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TRANSITION METAL—CARBON BONDS

XXXVIII*. ALKENYL—PLATINUM(II) COMPLEXES FROM PLATINUM ACETYLIDES

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Summary

Platinum(II) acetylides of the type *trans*-[Pt(C≡CR)$_2$(PMe$_2$Ph)$_2$] (R = CH$_2$OMe, CMe$_2$OH, Ph) are reduced by hydrazine hydrate to dialkenylplatinum(II) complexes of the type *trans*-[Pt(CH=CHR)$_2$(PMe$_2$Ph)$_2$] in which the hydrogens are mutually *cis* on the alkenyl double bonds. Some of the complexes exist as rotational isomers in solution due to restricted rotation about the Pt—C single bonds. Mono-alkenyl complexes [PtCl(CH=CHR)(PMe$_2$Ph)$_2$] (R = Ph or CMe$_2$OH) were prepared by the hydrogen chloride fission of the dialkenyl complexes. *trans*-[PtCl(CCl=CHCH$_2$OMe)(PMe$_2$Ph)$_2$] is formed when *trans*-[Pt(C≡CCH$_2$OMe)$_2$(PMe$_2$Ph)$_2$] is treated with hydrogen chloride whereas similar treatment of [Pt(C≡CCMe$_2$OH)(PMe$_2$Ph)$_2$] gives [PtCl(CCl=CHCMe=CH$_2$)(PMe$_2$Ph)$_2$]. ^{1}H, ^{13}C and ^{31}P NMR data are given and discussed.

Introduction

In 1959 Chatt and Rowe [2] reported briefly that [PtCl$_2$(P-n-Pr$_3$)$_2$] when treated with phenylacetylene in the presence of hydrazine hydrate gives the diphenylacetylide complex, *trans*-[Pt(C≡CPh)$_2$(P-n-Pr$_3$)$_2$] and the distyryl complex, *trans*-[Pt(CH=CHPh)$_2$(P-n-Pr$_3$)$_2$]. In their brief report structural evidence was not given and the stereochemistry about the double bonds in the styryl complex was not determined. They made the reasonable suggestion that *trans*-[PtHCl(P-n-Pr$_3$)$_2$] was an intermediate in the formation of the styryl complex. In our work we have found that compounds of the type *trans*-[Pt(*cis*-CH=CHR)$_2$(PMe$_2$Ph)$_2$] [where R = Ph, CH$_2$OMe or C$_6$H$_{10}$(OH)] are formed by treating

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* For Part XXXVII see ref. 1.

trans-$[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]$ with hydrazine hydrate in ethanol for three days. Similarly the styryl complex of Chatt and Rowe was also probably formed by hydrazine reduction of the corresponding diphenylacetylide.

We have also prepared alkenyl—platinum complexes by treating platinum acetylides with hydrogen chloride. Before discussing our results we will briefly review the work done previously on alkenyl—platinum complexes.

Attempts to prepare $[PtBr(CH{=}CHPh)(PEt_3)_2]$ or $[Pt(CH{=}CHPh)_2(PEt_3)_2]$ by treating $[PtCl_2(PEt_3)_2]$ with styrylmagnesium bromide gave *trans,trans*-1,4-diphenyl-1,3-butadiene, *trans*-$[PtHBr(PEt_3)_2]$, and *trans*-$[PtBr_2(PEt_3)_2]$: no styryl complexes were isolated [3]. The complex *cis*-$[PtBr(CH{=}CHPh)(PPh_3)_2]$ can, however, be prepared by the action of styryl bromide on $[Pt^0(PPh_3)_4]$ [4,5]. Treatment of the complex *trans*-$[PtCl_2(PEt_2Ph)_2]$ with $Me_3SnCH{=}CH_2$ gives the complex *trans*-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$ [6]. There are several examples where alkenyl—platinum complexes are formed by insertion of an acetylene into a platinum—hydrogen bond [7-11]. In addition a wide range of acetylene complexes of the type $[Pt(ac)(PPh_3)_2]$ (where ac is a substituted acetylene) react with HCl or CF_3CO_2H to give alkenyl—platinum complexes [12-14]. In all these compounds the platinum and added hydrogen are *cis* on the double bond and the addition (insertion) occurs in a Markownikoff manner.

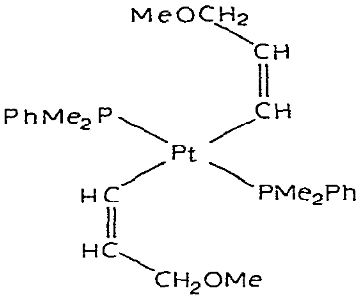
Results and discussion

Our new alkenyl compounds of type *trans*-$[Pt(CH{=}CHR)_2(PMe_2Ph)_2]$ were prepared by treating the corresponding acetylides with hydrazine hydrate in warm ethanol for three days. The complexes (see Table 1) were characterized by microanalysis, by ^1H, ^{13}C and ^{31}P NMR spectroscopy and by IR spectroscopy, which will be discussed later. The structure of the complex with R = CH_2OMe has been determined by means of X-ray diffraction [15] and is shown schematically in I. The alkenyl groups are *trans* and there is a *cis*-arrangement of the platinum and $-CH_2OMe$ groups about the C=C bond. The Pt—C distance of 2.13 (±0.02) Å is significantly larger than the Pt—C distance in *trans*-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$ [6], (2.03 ± 0.02 Å). This increased bond length is probably due to the large *trans*-bond weakening effect of carbon on the Pt—C bond

TABLE 1

YIELD, COLOUR, MELTING POINT AND ANALYTICAL DATA FOR SOME ALKENYL—PLATINUM COMPLEXES (L = PMe_2Ph)

	Yield (%)	Colour	M.p. (°C)	Analytical data found (calcd.) (%)		
				C	H	Halogen
$[Pt\{CH{=}CHCMe_2(OH)\}_2L_2]$	42	White	132-135	48.5 (48.65)	6.1 (6.3)	5.64 (6.00)
$[Pt\{CH{=}CHC_6H_{10}(OH)\}_2L_2]$	60	White	153-156	53.2 (53.4)	6.6 (6.45)	
$[Pt\{CH{=}CHCH_2OMe\}_2L_2]$	53	White	104-106	47.15 (47.0)	5.8 (5.9)	
$[Pt(CH{=}CHPh)_2L_2]$	64	White	142-145	56.55 (56.7)	5.4 (5.35)	
$[PtCl\{CH{=}CHCMe_2(OH)\}L_2]$	92	Cream	110-119	46.9 (47.25)	4.9 (4.8)	5.65 (6.0)
$[PtCl(CH{=}CHPh)L_2]$	79	White	146-148	43.0 (42.6)	5.25 (5.3)	5.6 (5.8)
$[PtCl(CCl{=}CHCH_2OMe)L_2]$	54	White	103-109	39.05 (39.25)	4.55 (4.6)	11.75 (11.6)
$[PtCl(CCl{=}CHCMe{=}CH_2)L_2]$	70	Yellow	100-105	42.05 (41.45)	4.65 (4.65)	11.2 (11.65)



(I)

trans to itself. The Pt—P bond length of 2.280 (±0.004) Å is approximately the same as that found for *trans*-[$PtCl_2(PEt_3)_2$] [16], (2.30 ± 0.02 Å).

The proton NMR spectrum of *trans*-[$Pt(CH{=}CHCH_2OMe)_2(PMe_2Ph)_2$] (Table 2) shows a phosphorus—methyl triplet pattern with satellites (due to 195-platinum) characteristic of *trans*-phosphines. The central resonance patterns of the β-vinylic protons (i.e. excluding satellites due to coupling with 195-platinum) consists of an 18-line pattern. The coupling $^3J(H^1—H^2)$ of 11.4 Hz is consistent with *cis*-hydrogens on the double bond. The value of the *trans*-coupling $^3J(Pt—H^2)$ = 64 Hz is much smaller than the value of the *trans*-coupling{$^3J(Pt—H)$ = 148 Hz} for *trans*-[$PtBr(CH{=}CH_2)(PMe_2Ph)_2$] and is probably due to carbon having a stronger *trans*-influence than bromine. Previously values of $^3J(Pt—H)$ in organo-platinum complexes have been shown to be strongly dependent on the nature of the *trans*-ligand [17-19]. The ^1H NMR spectrum of the complex *trans*-[$Pt(CH{=}CHPh)_2(PMe_2Ph)_2$] has a *P*-methyl triplet pattern showing *trans*-phosphines but the resonances of the vinylic protons were obscured by those of the phenyl protons. However, treatment of the complex with an ethereal solution of hydrogen chloride gives *trans*-[$PtCl(CH{=}CHPh)(PMe_2Ph)_2$]. Although most of the vinylic resonances of this complex were also obscured by the aromatic resonances, we could observe the upper field platinum-195 satellite of one of the vinyl hydrogens. This satellite appears as a doublet of triplets with $^3J(H—H)$ = 11, and $J(P—H)$ = 1.3 Hz. $^3J(H—H)$ is of the correct order for *cis*-hydrogens on the double bond. This value of the proton—proton coupling constant can be compared to those for *trans*-[$PtBr(CH{=}CHPh)(PPh_3)_2$], where $^3J(H—H)$ = 16.8 Hz when the CH=CH protons are mutually *trans* [14] or 10.5 Hz when they are *cis* [5]. We therefore think both our 2-phenylethynyl(β-styryl) complexes have *cis*-double bonds.

There is a considerable chemical shift difference (0.27 ppm) for the two in equivalent methyl resonances of PMe_2Ph for the complex *trans*-[$PtCl(CH{=}CHPh)(PMe_2Ph)_2$] indicating that there is no plane of symmetry through the phosphorus—metal bonds. This means that the styryl group is not rotating about the metal—carbon bond at a sufficient rate to cause equivalence of the phosphine methyls. A similar effect is found for *o*-substituted aryl—nickel complexes such as *trans*-[$NiBr(o\text{-tolyl})(PMe_2Ph)_2$] [20].

The product [$Pt\{CH{=}CHCMe_2OH\}_2(PMe_2Ph)_2$], obtained by the hydrazine reduction of the corresponding diacetylide, shows a strong broad absorption at ca. 3300 cm^{-1} due to ν(OH). The ^1H NMR spectrum is very complex and

TABLE 2. ^{1}H NMR DATA[a]

	P—Me resonance			Other resonances		
	δ	$\lvert ^2J(PH) + ^4J(PH)\rvert$	$^3J(PtH)$	δ	J	Assignment[b]
$[Pt(CH{=}CHCH_2OMe)_2L_2]$	1.66t	7.2	33.4	6.74m	$^3J(CH_2—H^2)$ 6.0	H^2
					$^3J(H^1—H^2)$ 11.4	
					$^4J(PH^2)$ 2.4	
					$^3J(PtH^2)$ 64	
				3.69d	$^3J(H^2—CH_2)$ 6.0	CH_2
					$^4J(PtCH_2)$ 8.0	
				3.18s		OMe
$[Pt\{CH{=}CHCMe_2(OH)\}_2L_2]$						
Isomer A	1.75t	7.2	33	6.99	$^3J(H^2—H^1)$ 12.8 ± 0.3	H^1
	1.71t	7.2	33	d of t	$^3J(PH^1)$ 2.2 ± 0.3	
					$^3J(PtH^1)$ 38 ± 2	
				6.66	$^3J(H^1—H^2)$ 12.8 ± 0.3	H^2
				d of t	$^4J(PH^2)$ 2.2 ± 0.3	
					$^3J(PtH^2)$ ≈76 ± 2	
				4.51s	$J(Pt—OH)$ 18.0 ± 1	OH
				0.90s		CH_3
Isomer B	1.75t	7.2	33	≈6.7s	$^3J(H^2—H^1)$ 12.5 ± 1	H^1 and H^2
	1.71t	7.2	33		$^3J(PH^1)$ 2 ± 0.5	
					$^4J(PH^2)$ 2 ± 0.5	
					$^2J(PtH^1)$ 38 ± 2	
					$^3J(PtH^2)$ 80 ± 2	
$[Pt(CH{=}CHPh)_2L_2]$	1.48t	7.0	33.2	7.24m		Ph[d]
$[PtCl(CCl{=}CHCH_2OMe)L_2]$	1.85t	7.3	31.5	6.29	$^4J(PH)$ 4.2	CH
	1.80t	7.2	31.5	t of t	$^3J(CH_2—H)$ 7.2	
					$^3J(Pt—H)$ 88	
				3.61d	$^3J(H—CH_2)$ 7.2	CH_2
					$^4J(PtH)$ 13.9	
				3.06s		OMe
$[PtCl\{CCl{=}CHC(Me){=}CH_2\}L_2]$	1.86t	7.3	30.8	6.69t	$^4J(PH)$ 3.5	CH
	1.81t	7.4	32.2		$^3J(PtH)$ 100	
				5.50s 4.63s } [e]		CH_2
				1.90s		CH_3

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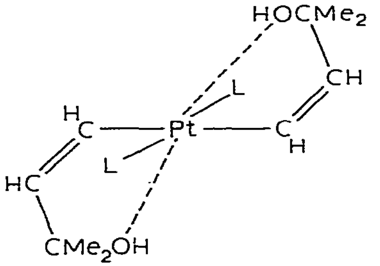
[a] In $CDCl_3$ at 90 MHz and ca. 25°C; δ values ± 0.01 ppm; J values ± 0.1 Hz unless shown otherwise, s = singlet, d = doublet, t = triplet, m = multiplet (multiplicities exclude satellites due to 195-platinum coupling). [b] H^1 *gem* to Pt H^2 *trans* to Pt. [c] The AB-pattern of the vinyl protons could not be resolved. [d] Vinylic resonances hidden by Ph resonances. [e] Broad resonances.

shows the presence of two isomers (A and B) in ca. 1/1 proportions. The data given and discussed below were calculated from spectra measured at 90 MHz in $CDCl_3$. A spectrum was also measured at 220 MHz and gave very similar data (the same within experimental error). The P—Me resonances occur as triplets at δ 1.71 and 1.75 ppm in each case $|^2J(\text{P—H}) + {}^4J(\text{P—H})| = 7.2 \pm 0.5$ Hz with satellites due to 195-platinum $^3J(\text{Pt—H}) = 33 \pm 1.5$ Hz. The *C*-methyls absorp at $\delta(\text{A}) = 0.90$ ppm and $\delta(\text{B}) = 1.15$ ppm for the two isomers, which are present in 1/1 proportion, from the intensity of the signals. Interestingly, the OH-resonances show coupling to 195-platinum at δ 4.43 and 4.51 ppm; $J(\text{Pt—H}) = 18 \pm 1$ Hz. On adding D_2O these resonances immediately disappear and the ratio of the intensities of the two *C*-methyl resonances, A/B, changes to ca. 1.5/1 from ca. 1/1 showing an isotope effect. The interaction of an alcohol hydroxyl group and platinum has been reported previously for complexes of type [PtCl(ac)(amine)] (where ac ≡ a tertairy ethynyl alcohol). The evidence for the interaction was based on IR spectroscopy and no NMR data were given. The phenyl resonance consists of two broad multiplets centred at δ 7.38 and 7.55 ppm. The resonance patterns of the vinylic protons are complex. One isomer gives a centre band in the form of an $AA'BB'X_2$ spectrum and the other appears as a broad singlet. Analysis shows for isomer A $\delta(\text{H}^1) = 6.99$, $\delta(\text{H}^2) = 6.66$ ppm; $J(\text{H}^1\text{—H}^2) = 12.8 \pm 0.3$, $J(\text{H}^1\text{—P}) = 2.2 \pm 0.3$ and $J(\text{H}^2\text{—P}) = 2.2 \pm 0.3$ Hz and for isomer B $\frac{1}{2}\{\delta(\text{H}^1) + \delta(\text{H}^2)\} = 6.7$. Analysis of the sidebands due to coupling with 195-platinum gives for isomer A $J(\text{Pt—H}^1) = 38 \pm 2$ and $J(\text{Pt—H}^2) = 76 \pm 2$ Hz and for isomer B $J(\text{H}^1\text{—H}^2) = 12.5 \pm 1$, $J(\text{P—H}^1) = 2 + 0.5$, $J(\text{P—H}^2) = 2 \pm 0.5$, $J(\text{Pt—H}^1) = 38 \pm 2$, $J(\text{Pt—H}^2) = 80 \pm 2$ Hz. The chemical shifts of the two protons H^1 and H^2 for isomer B must be very similar and the centre band could not be resolved. Because some of the satellite peaks overlap, the chemical shifts of these two protons could not be calculated accurately. However, assuming chemical shifts of 6.71 (H^1) and 6.69 (H^2) and using the above data satisfactory



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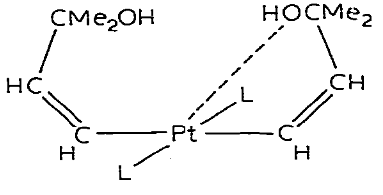

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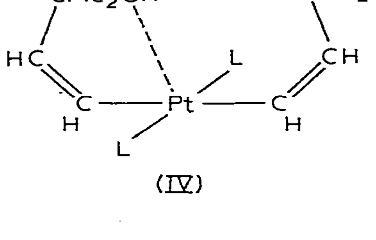
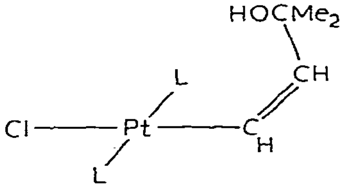


(IV)

simulations of the observed spectra were calculated. The ^1H NMR data for the mixture shows that (*i*) the PMe_2Ph ligands are mutually *trans*, (*ii*) the two hydrogens are on the double bond in a mutually *cis*-arrangement, (*iii*) the two isomers (A and B) are therefore probably rotational isomers (II) and (III) although we cannot say which is which, (*iv*) both hydroxyls are coupled equally to the platinum. This is clearly possible in (II) as shown and can be achieved in (III) by a dynamic interconversion with (IV). In the ^{31}P NMR spectrum the two isomers absorp at different chemical shifts $\delta(H_3PO_4) = -9.80$ ppm; $^1J(Pt-P) = 2692$ Hz and $\delta_{H_3PO_4} = -9.93$ ppm, $^1J(Pt-P) = 2682$ Hz. The intensity ratio is ca. 1/1 and changes to ca. 1.4/1 on treatment with D_2O. Thus the isomer which gives the low field ^{31}P resonances is responsible for the high field CH_3 resonance.

If *trans*-$[Pt\{CH{=}CHCMe_2(OH)\}_2(PMe_2Ph)_2]$ is treated with an ethereal solution of hydrogen chloride, *trans*-$[PtCl\{CH{=}CHCMe_2OH\}(PMe_2Ph)_2]$ is formed. This complex shows an OH-absorption band at 3295 cm^{-1} in its IR spectrum, and a singlet OH resonance at δ 4.49 ppm, with platinum-195 satellites, $J(Pt-OH) = 21$ Hz, in its ^1H NMR spectrum. Only one CMe_2 resonance, at δ 0.92 ppm is present in the ^1H NMR spectrum, and the vinylic region shows an ABX_2-pattern with $ABMX_2$-satellites. The coupling $^3J(H-H)$ of 10.8 Hz indicates *cis*-hydrogens on the double bond. The complex has thus configuration (V). The *trans*-coupling $^3J(Pt-H^2)$ of 151 Hz is considerably larger than that in



(V)

trans-$[Pt\{CH{=}CHCMe_2OH\}_2(PMe_2Ph)_2]$ but the *gem*-coupling $^2J(Pt-H^1)$ of 34 Hz is very similar.

The vinylic region of the ^1H NMR spectrum of *trans*-$[Pt\{CH{=}CHC_6H_{10}(OH)\}_2(PMe_2Ph)_2]$ could not readily be completely analysed, so data are only available for one isomer (Table 2).

The ^{31}P NMR data for the alkenyl—platinum complexes are recorded in Table 3. The complexes *trans*-$[Pt\{CH{=}CHC_6H_{10}(OH)\}_2(PMe_2Ph)_2]$ and *trans*-$[Pt(CH{=}CHPh)_2(PMe_2Ph)_2]$ like *trans*-$[Pt\{CH{:}CHCMe_2(OH)\}_2(PMe_2Ph)_2]$, show different phosphorus resonances for the two rotational isomers (Table 3). *trans*-$[Pt(CH{=}CHCH_2OMe)_2(PMe_2Ph)_2]$ shows only one type of phosphorus in its ^{31}P NMR spectrum, indicating it has only one configuration: this is probably consequent on the smaller bulk of the CH_2OMe group. The coupling $^1J(Pt-P)$ for the four complexes lie in the range 2680 to 2860 Hz, which is in the range expected for *trans*-phosphines on platinum [21-23].

The ^{13}C chemical shifts and coupling constants for *trans*-$[Pt\{CH{=}CHCMe_2(OH)\}_2(PMe_2Ph)_2]$ are recorded in Table 4. Since the complex exists as two isomers its ^{13}C NMR spectrum is difficult to interpret fully. The coupling $^1J(Pt-C)$ is 533 Hz for both isomers, which is the correct magnitude for platinum bonded to an sp^2-hybridized carbon atom cf. $^1J(Pt-C) = 594$ Hz found for *trans*-$[PtPh_2$-

TABLE 3

^{31}P NMR DATA [a] FOR SOME ALKENYL—PLATINUM COMPLEXES

Complex [b]	$\delta(H_3PO_4)$	$^1J(Pt—P)$
$[Pt\{CH{=}CHCMe_2(OH)\}_2L_2]$	−9.80	2692
	−9.93	2682
$[Pt\{CH{=}CHC_6H_{10}(OH)\}_2L_2]$ [c]	−10.65	2696
	−10.88	2685
$[Pt\{CH{=}CHPh\}_2L_2]$	−10.60	2859
	−11.80	2849
$[Pt\{CH{=}CHCH_2OMe\}_2L_2]$	−10.20	2810

[a] Spectra recorded at 36.43 MHz in deuteriochloroform, with all ^1H nuclei decoupled and $CDCl_3$ used to provide a frequency lock. Chemical shifts are given relative to 85% H_3PO_4 (±0.1 ppm), J values ±2.5 Hz. [b] L = PMe_2Ph. [c] Measured in C_6D_6.

$(PEt_3)_2]$ [24]. Unfortunately the coupling $^2J(Pt—C)$ could not be measured because the signals were obscured. Two different resonances could be seen for the carbon directly bonded to the metal, and for the methyl resonance of the phosphines, attributable to the two isomeric forms. The resonances due to the other types of carbon were not resolved for the two isomers.

Preparation of alkenyl—platinum complexes by treating platinum acetylides with HCl

The reaction of protic acids, HX, with platinum acetylide complexes of the type *trans*-$[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]$ depends very much on X, R, and the solvent used. Chisholm and Couch [25] found that on treating *trans*-$[Pt(C{\equiv}CMe)_2(PMe_2Ph)_2]$ with one mole of HCl per platinum atom in CH_2Cl_2, one of the acetylide ligands is cleaved giving *trans*-$[PtCl(C{\equiv}CMe)(PMe_2Ph)_2]$. If a second mole of HCl is added a mixture of *cis*- and *trans*-$[PtCl_2(PMe_2Ph)_2]$ is formed. If THF is used as solvent, and 2 moles of HCl per platinum atom are added then the main product is *trans*-$[PtCl(CCl{=}CHMe)(PMe_2Ph)_2]$ [26]. Similarly HCl adds across the triple bonds of *trans*-$[Pt(C{\equiv}CCF_3)_2(PEt_3)_2]$ to give a *trans*-alkenyl complex, *trans*-$[Pt(CCl{=}CHCF_3)_2(PEt_3)_2]$.

If *trans*-$[Pt(C{\equiv}CCH_2OMe)_2(PMe_2Ph)_2]$ in C_6H_6 is treated with dry HCl (2 moles per Pt atom) a complex is formed that shows no triple bond absorption in its IR spectrum, but shows a band of medium strength at 1600 cm^{-1} due to a carbon—carbon double bond. On the basis of analytical and IR and ^1H NMR evidence we assign to the complex the structure *trans*-$[PtCl(CCl{=}CHCH_2OMe)(PMe_2Ph)_2]$. In the ^1H NMR spectrum the vinylic proton is a triplet of triplets, coupling to the methylene group $^3J(H—H)$ = 7.2 Hz, and to phosphorus $^4J(P—H)$ = 4.2 Hz. The proton also couples to platinum-195: the value of $^3J(Pt—H)$ = 88.0 Hz, suggests that the platinum and the hydrogen are mutually *cis* on the double bond (since chlorine is the *trans*-ligand a $^3J(Pt—H)$ *trans*-coupling would be expected to be >100 Hz). The methylene protons couple to the vinylic hydrogen $^3J(H—H)$ = 7.2 Hz, and to platinum-195, $^4J(Pt—H)$ = 13.9 Hz.

The IR spectrum of the product formed by treating *trans*-$[Pt\{C{\equiv}CCMe_2(OH)\}_2(PMe_2Ph)_2]$ with dry HCl contains no absorption characteristic of a triple bond at ca. 2100 cm^{-1}, nor absorptions characteristic of an OH in the range

3400 to 3600 cm^{-1}, but shows strong absorption at 1600 cm^{-1} indicating a double bond. This evidence and that obtained from the ^1H NMR spectrum leads us to assign the structure *trans*-[PtCl{CCl=CHC(Me)=CH_2}$(PMe_2Ph)_2$] for the product. In the ^1H NMR spectrum the vinylic proton resonance is a triplet, $^4J(P-H)$ = 3.5 Hz at δ 6.69 ppm with platinum-195 satellites, $^3J(Pt-H)$ = 100 Hz. The two terminal proton resonances are broad singlets at τ 4.50, and τ 5.37, broadening probably being due to coupling to the methyl group, and possibly due to coupling to platinum-195. The ^1H NMR data for the complexes are recorded in Table 2.

If *trans*-[Pt{CH≡$CCMe_2$(OH)}$_2(PMe_2Ph)_2$] in C_6H_6 is treated with one mole of HCl per Pt atom then a mixture of off-white plates and yellow prisms is formed. The IR spectrum of this mixture shows no OH absorption, but shows peaks at 2110 and 2080 cm^{-1} indicating a triple bond, and a peak at 1600 cm^{-1} indicating a double bond. The product is probably a mixture of *trans*-[Pt{C≡CC(Me)=CH_2}$_2(PMe_2Ph)_2$] and *trans*-[PtCl{CCl=CHC(Me)=CH_2}$(PMe_2Ph)_2$].

trans-[PtCl{CCl=CHC(Me)=CH_2}$(PMe_2Ph)_2$] was pyrolysed at 150°C, in vacuo; the gas evolved was identified as HC≡CC(Me)=CH_2 by its IR spectrum and the residue was identified as *cis*-[$PtCl_2(PMe_2Ph)_2$]. A similar elimination occurs when *trans*-[$PtCl_2$(CCl=CClPh)$_2(PPr_3)_2$] (prepared by the action of Cl_2 on *trans*-[Pt(C≡CPh)$_2(PPr_3)_2$]) is refluxed in MeOH [27].

Experimental

Melting points were determined on a Kopler hot-stage apparatus and are corrected. Infrared spectra were determined on a Perkin—Elmer R 457 (4000-250 cm^{-1}) or Grubb—Parsons D.B.3/D.N.2 (500-200 cm^{-1}). ^1H NMR spectra were recorded in deuteriochloroform at 60 MHz on a Perkin—Elmer R12A spectrometer or at 90 MHz on a Bruker HFX spectrometer. ^{31}P (36.43 MHz) or ^{13}C (22.62 MHz) were also determined on a Bruker HFX spectrometer at ca. 25°C.

Preparation of trans-[Pt(CH=CHCH$_2$OMe)$_2$(PMe$_2$Ph)$_2$]

Trans-[Pt(C≡$CCH_2OMe)_2(PMe_2Ph)_2$] (0.20 g, 0.33 mmol) was dissolved in warm ethanol (5 ml). Hydrazine hydrate (0.13 ml, 2.64 mmol) was added, and the solution was put aside at room temperature. After three days white prisms of *trans*-[Pt(CH=$CHCH_2OMe)_2(PMe_2Ph)_2$] (0.11 g, 0.18 mmol, 53%) separated. It formed white prisms from benzene/hexane.

The following complexes were prepared in a similar manner. *trans*-[Pt(CH=CHPh)$_2(PMe_2Ph)_2$], *trans*-[Pt{CH=$CHCMe_2$(OH)}$_2(PMe_2Ph)_2$], *trans*-[Pt{CH=CHC_6H_{10}(OH)}$_2(PMe_2Ph)_2$]. These complexes crystallise from benzene/hexane.

Action of hydrogen chloride on trans-[Pt(CH=CHPh)$_2$(PMe$_2$Ph)$_2$]

Trans-[Pt(CH=CHPh)$_2(PMe_2Ph)_2$] (0.10 g, 0.15 mmol) in dry benzene (3 ml) was treated with an ethereal solution of hydrogen chloride (0.15 mmol). The solution was stirred for 40 min, when evaporation gave, as a white solid, *trans*-[PtCl(CH=CHPh)$(PMe_2Ph)_2$] (0.082 g, 0.13 mmol, 79%). It formed cream prisms from benzene/hexane.

Action of hydrogen chloride on trans-[Pt{CH=CHCMe$_2$(OH)}$_2$(PMe$_2$Ph)$_2$]

Trans-[Pt{CH=CHCMe$_2$(OH)}$_2$(PMe$_2$Ph)$_2$] (0.10 g, 0.16 mmol) in wet benzene (3 ml) was treated with an ethereal solution of hydrogen chloride (0.16 mmol). The solution was stirred for 30 min, when evaporation gave *trans*-[PtCl{CH=CHCMe$_2$(OH)}(PMe$_2$Ph)$_2$] (0.073 g, 0.12 mmol, 92%) as a white solid. It formed white needles from n-hexane.

Preparation of alkenyl—platinum complexes by the action of hydrogen chloride on platinum acetylides

Trans-[PtCl(CCl=CHCH$_2$OMe)(PMe$_2$Ph)$_2$]. *Trans*-[Pt(C≡CCH$_2$OMe)$_2$(PMe$_2$Ph)$_2$] (0.70 g, 1.15 mmol) in dry benzene (5 ml) was treated with an ethereal solution of hydrogen chloride (2.30 mmol). The solution was stirred for 1 h, and evaporation, followed by trituration with light petroleum (b.p. 30-40°C) gave a white solid *trans*-[PtCl(CCl=CHCH$_2$OMe)(PMe$_2$Ph)$_2$] (0.38 g, 0.62 mmol. 54%). It forms as white prisms from n-hexane.

Trans-[PtCl{CCl=CHC(CH$_3$):CH$_2$}(PMe$_2$Ph)$_2$]. *Trans*-[Pt{C≡CCMe$_2$(OH)}$_2$(PMe$_2$Ph)$_2$] (0.20 g, 0.315 mmol) in dry benzene (4 ml) was treated with an ethereal solution of hydrogen chloride (0.63 mmol). The resulting orange solution was stirred for 20 min, and evaporation followed by trituration with light petroleum (b.p. 30-40°C) gave a yellow solid, *trans*-[PtCl{CCl=CHC(CH$_3$)=CH$_2$}(PMe$_2$Ph)$_2$] (0.13 g, 0.22 mmol, 70%). It forms as yellow prisms from n-hexane.

Pyrolysis of trans-[PtCl{CCl=CHC(CH$_3$)=CH$_2$}(PMe$_2$Ph)$_2$]

Trans-[PtCl{CCl=CHC(CH$_3$)=CH$_2$}(PMe$_2$Ph)$_2$] was heated to 150°C in vacuo. The gas given off was collected in an IR gas cell. Its IR spectrum was identical with that of HC≡CC(CH$_3$)=CH$_2$. Ethanol was added to the residue at room temperature, giving an off-white solid, *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (0.05 g, 0.12 mmol, 67%).

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