

Transition Metal–Carbon Bonds. Part 48.¹ Allene Complexes from Halogeno-bridged Platinum(II) Complexes: Crystal Structures of *cis*-[PtCl₂(PPrⁿ₃)(C₃H₄)] and *cis*-[PtCl₂(PMe₂Ph)(C₃H₄)] †

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A ³¹P n.m.r. study of the system [Pt₂Cl₄(PMe₂Ph)₂]-allene shows that at low temperatures (e.g. 213 K) *trans*-[PtCl₂(PMe₂Ph)(C₃H₄)] forms rapidly and reversibly. At 20 °C [Pt₂Cl₄(PR₃)₂] (PR₃ = PPrⁿ₃, PMe₂Et, or PMe₂Ph) react with allene to give colourless complexes *cis*-[PtCl₂(PR₃)(C₃H₄)], the crystal structures of the PPrⁿ₃ and PMe₂Ph complexes were determined by X-ray diffraction. Crystal data are for [PtCl₂(PPrⁿ₃)(C₃H₄)] *a* = 15.461(2), *b* = 11.437(2), *c* = 9.606(2) Å, space group *Pna*2₁, with *Z* = 4 and for [PtCl₂(PMe₂Ph)(C₃H₄)] *a* = 8.398(2), *b* = 10.209(3), *c* = 15.677(4) Å, space group *P2*₁2₁2₁, and *Z* = 4. Final *R* factors are *R* = 0.026 and 0.029 respectively. These *cis* complexes dissociate very slowly in solution, in contrast with *cis*-[PtCl₂(PPh₃)(C₃H₄)], which was previously reported to be unstable. Treatment of *cis*-[PtCl₂(PMe₂Ph)(C₃H₄)] with [Pt₂Cl₄(PMe₂Ph)₂] gives what is probably the μ -allene complex *cis,cis*-[(PhMe₂P)Cl₂Pt(C₃H₄)PtCl₂(PMe₂Ph)] which was too insoluble to characterize fully. Treatment of [NBuⁿ₄]₂[Pt₂X₆] (X = Cl, Br, or I) with an excess of allene gives the salts [NBuⁿ₄][PtX₃(C₃H₄)]. Treatment of [NBuⁿ₄][PtX₃(C₃H₄)] with [NBuⁿ₄]₂[Pt₂X₆] (X = Cl or Br) gave the μ -allene complexes [NBuⁿ₄]₂[X₃Pt(C₃H₄)PtX₃]. The NPrⁿ₄ salt was also made. Proton, ¹³C, and ³¹P n.m.r. data and i.r. data are given and discussed.

In two recent papers^{2,3} from these laboratories we described investigations into the action of various functionalized olefins (allyl alcohol, allyl acetate, vinyl acetate *etc.*) on halogeno-bridged platinum(II) complexes of type [Pt₂Cl₄(PR₃)₂]. We now describe a study of the action of allene on both [Pt₂Cl₄(PR₃)₂] and the ions [Pt₂X₆]²⁻ (X = Cl, Br, or I).

Allene complexes of platinum(II) are rare.^{4,5} Chloro-bridged complexes of the type [Pt₂Cl₄(alln)₂] (alln = an allene) have been prepared by treating ethyleneplatinum(II)

complex of 1,1-dimethylallene is more stable and was studied in more detail, including its reactions with amines.

RESULTS AND DISCUSSION

We have shown previously that complexes of the type [Pt₂Cl₄(PR₃)₂] interact with olefins at low temperatures to give very labile complexes of type *trans*-[PtCl₂(PR₃)(olefin)] in equilibrium with the bridged complexes.^{2,3} In a similar manner we have now studied the interaction of [Pt₂Cl₄(PMe₂Ph)₂] with allene in CH₂Cl₂-CD₂Cl₂ by

TABLE I
Analytical and i.r. (cm⁻¹) data

Complex	Analyses (%) ^a				M.p. (θ/°C)	ν(Pt–Cl)	ν ⁻ (C=C) _{unco-ord.}
	C	H	N	Cl			
<i>cis</i> -[PtCl ₂ (PPr ⁿ ₃)(CH ₂ =C=CH ₂)] ^b	31.0 (30.9)	5.3 (5.4)		15.0 (15.2)	123–128 ^c	275, 328	1 791
<i>cis</i> -[PtCl ₂ (PMe ₂ Ph)(CH ₂ =C=CH ₂)]	29.95 (29.75)	3.4 (3.4)		16.05 (15.95)	140 ^d	293, 323	1 800
<i>cis</i> -[PtCl ₂ (PMe ₂ Et)(CH ₂ =C=CH ₂)]	21.5 (21.2)	3.8 (3.8)		17.6 (17.9)	112–120 ^c	297, 338	1 795
[NBu ⁿ ₄][PtCl ₃ (CH ₂ =C=CH ₂)] ^e	39.1 (39.1)	7.1 (6.9)	2.55 (2.4)		65–69	304, 311, 330	1 795
[NBu ⁿ ₄][PtBr ₃ (CH ₂ =C=CH ₂)]	31.8 (31.75)	5.6 (5.5)	1.9 (1.95)		88–92		1 800
[NBu ⁿ ₄][PtI ₃ (CH ₂ =C=CH ₂)]	26.45 (26.6)	4.45 (4.7)	1.6 (1.65)		105 ^c		1 785
<i>cis,cis</i> -[Pt ₂ Cl ₄ (PMe ₂ Ph) ₂ (CH ₂ =C=CH ₂)]	26.9 (26.9)	3.05 (3.1)		17.0 (16.7)	203–205 ^c	292, 320	
<i>cis,cis</i> -[Pt ₂ Cl ₄ (PMe ₂ Et) ₂ (CH ₂ =C=CH ₂)]	17.55 (17.55)	3.55 (3.5)		18.6 (18.85)	135 ^d	294, 330	
[NBu ⁿ ₄] ₂ [Pt ₂ Cl ₆ (CH ₂ =C=CH ₂)] ^f	37.25 (37.25)	6.8 (6.8)	2.45 (2.5)		42–50	286, 301, 333	
[NBu ⁿ ₄] ₂ [Pt ₂ Br ₆ (CH ₂ =C=CH ₂)]	29.8 (30.15)	5.4 (5.5)	2.0 (2.0)		88–95		
[NPr ⁿ ₄] ₂ [Pt ₂ Cl ₆ (CH ₂ =C=CH ₂)]	31.5 (31.9)	5.85 (5.95)	2.6 (2.8)		170 ^d	292, 315, 340	

^a Calculated values are given in parentheses. ^b Molecular weight 477 (466). ^c Melts with decomposition. ^d Decomposes without melting. ^e Conductivity in acetone = 81.0 Ω⁻¹ cm² mol⁻¹ (20 °C). ^f Conductivity in acetone = 115 Ω⁻¹ cm² mol⁻¹ (20 °C).

chloride with the allene,⁶ although an allene analogue of Zeise's anion *viz.* [PtCl₃(C₃H₄)]⁻ has not hitherto been described nor have allene-bridged complexes of platinum(II) *i.e.* with the two double bonds of allene bonded to different platinum atoms. Moreover it has been reported that *cis*-[PtCl₂(PPh₃)(C₃H₄)] is rather unstable, decomposing readily in solution.⁷ This allene complex was not fully characterized although the corresponding

† *cis*-Allenedichloro(triisopropylphosphine)platinum(II) and *cis*-allenedichloro(dimethylphenylphosphine)platinum(II).

³¹P n.m.r. spectroscopy and find a similar behaviour. At 213 K the n.m.r. parameters of *trans*-[PtCl₂(PMe₂Ph)(CH₂=C=CH₂)] were δ (P) –8.5 p.p.m., ¹J(PtP) 3 332 Hz. For comparison, the values of ¹J(PtP) for the analogous complexes with allyl alcohol and vinyl acetate under these conditions are 3 441 and 3 544 Hz respectively.

At room temperature in dichloromethane solution we find that the chloro-bridged complexes [Pt₂Cl₄(PR₃)₂] (PR₃ = PPrⁿ₃, PMe₂Et, or PMe₂Ph) react with an excess of allene to give colourless crystalline complexes of the

type *cis*-[PtCl₂(PR₃)(C₃H₄)] which have been fully characterized (see Tables 1—4). They are thus much more stable than *cis*-[PtCl₂(PPh₃)(C₃H₄)].⁷ The crystal structures of the PPr₃ and PMe₂Ph derivatives were determined by X-ray diffraction and are shown in Figures 1 and 2 respectively.

Selected bond lengths and angles with their estimated

(L = PPr₃ or PMe₂Et) showed that dissociation in solution is slow, only a small proportion of free allene being observed after several days (studies on the PMe₂Ph complex were hampered by its low solubility). The allene part of the ¹H n.m.r. spectrum of *cis*-[PtCl₂(PPr₃)(CH₂=C=CH₂)] is shown in Figure 3. The observation of four proton resonances indicates that the

TABLE 2
Hydrogen-1 n.m.r. parameters^a

	CH ₂ (co-ord.)		CH ₂ (unco-ord.)		Coupling constants (J/Hz)											
	δ(H ¹)	δ(H ²)	δ(H ³)	δ(H ⁴)	H ¹ H ²	H ¹ H ³	H ¹ H ⁴	H ² H ³	H ² H ⁴	H ³ H ⁴	PtH ¹	PtH ²	PtH ³	PtH ⁴	PH ¹	PH ²
<i>cis</i> -[PtCl ₂ (PPr ₃)(CH ₂ =C=CH ₂)] ^b	3.14	4.10	5.41	5.71	-6.1	-3.9	-3.9	-3.9	-3.9	-7.7	-58.7	-72.2	+66.8	+88.6	2.8	0.5
<i>cis</i> -[PtCl ₂ (PMe ₂ Et)- (CH ₂ =C=CH ₂)] ^b	3.44	4.15	5.47	5.77	6.2	3.9	3.9	3.9	3.9	7.8	58.5	71.2	69.6	93.0	2.6	0.7
[NBu ₄][PtCl ₂ (CH ₂ =C=CH ₂)]	3.85	5.22	5.30	<i>c</i>	<i>c</i>	-3.8	<i>c</i>	-3.8	<i>c</i>	7.0	-66.3	<i>c</i>	+51.4	+65.9	<i>c</i>	<i>c</i>
[NBu ₄][PtBr ₂ (CH ₂ =C=CH ₂)]	4.02	5.04	5.04	<i>c</i>	<i>c</i>	3.8	<i>c</i>	7.0	<i>c</i>	7.0	-66.8	<i>c</i>	+56	+63	<i>c</i>	<i>c</i>
[NBu ₄][PtI ₂ (CH ₂ =C=CH ₂)]	4.34	4.79	4.57	<i>c</i>	<i>c</i>	3.7	<i>c</i>	3.7	<i>c</i>	7.0	-67.6	<i>c</i>	+59	+70	<i>c</i>	<i>c</i>
[NBu ₄] ₂ [Pt ₂ Cl ₆ (CH ₂ =C=CH ₂)]	3.70	5.00			J(H ¹ H ²) + J'(H ¹ H ²) = 3.1					{ 74 54	{ 70 36					
[NPr ₄] ₂ [Pt ₂ Cl ₆ (CH ₂ =C=CH ₂)]	3.75	5.02			J(H ¹ H ²) + J'(H ¹ H ²) = 3.3					{ 73 55	{ 70 36					
[NBu ₄] ₂ [Pt ₂ Br ₆ (CH ₂ =C=CH ₂)]	<i>d</i>	5.36			J(H ¹ H ²) + J'(H ¹ H ²) = 2.7					{ <i>d</i> <i>d</i>	{ 71 37					

^a For the allene ligand only; in CDCl₃. The absence of + or - for some coupling constants indicates that the sign was not determined. ^b J(PH³) ~ J(PH⁴) ~ 0. ^c Not determinable. ^d Obscured by cation resonance.

standard deviations are listed in Table 5. Corresponding dimensions in the two complexes are in close agreement. The 0.018 Å difference in the Pt-P bond lengths and the 0.019 Å difference in the Pt-Cl bond lengths *trans* to

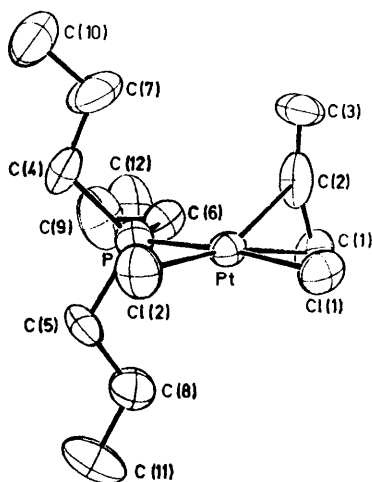


FIGURE 1 The molecular structure and atom numbering of *cis*-[PtCl₂(PPr₃)(C₃H₄)]

them may reflect real differences between the two phosphines, but they are on the borderline of significance. There is also a 5° difference between the *trans* Cl-Pt-C angles for the two compounds.

The co-ordinated C=C bond lengths are longer, but not significantly so, than those in Zeise's salt,⁸ but the Pt-Cl bond lengths *trans* to carbon are significantly shorter than the 2.340(2) Å in Zeise's salt. The unco-ordinated C=C bond lengths are normal.

Hydrogen-1 n.m.r. studies of *cis*-[PtCl₂L(CH₂=C=CH₂)]

molecule is not fluxional at room temperature. However, on raising the temperature to 60 °C the lines of the two low-frequency resonances broadened. Since the two high-frequency resonances were unchanged at 60 °C the explanation for the broadening must be slow rotation about the platinum-olefin bond {rather than movement of the metal between the two double bonds, as occurs in [Pt₂Cl₄(Me₂C=C=CMe₂)₂]^{6,9}.

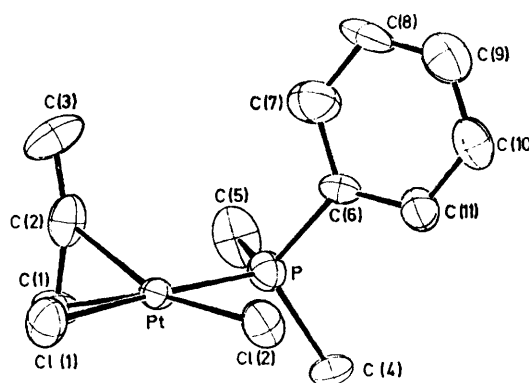


FIGURE 2 The molecular structure and atom numbering of *cis*-[PtCl₂(PMe₂Ph)(C₃H₄)]. The crystal consists of molecules of one enantiomer only (see Experimental section)

The unusual symmetry of the pattern in Figure 3 stems from the equality of all four long-range proton-proton coupling constants. Since four-bond couplings in allenes are dominated by a π-electron mechanism,¹⁰ the reduction in magnitude of ⁴J(HH) (-3.9 Hz) compared to that in free allene (-7.1 Hz)¹¹ is consistent with the decrease in C=C bond order on complexation. Coupling constant data on other complexes of allene are sparse,

but in the nickel(0) complex $[\text{Ni}(\text{PPh}_3)_2(\text{CH}_2=\text{C}=\text{CH}_2)]$ the value of $^4J(\text{HH})$ is <0.5 Hz¹² and in $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{C}=\text{CH}_2)]$ ¹³ it is also unresolved. This could indicate an almost zero π -bond order in the co-ordinated C-C bond in the zerovalent complexes (consistent with the crystal structure of the Pt⁰ complex). With the anions $[\text{PtX}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$ (see below) the values of

TABLE 3

Phosphorus-31 and platinum-195 n.m.r. parameters^a

Complex	$\delta(\text{P})^b$	$^1J(\text{PtP})$	$\delta(\text{Pt})^c$
<i>cis</i> - $[\text{PtCl}_2(\text{PPr}^n)_3](\text{CH}_2=\text{C}=\text{CH}_2)$	6.2	2 963	900
<i>cis</i> - $[\text{PtCl}_2(\text{PMe}_2\text{Et})(\text{CH}_2=\text{C}=\text{CH}_2)]$	-3.3	2 994	894
<i>cis</i> - $[\text{PtCl}_2(\text{PMe}_2\text{Ph})(\text{CH}_2=\text{C}=\text{CH}_2)]$	9.3	3 023	
$[\text{NBu}^n_4][\text{PtCl}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$			2 037

^a In CDCl_3 . ^b In p.p.m. to high frequency of H_3PO_4 . ^c In p.p.m. to high frequency of $\Xi(^{195}\text{Pt}) = 21.4$ MHz.

$^4J(\text{HH})$ are much the same as in *cis*- $[\text{PtCl}_2(\text{PPr}^n)_3](\text{CH}_2=\text{C}=\text{CH}_2)$ (Table 2).

In order to see whether the uncomplexed double bond of the allene ligand in *cis*- $[\text{PtCl}_2(\text{PMe}_2\text{Ph})(\text{CH}_2=\text{C}=\text{CH}_2)]$ could be made to interact with a second platinum atom we treated this complex with an equivalent amount of $[\text{Pt}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_2]$ in dichloromethane solution. A white powder slowly precipitated over a period of 3 days. This product was insoluble in common organic solvents and we were unable to obtain n.m.r. spectra or measure its molecular weight. However, on the basis of micro-analytical data (Table 1), the absence of a band due to C=C (unco-ordinated) in the i.r. absorption spectrum, and the presence of two very strong bonds due to $\nu(\text{Pt}-\text{Cl})$ we formulate the complex as *cis,cis*- $[(\text{PhMe}_2\text{P})\text{Cl}_2\text{Pt}(\mu\text{-C}_3\text{H}_4)\text{PtCl}_2(\text{PMe}_2\text{Ph})]$, containing a bridging allene ligand. The analogous PMe_2Et complex was also very insoluble and we were unable to prepare the PPr^n_3 complex, which one would expect to be much more

(X = Cl, Br, or I) with an excess of allene in dichloromethane or acetone gives the salts $[\text{NBu}^n_4][\text{PtX}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$. The isolation of the iodide is of especial interest since iodo-olefin complexes of platinum are exceedingly rare. It is worth noting that ethylene does not give a product with $[\text{Pt}_2\text{I}_6]^{2-}$, nor is there any indication (from the colour of the solution) of formation of $[\text{PtI}_3(\text{C}_2\text{H}_4)]^-$ *in situ*. In solution, the salt $[\text{NBu}^n_4][\text{PtI}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$ begins to decompose after a few hours but in the solid state it is stable.

As mentioned above, allene will displace ethylene from its complexes and has been used as a method of prepar-

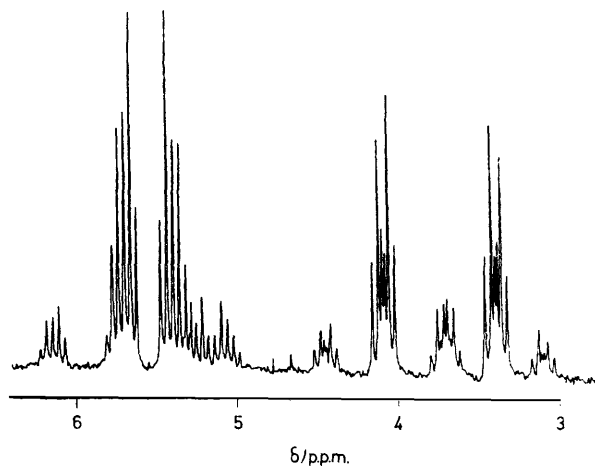


FIGURE 3 100 MHz ^1H n.m.r. spectrum of the allene resonances of *cis*- $[\text{PtCl}_2(\text{PPr}^n_3)(\text{CH}_2=\text{C}=\text{CH}_2)]$ in CDCl_3 with ^{31}P decoupling

ation. It is possible therefore that the allene-platinum(II) is stronger than the ethylene-platinum(II) bond and that the origin of this greater strength lies in the relief of strain in the allene system on complexation.

TABLE 4

Carbon-13 n.m.r. parameters^a

	Pt-CH ₂		Pt-C		CH ₂ (unco-ord.)	
	$\delta(\text{C})^b$	$J(\text{PtC})$	$\delta(\text{C})$	$J(\text{PtC})$	$\delta(\text{C})$	$J(\text{PtC})$
<i>cis</i> - $[\text{PtCl}_2(\text{PPr}^n_3)(\text{CH}_2=\text{C}=\text{CH}_2)]$	36.7	118	164.7	287	93.0	39
$[\text{NBu}^n_4][\text{PtCl}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$	34.8	136	162.8	308	92.5	44
$[\text{NBu}^n_4][\text{PtBr}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$	35.5	122	162.1	299	92.9	44
$[\text{NBu}^n_4][\text{PtI}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$	37.1	105	161.8	283	93.3	40
$[\text{NBu}^n_4]_2[\text{Pt}_2\text{Cl}_6(\text{CH}_2=\text{C}=\text{CH}_2)]^-$	46.6	{ 160 18	108.0	356		

^a For the allene ligand only. In CDCl_3 unless otherwise stated. ^b In p.p.m. to high frequency of SiMe_4 . ^c In $(\text{CH}_3)_2\text{CO}-(\text{CD}_3)_2\text{CO}$.

soluble. A ^{31}P n.m.r. study on a mixture of *cis*- $[\text{PtCl}_2(\text{PPr}^n_3)(\text{C}_3\text{H}_4)]$ and $[\text{Pt}_2\text{Cl}_4(\text{PPr}^n_3)_2]$ (2 : 1) in deuteriochloroform solution showed no evidence of a reaction even after 14 days at *ca.* 20 °C. Presumably the steric effect of the PPr^n_3 ligands prevents the allene acting as a bridging group. Rhodium and molybdenum complexes containing a bridging allene ligand have been reported.¹⁴⁻¹⁶

The allene analogues of Zeise's anion *viz.* anions of the type $[\text{PtX}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$ have not previously been reported. We find that treatment of $[\text{NBu}^n_4]_2[\text{Pt}_2\text{X}_6]$

The enthalpy of hydrogenation of the first double bond in allene (-40.75 kcal mol⁻¹)^{*} is much greater than the second (-29.71 kcal mol⁻¹) which is similar to that of ethylene (-32.69 kcal mol⁻¹).¹⁷

The ^1H n.m.r. spectra of the anions, $[\text{PtX}_3(\text{CH}_2=\text{C}=\text{CH}_2)]^-$, show ABX_2 patterns, indicating that there is no fluxional process involving movement of the $[\text{PtX}_3]$ unit between the two allene double bonds. From the variations in $\delta(\text{H})$ and $J(\text{PtH})$ with change of halide (see Table 2) it appears that the order of $\delta(\text{H}^3)$ and $\delta(\text{H}^4)$ is

* Throughout this paper: 1 cal = 4.184 J.

reversed on going from chloride to iodide and since $\delta(\text{H}^4)$ changes by most we suggest that this proton is the one closest to the co-ordination plane. The ^{13}C n.m.r. parameters are given in Table 4. The parameters of these complexes and of *cis*-[PtCl₂(PPrⁿ₃)(CH₂=C=CH₂)]

TABLE 5

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

	PPr ⁿ compound	PMe ₂ Ph compound
(a) Bond lengths		
PtP	2.268(5)	2.250(5)
Pt-Cl(1)	2.374(4)	2.354(5)
Pt-Cl(2)	2.307(5)	2.316(3)
Pt-C(1)	2.152(19)	2.153(19)
Pt-C(2)	2.101(14)	2.088(18)
C(1)-C(2)	1.42(4)	1.40(3)
C(2)-C(3)	1.29(4)	1.31(3)
P-C(4)	1.87(2)	1.83(2)
P-C(5)	1.82(2)	1.80(2)
P-C(6)	1.83(2)	1.80(2)
C-C	1.49-1.53(3)	1.38-1.41(3)
(b) Bond angles		
C(1)-C(2)-C(3)	158.4(18)	157.8(16)
Cl(2)-Pt-C(1)	167.5(5)	162.8(5)
Cl(2)-Pt-C(2)	153.2(11)	158.5(6)
Cl(2)-Pt-Cl(1)	90.5(2)	89.6(2)
Cl(2)-Pt-P	87.0(2)	87.6(2)
Pt-P-C(4)	113.3(6)	111.4(6)
Pt-P-C(5)	109.8(6)	117.1(7)
Pt-P-C(6)	114.7(6)	110.9(6)

do not differ greatly from those reported by Cooper and Powell¹⁸ for *trans*-[PtCl₂(NC₅H₄Me)(CH₂=C=CMe₂)]. The values of $J(\text{PtC})$ for the two co-ordinated ^{13}C nuclei show the expected dependence on the *trans* influence of the halide.

We then studied the possibility of an allene bridging two PtX₃ moieties and found it would readily do this with X = Cl or Br. Thus the salts [NBuⁿ₄]₂[Pt₂X₆-(CH₂=C=CH₂)] (X = Cl or Br) were prepared by mixing together [NBuⁿ₄][PtX₃(CH₂=C=CH₂)] and [NBuⁿ₄]₂[Pt₂X₆], ratio 2:1, in acetone. For the chloride the reaction required 10 days for completion but for the bromide only 20 min; we did not succeed in isolating an

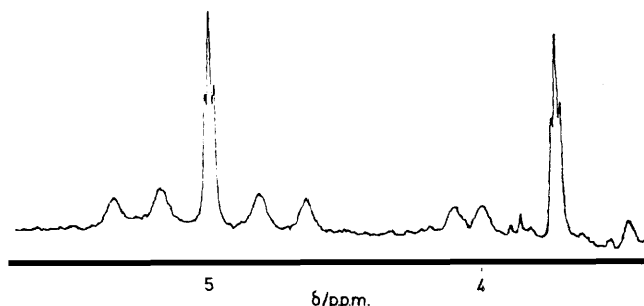


FIGURE 4 100 MHz ^1H n.m.r. spectrum of the allene resonances of [NPrⁿ₄]₂[Pt₂Cl₆(CH₂=C=CH₂)] in CDCl₃

analogous iodo-complex. The tetra-*n*-propylammonium salt of [Pt₂Cl₆(CH₂=C=CH₂)]²⁻ was prepared by treatment of allene with [NPrⁿ₄]₂[Pt₂Cl₆] in dichloromethane over 8 h. Nuclear magnetic resonance spectra establish unambiguously the presence of a bridging allene ligand.

The ^1H n.m.r. spectrum of the allene resonance of [NPrⁿ₄]₂[Pt₂Cl₆(CH₂=C=CH₂)] is shown in Figure 4. The two protons in a CH₂ group are chemically inequivalent and the C₂ molecular symmetry of the anion gives rise to an [AX]₂ spin system. The A and X resonances appear as 1:2:1 triplets which suggests that $^2J(\text{HH}') \approx ^4J(\text{HH}')$. However, in view of the poor resolution of the spectral lines, other solutions are possible.¹⁹ Both types of proton show large couplings to each of the two ^{195}Pt nuclei (probably of opposite sign) but the ^{195}Pt satellites are broad. Irradiation of one of the ^{195}Pt satellites causes collapse of the three adjacent satellites and raising the temperature to 60 °C sharpens the ^{195}Pt satellites while leaving the central resonances unchanged. Both these observations suggest that the broadening stems from fast ^{195}Pt relaxation. A similar phenomenon has been observed with some π -allylic platinum(II) complexes²⁰ and with the anions [PtCl₃(CH₂=CHCH₂OH)]⁻ and [PtCl₃(CH₂=CHOCOCH₃)]⁻.²¹

The ^{13}C n.m.r. spectrum of [NBuⁿ₄]₂[Pt₂Cl₆(CH₂=C=CH₂)] also indicates a symmetrically bridging allene ligand, the terminal carbon showing coupling to two ^{195}Pt nuclei (Table 4).

EXPERIMENTAL

The general techniques used were the same as in other recent papers from this laboratory.²²

The ^1H , $^1\text{H}\{-^{31}\text{P}\}$, $^{31}\text{P}\{-^1\text{H}\}$, and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra were recorded with a JEOL FX100Q n.m.r. spectrometer using an internal deuterium lock. Except where otherwise stated, measurements were made at ambient temperature (*ca.* 296 K). ^{195}Pt chemical shifts were determined by $^1\text{H}\{-^{195}\text{Pt}\}$ INDOR as described elsewhere.²³ For the complexes *cis*-[PtCl₂(PPrⁿ₃)(CH₂=C=CH₂)] and [NBuⁿ₄]₂[Pt₂Cl₆(CH₂=C=CH₂)], signs of coupling constants were determined by $^1\text{H}\{-^1\text{H}\}$ and $^1\text{H}\{-^{31}\text{P}\}$ selective decoupling and $^1\text{H}\{-^{195}\text{Pt}\}$ INDOR and are based on the assumption that $^1J(\text{PtP})$ is positive.²⁴

cis-[PtCl₂(PPrⁿ₃)(CH₂=C=CH₂)]-[Pt₂Cl₆(PPrⁿ₃)₂] (0.102 g) was dissolved in dichloromethane (2 cm³) and propadiene bubbled through this solution for 2 min. The flask was sealed and set aside for *ca.* 4 h until the solution became colourless. Light petroleum (b.p. 60-80 °C) was then added and the flask cooled to -30 °C to give the required product (0.091 g, 80%) as white prisms. *cis*-[PtCl₂(PMe₂Ph)₂(CH₂=C=CH₂)] (84%), *cis*-[PtCl₂(PMe₂Et)₂(CH₂=C=CH₂)] (81%), [NBuⁿ₄][PtCl₃(CH₂=C=CH₂)] (58%), [NBuⁿ₄][PtBr₃(CH₂=C=CH₂)] (67%), and [NBuⁿ₄][PtI₃(CH₂=C=CH₂)] (97%) were prepared similarly, the salts being recrystallised from acetone-diethyl ether.

cis,cis-[Pt₂Cl₆(PMe₂Ph)₂(CH₂=C=CH₂)]-[PtCl₂(PMe₂Ph)₂(CH₂=C=CH₂)] (0.062 g) and [Pt₂Cl₆(PMe₂Ph)₂] (0.057 g) were mixed and dissolved in dichloromethane (5 cm³). After 3 days, the solution had become pale and the required product (0.061 g, 52%) had precipitated as a fine white powder. The compounds *cis,cis*-[Pt₂Cl₆(PMe₂Et)₂(CH₂=C=CH₂)] (19%), [NBuⁿ₄]₂[Pt₂Cl₆(CH₂=C=CH₂)] (70%) (*ca.* 10 days reaction time), and [NBuⁿ₄]₂[Pt₂Br₆(CH₂=C=CH₂)] (38%) (*ca.* 20 min reaction time) were prepared similarly, the salts being recrystallised from acetone-diethyl ether.

[NPrⁿ₄]₂[Pt₂Cl₆(CH₂=C=CH₂)]-[PtCl₂]

(0.060 g) was suspended in dichloromethane (10 cm³) and propadiene bubbled through the solvent for 2 min. The flask was sealed and shaken for 8 h until the solid had dissolved to give a pale yellow solution. Addition of light petroleum (b.p. 60–80 °C) gave the required product (0.035 g, 56%) as yellow needles.

Crystal Data.—(a) PPrⁿ₃ complex, C₁₃H₂₅Cl₂PPr, *M* = 466.3, Orthorhombic, *a* = 15.461(2), *b* = 11.437(2), *c* = 9.606(2) Å, *U* = 1 698.6(5) Å³, *Z* = 4, *D*_c = 1.823 g cm⁻³, *F*(000) = 896, space group *Pna*2₁, Mo-*K*_α radiation, graphite monochromatised, λ = 0.710 69 Å, μ(Mo-*K*_α) = 87.36 cm⁻¹. (b) PMe₂Ph complex, C₁₁H₁₅Cl₂PPr, *M* = 444.2, Orthorhombic, *a* = 8.398(2), *b* = 10.209(3), *c* = 15.677(4) Å, *U* = 1 344.2(5) Å³, *Z* = 4, *D*_c = 2.195 g cm⁻³, *F*(000) = 832, space group *P*2₁2₁2₁, μ(Mo-*K*_α) = 110.35 cm⁻¹.

Structure Determinations.—All measurements were made on a Syntex *P*2₁ diffractometer. Cell dimensions and their standard deviations were obtained for each compound by least-squares treatment of the setting angles for 15 reflections having 35 < 2θ < 40°. Intensities of all independent reflections with 2θ < 45° were measured in the ω–2θ scan

TABLE 6

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
(a) Tripropylphosphine complex			
Pt(1)	0.021 77(4)	0.102 77(5)	0.000 00(0)
Cl(1)	–0.124 2(3)	0.042 2(4)	0.026 1(8)
Cl(2)	–0.010 8(3)	0.281 6(4)	0.098 0(7)
P(1)	0.155 9(3)	0.175 1(4)	–0.041 5(4)
C(1)	0.035 5(13)	–0.050 2(16)	–0.128 5(21)
C(2)	0.067 0(10)	–0.070 3(12)	0.008 3(43)
C(3)	0.099 4(14)	–0.126 9(16)	0.112 1(25)
C(4)	0.211 2(12)	0.230 2(17)	0.118 8(22)
C(5)	0.148 5(13)	0.301 8(16)	–0.155 0(21)
C(6)	0.229 7(11)	0.073 4(16)	–0.128 2(21)
C(7)	0.229 4(17)	0.132 9(22)	0.224 5(24)
C(8)	0.103 2(15)	0.276 1(18)	–0.288 8(22)
C(9)	0.317 3(14)	0.125 7(17)	–0.160 8(29)
C(10)	0.277 8(14)	0.183 4(24)	0.348 5(25)
C(11)	0.102 3(18)	0.372 6(19)	–0.374 9(25)
C(12)	0.373 5(15)	0.039 4(21)	–0.242 0(27)
(b) Dimethylphenylphosphine complex			
Pt(1)	0.217 67(7)	0.015 69(5)	0.236 40(4)
Cl(1)	0.085 3(7)	–0.124 0(5)	0.332 6(3)
Cl(2)	0.232 8(6)	–0.154 6(4)	0.139 2(3)
P(1)	0.338 7(6)	0.142 3(5)	0.138 5(3)
C(1)	0.131 9(22)	0.176 8(18)	0.312 2(12)
C(2)	0.285 3(28)	0.138 4(16)	0.336 6(11)
C(3)	0.418 8(29)	0.139 9(20)	0.379 6(13)
C(4)	0.216 2(22)	0.161 1(19)	0.043 0(11)
C(5)	0.384 0(25)	0.308 2(16)	0.168 8(13)
C(6)	0.526 5(18)	0.073 3(16)	0.107 4(10)
C(7)	0.658 2(25)	0.090 0(21)	0.161 9(13)
C(8)	0.805 8(19)	0.035 7(19)	0.141 8(13)
C(9)	0.819 1(24)	–0.035 4(18)	0.066 9(13)
C(10)	0.691 0(22)	–0.050 3(18)	0.012 4(11)
C(11)	0.543 2(20)	0.002 7(18)	0.032 6(10)

mode, using scans from 0.8° below *K*_{α1} to 0.8° above *K*_{α2}. The structure used only those reflections for which *I* > 3σ(*I*), 992 for (a) and 1 018 for (b). A further 207 reflections for (a) and 25 reflections for (b) had *I* < 3σ(*I*), σ(*I*) being calculated from counting statistics. Lorentz, polarisation, and transmission factors were applied [*A** = 1.83–2.24 for (a), 5.04–9.82 for (b)] and the structures were solved from Patterson and difference syntheses. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms converged at *R* = 0.026

for (a) and *R* = 0.029 for (b) with *R*' values of 0.034 and 0.042 respectively. Since the space group for (a) is polar, and that for (b) is enantiomorphic, refinements were also carried out with the polarity of (a) and the chirality of (b) reversed. These converged at *R* = 0.029, *R*' = 0.038 for (a) and *R* = 0.047, *R*' = 0.063 for (b), indicating that both initial assignments were correct. Hydrogen atoms were not included, and atomic scattering factors were calculated using the analytical approximation and coefficients given in ref. 25. Least-squares weights were derived from the modified variances σ²(*I*) = σ_c²(*I*) + (0.02*I*)², where σ_c²(*I*) is the variance from counting statistics; the derived expression for the weight is *w*⁻¹ = σ²(*F*_o) = σ_c²(*F*_o) + ¼(0.02*F*_o)². The final atomic co-ordinates and their estimated standard deviations are given in Table 6; the anisotropic temperature factors and a list of observed and calculated structure factors are given in Supplementary Publication No. SUP 22914 (16 pp.).*

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

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