), 1969, 53.
[8] J. Ashley-Smith, I. Donek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 128.
[9] R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews, and R. Bau, *Inorg. Chem.*, 1975, **14**, 2653.
[10] B. E. Mann, C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 1103.
[11] ' International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.