

Hydrido-organometallic Complexes of Platinum(II). X-Ray Crystal Structure of *trans*-[PtH(C₆H₄F-*p*)(PPh₃)₂][†]

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A series of compounds *trans*-[PtH(R)(PPh₃)₂] [R = C₆H₄Y-*p* (Y = Me, OMe, F, or Cl), C₆H₄Me-*o*, C₆H₃Cl₂-2,5, C₆HCl₄-2,3,4,5, C₆HCl₄-2,3,4,6, C₆Cl₅, or C₆F₅], *cis*-[PtH(C₆F₅)(PPh₃)₂], and *cis*-[PtH(Ph)(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂) have been obtained by decarboxylation of formate complexes, or by the reaction of the halogeno complexes with NaBH₄. The compounds have been characterized by i.r. and n.m.r. (¹H, ³¹P, and ¹⁹⁵Pt) spectroscopy. The molecular structure of *trans*-[PtH(C₆H₄F-*p*)(PPh₃)₂] has been determined by a single-crystal X-ray structural analysis. The crystals are orthorhombic, space group *Pcab*, with *a* = 25.304(5), *b* = 23.963(5), *c* = 11.530(3) Å, and *Z* = 8. Dimethyl acetylenedicarboxylate inserts into the Pt-H bond of *trans*-[PtH(R)(PPh₃)₂] (R = C₆H₄Cl-*p*, C₆H₄Me-*p*, or C₆H₄Me-*o*) to give the corresponding σ-vinyl complexes, but other alkynes and olefins do not react. The thermal stability in solution has also been studied; decomposition takes place *via* reductive elimination to give RH. The results obtained are explained in terms of the electronegativity and the size of the ligands and the configuration of the complexes.

Transition-metal complexes containing hydride and σ-carbon-bonded ligands are of current interest since they are involved as intermediates in homogeneously catalysed hydrogenation of unsaturated hydrocarbons and as the products of oxidative addition of C-H bonds to low-valent transition-metal complexes.

While the platinum hydrido complexes have a widely known chemistry, there are relatively few organometallic complexes of this type. Most are of the type *trans*-[PtH(R)L₂], in which the σ-bonded group is electron withdrawing and L are tertiary phosphines, in general PEt₃.¹⁻³ Even fewer complexes of *cis* configuration, usually with bidentate phosphine, have been described because of their instability even at low temperatures.⁴

In order to study the steric and electronic effects on their stability and reactivity, new compounds *trans*-[PtH(R)L₂] with bulky ligands such as PPh₃ and substituted phenyl groups, and *cis*-[PtH(C₆F₅)(PPh₃)₂] and *cis*-[PtH(C₆H₅)(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂), have been prepared.

Results and Discussion

The previously reported hydrido organometallic complexes of platinum were obtained by the reaction between [PtH(Cl)L₂] and Grignard reagents MgR(X)^{4,5} or, more generally, by the action of BH₄⁻ on the halogeno complexes,⁶ or by thermal decomposition of hydroxo-, alkoxo-, or formato-complexes.¹⁻³

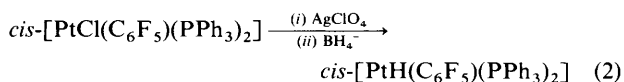
The decarboxylation of the compounds *trans*-[Pt(OCHO)(R)(PPh₃)₂] (R = C₆F₅, C₆Cl₅, C₆HCl₄-2,3,4,6, C₆HCl₄-2,3,4,5, or C₆H₃Cl₂-2,5)⁷ in refluxing methanol leads to *trans*-[PtH(R)(PPh₃)₂]. These can also be obtained by decarboxylation of the *cis* formate complexes, since the *cis*-to-*trans* isomerization occurs easily for these compounds.

The compound *cis*-[Pt(OCHO)(C₆F₅)(PPh₃)₂] is decomposed by the action of heat and does not lead to any hydrido complex. We have noticed that the decarboxylation occurs in 2 h when R is C₆H₃Cl₂-2,5 while when R is C₆Cl₅ 24 h are required for completion. This result shows that the elimination of CO₂ is less favoured when bulky and electron-withdrawing groups are bound to platinum, in a similar way to the β elimination of formaldehyde from the compounds *trans*-[Pt(OMe)RL₂]. The action of AgClO₄ and Na(OCHO) on the compounds *trans*-[PtBr(R)(PPh₃)₂], when R is less bulky than a polychlorophenyl group, leads directly to the compounds with a hydrido ligand, showing that the decarboxylation occurs at room temperature in this case. The compounds *trans*-[PtH(R)(PPh₃)₂] (R = C₆H₄Me-*p*, C₆H₄Cl-*p*, C₆H₄F-*p*, C₆H₄OMe-*p*, Ph, or C₆H₄Me-*o*) have been obtained in this fashion.

The action of Na(OCHO) on the compounds [Pt(O₂CCF₃)(R)(PPh₃)₂] has been studied; in refluxing methanol this reaction leads to *trans*-[PtH(R)(PPh₃)₂], when R is C₆H₃Cl₂-2,5 or C₆HCl₄-2,3,4,5, by metathesis followed by decarboxylation. However when R is a bulkier group no reaction occurs.

The action of NaBH₄ on the compounds *trans*-[PtX(R)(PPh₃)₂] leads to *trans*-[PtH(R)(PPh₃)₂], when R is a *para*-substituted group or *o*-tolyl. However, for bulkier groups, such as polychlorophenyl, no reaction takes place, and hence the applicability of the preparation methods depends mainly on the volume of the ligands bound to platinum (see Scheme).

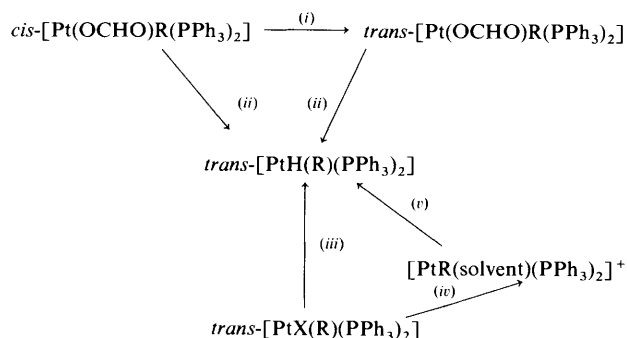
In an attempt to obtain compounds with *cis* configuration, [PtH(Ph)(dppe)] was prepared by the action of NaBH₄ on [PtCl(Ph)(dppe)]. Owing to the small tendency of the compounds with C₆F₅ to isomerize from *cis* to *trans*, it is possible to obtain *cis*-[PtH(C₆F₅)(PPh₃)₂] by the reaction of *cis*-[PtCl(C₆F₅)(PPh₃)₂] with AgClO₄, followed by reaction with NaBH₄ at low temperature [equations (1) and (2)]. The



[†] *trans*-(*p*-Fluorophenyl)hydridobis(triphenylphosphine)platinum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii-xx.

Non-S.I. unit employed: atm = 101 325 Pa.



Scheme. (i) In benzene at 50 °C; (ii) in refluxing methanol, R = C₆Cl₅, C₆HCl₄-2,3,4,6, C₆HCl₄-2,3,4,5, or C₆H₃Cl₂-2,5; (iii) NaBH₄ in CH₂Cl₂ at 0 °C, R = C₆F₅, C₆H₄Me-*o*, C₆H₄Me-*p*, C₆H₄OMe-*p*, C₆H₄Cl-*p*, or C₆H₄F-*p*; (iv) AgClO₄ in methanol; (v) Na(OCHO) in methanol

same method leads to $trans\text{-[PtH(C}_6\text{F}_5\text{)(PPh}_3\text{)}_2\text{]}$ from the *trans* chloro compound.

The new compounds are air stable, white solids, soluble in CH₂Cl₂, CHCl₃, benzene, or toluene, and have been characterized by elemental analysis, decomposition temperatures, and i.r. and n.m.r. spectra. The analytical data are reported in Table 1. The i.r. spectra show bands due to the coordinated ligands and a band due to $\nu(\text{Pt-H})$, characteristic of compounds with a terminal hydrido ligand, which appears in the region 1870—2040 cm⁻¹. The compounds with a *cis* configuration show the highest frequencies due to the smaller *trans* influence of the phosphine as compared to the R group. In the ¹H n.m.r. spectra the hydrido resonance appears at high field, as a triplet with platinum satellites when the configuration is *trans*. In some cases, coupling between the hydrido and the *o*-hydrogen in the R group has been observed, and ⁴*J*(H-H) is about 3 Hz. The values for ¹*J*(H-Pt) are in the range 602—713 Hz and for ²*J*(H-P) between 14 and 18.5 Hz; these values are similar to those reported by Arnold and Bennett.² For the compound $cis\text{-[PtH(C}_6\text{F}_5\text{)(PPh}_3\text{)}_2\text{]}$ the spectrum is more complex, the hydrido resonance appearing as a doublet of doublets with platinum satellites and each signal being split into a triplet due to coupling with the fluorine atoms in *ortho* positions. For the *trans* isomer, the spectrum is not well resolved and the signals appear as multiplets from which the coupling constant with fluorine atoms cannot be measured.

From the values of ¹*J*(Pt-H) for the compounds $trans\text{-[PtH(R)(PPh}_3\text{)}_2\text{]}$ the order of *trans* influence of the R group can be deduced: C₆F₅ < C₆Cl₅ < C₆HCl₄-2,3,4,6 < C₆HCl₄-2,3,4,5 < C₆H₃Cl₂-2,5 < C₆H₄Me-*o* ≈ C₆H₄OMe-*p* ≈ C₆H₄F-*p* ≈ C₆H₄Me-*p* ≈ C₆H₄Cl-*p* ≈ Ph. In fact when R is a *para*-substituted phenyl group, *J*(Pt-H) is nearly constant as observed for analogous compounds with PEt₃;² however, for the other groups ¹*J*(Pt-H) increases with the electron-withdrawing ability of R.

In the ³¹P n.m.r. spectra singlet with platinum satellites is observed when the configuration is *trans* and a doublet of doublets with platinum satellites when the configuration is *cis*. For the compound $cis\text{-[PtH(Ph)(dppe)]}$ the values of ¹*J*(Pt-P) are very similar and hence the *trans* influences of H and phenyl are similar. For the compound $cis\text{-[PtH(C}_6\text{F}_5\text{)(PPh}_3\text{)}_2\text{]}$ the coupling constant ¹*J*(P-Pt) = 2630 Hz is assigned to the phosphorus atom *trans* to the C₆F₅ group, since this signal appears as a broad multiplet due to coupling with F atoms; the well defined doublet [*J*(P-Pt) = 1938 Hz] is then assigned to the phosphorus *trans* to H. From these values it can be deduced that the *trans* influence of C₆F₅ is smaller than those of the hydrido and phenyl ligands.

Table 1. Analytical data, decomposition temperatures, and i.r. data

Compound <i>trans</i> - [PtH(R)(PPh ₃) ₂]	I.r. (cm ⁻¹) $\nu(\text{Pt-H})$	Decomp. temp. (°C)	Analysis (%) [*]		
			C	H	Cl
R					
C ₆ Cl ₅	2 000	214	51.9 (52.0)	3.1 (3.2)	19.0 (18.25)
C ₆ HCl ₄ -2,3,4,6	1 995	218	53.0 (53.9)	3.3 (3.4)	15.2 (15.15)
C ₆ HCl ₄ -2,3,4,5	2 010	212	53.9 (53.9)	3.3 (3.4)	15.3 (15.15)
C ₆ H ₃ Cl ₂ -2,5	1 985	204	58.2 (58.2)	3.8 (3.95)	7.9 (8.2)
C ₆ H ₄ F- <i>p</i>	1 895	205	61.8 (61.85)	4.2 (4.3)	
C ₆ H ₄ Cl- <i>p</i>	1 895	210	60.4 (60.6)	4.2 (4.25)	4.4 (4.25)
C ₆ H ₄ OMe- <i>p</i>	1 880	176	62.1 (62.4)	4.4 (4.65)	
C ₆ H ₄ Me- <i>p</i>	1 870	198	63.6 (63.6)	4.7 (4.7)	
C ₆ H ₄ Me- <i>o</i>	1 960	190	63.8 (63.6)	4.7 (4.7)	
C ₆ F ₅	1 980	130	55.6 (56.8)	3.4 (3.5)	
<i>cis</i> -[PtH(C ₆ F ₅)- (PPh ₃) ₂]	2 040	125	54.8 (56.8)	3.5 (3.5)	
<i>cis</i> -[PtH(Ph)(dppe)]	2 020	175—180	55.9 (57.25)	4.5 (4.45)	

^{*} Calculated values are given in parentheses.

An inverse linear correlation between ¹*J*(P-Pt) and $\nu(\text{Pt-H})$ can be established for the compounds $trans\text{-[PtH(R)(PPh}_3\text{)}_2\text{]}$, thus the *cis* and *trans* influence act in opposite directions. The electron-withdrawing substituents weaken the Pt-P bond while they strengthen the Pt-H bond. Due to the importance of steric effects on those parameters, the compounds with one substituent in *ortho* (R = C₆HCl₄-2,3,4,5, C₆H₃Cl₂-2,5, or C₆H₄Me-*o*; *r* = 0.972) or no substituent in *ortho* positions (R = C₆H₄OMe-*p*, C₆H₄F-*p*, C₆H₄Me-*p*, C₆H₄Cl-*p*, Ph, or C₆F₅; *r* = 0.998) have to be considered separately.

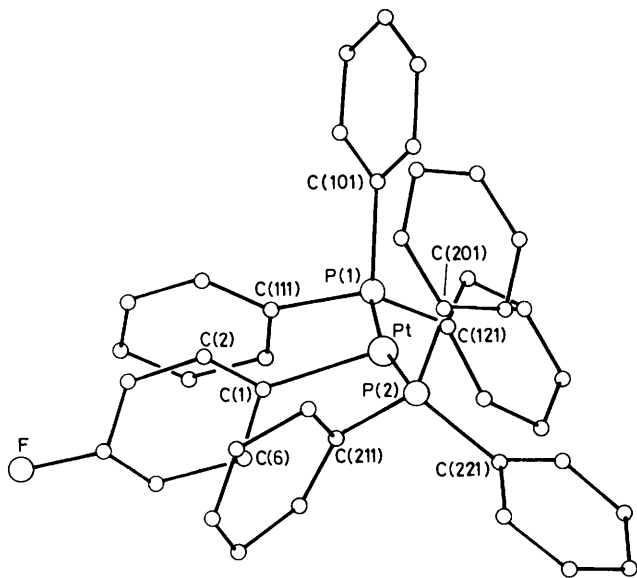
For the compounds $trans\text{-[PtH(R)(PPh}_3\text{)}_2\text{]}$ both ¹H-coupled and ¹H-decoupled ¹⁹⁵Pt-H n.m.r. spectra have been studied. The $\delta(^{195}\text{Pt})$ values are characteristic for platinum(II) compounds, and the values of *J*(Pt-P) and *J*(Pt-H) are in accord with those found by ³¹P or ¹H n.m.r. spectroscopy. A linear correlation has been established between $\delta(\text{H})$ and $\delta(\text{Pt})$ (*r* = 0.986) from which it can be deduced that the chemical shift for both nuclei, directly bound, is affected by the paramagnetic shield of the 5*d* electrons of platinum.

The crystal structure of $trans\text{-[PtH(C}_6\text{H}_4\text{F-}p\text{)(PPh}_3\text{)}_2\text{]}$ is composed of discrete molecules separated by van der Waals distances (Figure). Selected bond lengths and angles are listed in Table 3. The compound exhibits the typical square-planar coordination of Pt, but it is somewhat distorted by the reduced steric requirements of the hydrido ligand. The two P atoms of the phosphine ligands are approximately *trans* to each other; the angle P(1)-Pt-P(2) of 169.6(2)° is nearly equal to that observed in analogous platinum compounds with two triphenylphosphine ligands.^{8,9} The two remaining co-ordination sites are occupied by the carbon atom of the fluorophenyl ligand and by the hydrido ligand. Although the position of the latter has not been detected, its presence has been unambiguously verified by i.r. and ¹H n.m.r. spectroscopy (see above). The P(1), P(2), and C(1) atoms are on a plane, while the Pt atom deviates -0.071(6) Å from this plane. The fluorophenyl ligand is planar, with the

Table 2. ^1H , ^{31}P - $\{^1\text{H}\}$, and ^{195}Pt - $\{^1\text{H}\}$ n.m.r. data^a

<i>trans</i> -[PtH(R)(PPh ₃) ₂]	$\delta(\text{H})^b$	$^1J(\text{H-Pt})$	$^2J(\text{H-P})$	$\delta(^{31}\text{P})$	$^1J(\text{P-Pt})$	$\delta(\text{H})^c$	$\delta(^{195}\text{Pt})^d$
R							
C ₆ Cl ₅	-8.1	684	15.0	-122.8	3 103		-4 968
C ₆ HCl ₄ -2,3,4,6	-7.7	669	15.5	-113.2	3 105		-4 947
C ₆ HCl ₄ -2,3,4,5	-7.1 ^e	650	16.0	-111.1	3 070		-4 938
C ₆ H ₃ Cl ₂ -2,5	-6.7 ^f	631	17.0	-111.3	3 092		-4 923
C ₆ H ₄ F- <i>p</i>	-5.7	605	18.0	-108.5	3 106		-4 882
C ₆ H ₄ Cl- <i>p</i>	-5.7	604	18.0	-109.0	3 103		-4 879
C ₆ H ₄ OMe- <i>p</i>	-5.5	607	18.0	-108.6	3 121	3.5	-4 884
Ph	-5.6	602	18.0	-108.7	3 128		-4 885
C ₆ H ₄ Me- <i>p</i>	-5.5	604	18.5	-108.7	3 142	2.0	-4 878
C ₆ H ₄ Me- <i>o</i>	-5.2	610	18.5	-110.8	3 146	1.6	-4 854
C ₆ F ₅	-6.2	713	14.0	-110.3 ^g	2 989		
<i>cis</i> -[PtH(C ₆ F ₅)(PPh ₃) ₂]	-4.9 ^h	1 040	185.0	-113.8 ⁱ	1 938		
			19.5	-118.2	2 630		
<i>cis</i> -[PtH(Ph)(dppf)]	-1.0	1 272	195.0	-88.4	1 732		
			16.0	-94.3	1 720		

^a In CDCl₃ or CHCl₃ solvent, and at room temperature, unless otherwise stated, referenced to SiMe₄, P(OMe)₃, or PtCl₆²⁻ in D₂O. ^b Hydrido resonance. ^c Other resonances in the R group. ^d At 312 K. ^e $^4J(\text{H-H}) = 2.6$ Hz. ^f $^4J(\text{H-H}) = 3.0$ Hz. ^g In benzene. ^h $^4J(\text{H-F}) = 5.2$ Hz. ⁱ In toluene at 213 K, $^2J(\text{P-P}) = 14.5$ Hz.

**Figure.** Molecular structure of *trans*-[PtH(C₆H₄F-*p*)(PPh₃)₂]

largest deviation of 0.05(2) Å being for C(4). Unlike other square-planar aryl complexes of Ni^{II} and Pt^{II},^{10,11} the fluorophenyl ligand is not perpendicular to the platinum square plane, the dihedral angle being 109.7(7)°.

The Pt-P distances [2.256(6) and 2.264(5) Å] are similar to those found in analogous hydrido compounds as in *trans*-[PtH(CH₂CN)(PPh₃)₂] [2.276(4) and 2.272(4) Å]⁸ and in *trans*-[PtH{N₂(C₆H₄Me-*p*)₂}(PPh₃)₂] [2.268(5) and 2.267(5) Å],⁹ but are somewhat longer than those found in the analogous chloro complexes.^{8,12}

The Pt-C bond length [2.066(23) Å] is longer than the predicted value, but is very similar to those found in other platinum compounds such as *trans*-[Pt(CO)(C₆H₄Cl-*p*)(PEt₃)₂]PF₆ [2.06(4) Å],¹¹ *cis*-[PtCl(C₆H₄Me-*p*)(PEt₃)₂] [2.05(3) Å],¹³ *cis*-[PtCl(C₆F₅)(PEt₃)₂] [2.08(2) Å],¹³ and *cis*-[Pt(C₆H₄NO₂-*o*)₂(PPh₃)₂] [2.061(6) and 2.060(6) Å],¹⁴ indicating that the *trans* influence of H is similar to that of CO and the phosphine ligands.

Table 3. Selected bond lengths (Å) and angles (°) for *trans*-[PtH(C₆H₄F-*p*)(PPh₃)₂]

Pt-P(1)	2.256(6)	C(3)-C(2)	1.361(33)
Pt-P(2)	2.264(5)	C(4)-C(3)	1.447(40)
Pt-C(1)	2.066(23)	C(5)-C(4)	1.336(46)
C(2)-C(1)	1.395(33)	F-C(4)	1.382(31)
C(6)-C(1)	1.506(33)	C(6)-C(5)	1.502(35)
P(2)-Pt-P(1)	169.6(2)	C(6)-C(1)-Pt	116.0(16)
C(1)-Pt-P(1)	96.0(7)	C(6)-C(1)-C(2)	120.1(20)
C(1)-Pt-P(2)	93.6(7)	C(3)-C(2)-C(1)	122.1(22)
C(101)-P(1)-Pt	115.0(7)	C(4)-C(3)-C(2)	120.0(23)
C(111)-P(1)-Pt	117.4(8)	C(5)-C(4)-C(3)	121.3(25)
C(121)-P(1)-Pt	109.1(7)	F-C(4)-C(3)	114.8(26)
C(201)-P(2)-Pt	112.4(7)	F-C(4)-C(5)	123.1(27)
C(211)-P(2)-Pt	115.5(7)	C(6)-C(5)-C(4)	121.6(26)
C(221)-P(2)-Pt	111.9(8)	C(5)-C(6)-C(1)	114.0(22)
C(2)-C(1)-Pt	123.6(17)		

The packing forces determine an eclipsed form for Pt-P(1) and Pt-P(2); the atoms C(111), P(1), Pt, P(2), C(211) are nearly on a plane with torsion angles of -2.1(7) and -6.5(7)°.

The thermal decomposition of the hydridoalkyl or hydridoaryl complexes of platinum occurs by an intramolecular reductive elimination with formation of the corresponding RH, and therefore the *cis* isomers are less stable than the *trans* because in the former the R and H ligands are in adjacent positions. For instance, while the compound *cis*-[PtH(Me)(PPh₃)₂] is decomposed in solution at -25 °C to give CH₄,⁴ the analogous *trans* complex is stable in solution at room temperature, even with smaller phosphines such as PEt₃. The thermal stability in solution has been studied for the new complexes, and a considerably greater stability is observed than for the PEt₃ analogues.² Where R is a *para*-substituted group, the compounds *trans*-[PtH(R)(PPh₃)₂] decompose partially after 24 h in refluxing xylene to give RH, phosphine, and a red compound which could not be identified, and which is believed to arise from the oligomerization of [Pt(PPh₃)₂]. When the refluxing period is 48 h, there is total decomposition to give RH, PPh₃O, and metallic platinum. When R is C₆F₅, C₆Cl₅, or C₆H₃Cl₂-2,5, the corresponding hydrido complexes are recovered and are only decomposed in refluxing *n*-decane to

Table 4. Positional parameters with estimated standard deviations in parentheses

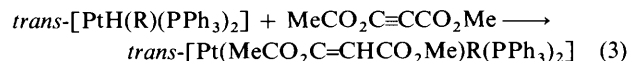
Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pt	14 774(3)	17 147(3)	9 976(8)	C(203)	725(9)	494(12)	-1 968(25)
P(1)	1 397(2)	2 651(2)	911(5)	C(204)	484(10)	-17(13)	-1 794(24)
C(101)	1 071(8)	2 913(9)	-374(17)	C(205)	526(12)	-314(11)	-813(32)
C(102)	694(10)	2 627(11)	-960(25)	C(206)	785(10)	-86(10)	134(25)
C(103)	462(11)	2 829(11)	-1 913(29)	C(211)	2 036(7)	388(9)	1 239(20)
C(104)	575(10)	3 367(12)	-2 323(29)	C(212)	2 195(10)	58(11)	342(23)
C(105)	934(10)	3 676(11)	-1 757(26)	C(213)	2 708(10)	-181(11)	319(27)
C(106)	1 193(9)	3 475(9)	-752(19)	C(214)	3 039(10)	-55(11)	1 264(25)
C(111)	1 995(8)	3 061(10)	1 054(25)	C(215)	2 865(10)	285(11)	2 141(23)
C(112)	2 378(8)	3 004(10)	268(26)	C(216)	2 364(9)	497(9)	2 158(24)
C(113)	2 864(10)	3 278(14)	184(26)	C(221)	1 074(8)	531(11)	2 561(20)
C(114)	2 931(12)	3 656(14)	1 095(31)	C(222)	1 153(9)	45(12)	3 071(26)
C(115)	2 601(14)	3 720(12)	1 989(27)	C(223)	910(18)	-90(12)	4 057(26)
C(116)	2 074(10)	3 450(11)	1 947(23)	C(224)	581(12)	292(19)	4 625(25)
C(121)	993(8)	2 886(8)	2 102(23)	C(225)	516(10)	800(15)	4 154(24)
C(122)	641(11)	3 350(11)	2 081(35)	C(226)	761(8)	944(10)	3 104(20)
C(123)	366(12)	3 533(15)	3 119(40)	C(1)	2 290(9)	1 706(10)	1 167(21)
C(124)	452(15)	3 225(15)	4 085(31)	C(2)	2 557(9)	1 920(9)	2 126(21)
C(125)	803(12)	2 781(15)	4 185(33)	C(3)	3 093(10)	1 904(9)	2 214(22)
C(126)	1 066(9)	2 642(10)	3 177(23)	C(4)	3 408(11)	1 713(12)	1 244(29)
P(2)	1 404(2)	778(2)	1 189(5)	C(5)	3 183(10)	1 489(11)	305(32)
C(201)	1 031(8)	463(8)	6(22)	C(6)	2 595(9)	1 503(9)	127(20)
C(202)	1 003(8)	737(10)	-1 030(21)	F	3 946(6)	1 698(7)	1 448(18)

give metallic platinum, RH, and PPh_3O . The decomposition process is an intramolecular reductive elimination as inferred from the facts that no R-R is formed, and that the decomposition of mixtures of *trans*-[PtH(C₆H₄Cl-*p*)(PPh₃)₂] and *trans*-[PtH(C₆H₄Me-*p*)(PPh₃)₂] leads only to chlorobenzene and toluene. The addition of PPh₃ to a refluxing xylene solution of the compound *trans*-[PtH(C₆H₄Me-*p*)(PPh₃)₂] does not affect the rate of formation of RH but the formation of metallic platinum is retarded. In the presence of a phosphine-trapping agent, such as sulphur, the decomposition is notably accelerated, and within 1 h the resulting products are PPh₃S, RH, and metallic platinum. This result shows that the mechanism for the thermal decomposition is dissociative. On the other hand, the thermal decomposition is accelerated when carbon monoxide is bubbled through the solution, similarly to the result of Arnold and Bennett² for the analogous triethylphosphine compounds.

The observed trend in stability of these hydrido complexes with *trans* configuration is consistent with the steric effects arising from *ortho* substituents in the R group and with the greater volume of PPh₃, as compared to PEt₃. The *cis* compounds reported in this paper are fairly stable, although they are decomposed more easily than the *trans* complexes. The compound *cis*-[PtH(C₆F₅)(PPh₃)₂] is decomposed in benzene or toluene at room temperature within several hours to give metallic platinum, [Pt(PPh₃)₃], and C₆HF₅; its stability is less than that of *cis*-[PtH(C₆Cl₅)(PEt₃)₂],³ which may be due to the *ortho* effect of the chlorine atoms in the C₆Cl₅ group of similar electronegativity as C₆F₅, since PPh₃ is bulkier than PEt₃. The compound *cis*-[PtH(Ph)(dppe)] is much more stable since it can be recovered after 24 h in xylene at 80 °C, and is only decomposed in refluxing xylene. Its greater stability, despite C₆F₅ being more electron withdrawing than Ph, may be due to the bidentate phosphine as the mechanism for the reductive elimination is dissociative. The lower stability of the compounds with a *cis* configuration is consistent with the easier reductive elimination of adjacent groups.

The insertion of unsaturated molecules into M-H bonds is a well established reaction which is relevant to different catalytic

processes. This reaction takes place easily for [PtH(X)L₂] but much less readily for [PtH(R)L₂].² Insertion products have been obtained only for strongly activated alkynes such as MeCO₂C≡CCO₂Me and platinum complexes with not too bulky R groups [equation (3); R = C₆H₄Cl-*p*, C₆H₄Me-*p*, or C₆H₄Me-*o*].



The compounds obtained have been characterized by elemental analyses, i.r., ¹H and ³¹P n.m.r. spectra. The bands due to ν(C=O) appear at 1 690–1 675 cm⁻¹ and those due to ν(C–O) at 1 170–1 150 and 1 230–1 205 cm⁻¹, while the band due to the double bond C=C, in the vinyl ligand, appears at 1 570–1 580 cm⁻¹. In the ¹H n.m.r. spectrum two signals of the non-equivalent methyl substituents of the ester groups appear in the region 3–3.6 p.p.m., but the resonance due to the vinyl proton has not been observed, probably being hidden under the intense signal of PPh₃ at 7–7.6 p.p.m. The ³¹P n.m.r. spectrum shows the *trans* arrangement of the phosphines. For bulkier R groups such as polychlorophenyl no insertion occurs even when more strenuous conditions are used. This result can be related to the greater difficulty of acetylene in co-ordinating to platinum, in a previous step, and to the greater strength of the Pt–H bond in these compounds, as can be deduced from the ¹J(Pt–H) values. No insertion takes place for the reagents PhC≡CPh, PhC≡CH, and CH₂=CHCO₂Me, showing that highly electron-withdrawing groups are required for insertion into the electron-rich Pt–H bond.

The reaction of the compounds *trans*-[PtH(R)(PPh₃)₂] with CO, at high pressure, does not lead to insertion into Pt–H or Pt–C bonds. For R = C₆H₄Cl-*p* or C₆H₃Cl₂-2,5, at a pressure of 50 atm, the compounds decompose within 12 h to give RH and [Pt(PPh₃)₂(CO)₂], showing the greater tendency towards reductive elimination than to insertion. However for R = C₆Cl₅ the starting material is recovered due to the high stability of the Pt–C₆Cl₅ bond.

Experimental

Chemical analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona. The ^1H , ^{31}P - $\{^1\text{H}\}$, and ^{195}Pt n.m.r. spectra were obtained on a Bruker FT-80-SY spectrometer, i.r. spectra with a Beckman Acculab 4. Gas chromatography was carried out on a Hewlett-Packard 5710A instrument.

Crystallography.—*Crystal data.* $\text{C}_{42}\text{H}_{35}\text{FP}_2\text{Pt}$, $M = 815.78$, orthorhombic, $a = 25.304(5)$, $b = 23.963(5)$, $c = 11.530(3)$ Å, $U = 6991(3)$ Å³, space group $Pcab$, $Z = 8$, $D_c = 1.550$ g cm⁻³, $F(000) = 3232$, $\lambda(\text{Mo-K}_\alpha) = 0.71069$ Å, $\mu(\text{Mo-K}_\alpha) = 43.49$ cm⁻¹, 288 K.

Data collection. A tabular crystal (0.1 × 0.1 × 0.07 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12^\circ$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-K α radiation, using the ω -scan technique, with scan width 0.8° and scan speed $0.03^\circ \text{ s}^{-1}$. 2791 Reflections were measured in the range $2 \leq \theta \leq 22.5^\circ$, 2275 being observed [$I \geq 2.5\sigma(I)$]. Three reflections were measured every 2 h as orientation and intensity control, but significant intensity decay was not observed. Lorentz polarization and absorption corrections were made.

Structure solution and refinement. The structure was solved by direct methods, using the MULTAN system of computer programs¹⁵ and refined by full-matrix least-squares, using the SHELX 76 program.¹⁶ The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma|F_o|^2 + 0.014|F_o|^2]^{-1}$; f , f' , and f'' were taken from ref. 17.

The positions of hydrogen atoms were computed and refined with an overall isotropic thermal parameter, and the remaining atoms were treated anisotropically. The final R was 0.067 ($R' = 0.068$) for all observed reflections. Maximum peak in the final difference synthesis $0.06 \text{ e } \text{Å}^{-3}$. Maximum shift/error = -0.25 in U_{11} of C(1).

Additional material available from the Cambridge Crystallographic Centre comprises thermal parameters and remaining bond lengths and angles.

Materials.—The compounds $\text{trans}[\text{PtBr}(\text{R})(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Y-}p$; $\text{Y} = \text{H, Cl, F, or Me}$),¹⁸ $\text{cis- and trans}[\text{Pt}(\text{OCHO})\text{R}(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{Cl}_5, \text{C}_6\text{F}_5, \text{C}_6\text{HCl}_4\text{-}2,3,4,6, \text{C}_6\text{HCl}_4\text{-}2,3,4,5, \text{ or } \text{C}_6\text{H}_3\text{Cl}_2\text{-}2,5$),⁷ $[\text{Pt}(\text{O}_2\text{CCF}_3)\text{R}(\text{PPh}_3)_2]$,¹⁹ $\text{cis- and trans}[\text{PtCl}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2]$,²⁰ and $[\text{PtCl}(\text{Ph})(\text{dppe})]$ ²¹ were prepared by previously described procedures.

Preparations.— $[\text{PtCl}(\text{C}_6\text{H}_4\text{Me-}o)(\text{PPh}_3)_2]$. The compounds $[\text{Pt}(\text{PPh}_3)_3]$ (1 mmol) and $\text{Hg}(\text{C}_6\text{H}_4\text{Me-}o)\text{Cl}$ (1 mmol) were dissolved in toluene and stirred under a nitrogen atmosphere for 6 h. The metallic mercury was filtered off and the solvent removed; the residue was washed with hexane and recrystallized from dichloromethane-methanol. Yield 70%. ^{31}P N.m.r. in CHCl_3 , reference $\text{P}(\text{OMe})_3$; $\delta(\text{P}) - 117.6$ p.p.m., $J(\text{P-Pt}) = 3135$ Hz.

$\text{trans}[\text{PtH}(\text{R})(\text{PPh}_3)_2]$. (a) From $[\text{Pt}(\text{OCHO})\text{R}(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{Cl}_5, \text{C}_6\text{HCl}_4\text{-}2,3,4,6, \text{C}_6\text{HCl}_4\text{-}2,3,4,5, \text{ or } \text{C}_6\text{H}_3\text{Cl}_2\text{-}2,5$). The corresponding formate complex (*cis* or *trans*) (1.0 mmol) was dissolved in the minimum amount of CH_2Cl_2 , and methanol (20 cm³) was added. The mixture was refluxed with stirring for several hours. On cooling, a white precipitate was formed. This was recrystallized from dichloromethane-methanol. Yield 80–85%.

(b) From $[\text{Pt}(\text{O}_2\text{CCF}_3)\text{R}(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{HCl}_4\text{-}2,3,4,5$ or $\text{C}_6\text{H}_3\text{Cl}_2\text{-}2,5$). A mixture of $[\text{Pt}(\text{O}_2\text{CCF}_3)\text{R}(\text{PPh}_3)_2]$ (1 mmol), $\text{Na}(\text{OCHO})$ (6.0 mmol), and methanol (20 cm³) was refluxed with stirring for 4 h. The solvent was removed and the solid extracted with dichloromethane. On adding methanol, the compounds $[\text{PtH}(\text{R})(\text{PPh}_3)_2]$ were formed. Yield 50%.

(c) From $[\text{PtX}(\text{R})(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Y-}p$; $\text{Y} = \text{H, Cl, Me, or OMe}$, $\text{X} = \text{Br}$; $\text{R} = \text{C}_6\text{H}_4\text{Me-}o$, $\text{X} = \text{Cl}$). Two methods were used.

A solution of AgClO_4 (1.2 mmol) in methanol (20 cm³) was added to a solution of $\text{trans}[\text{PtX}(\text{R})(\text{PPh}_3)_2]$ (1.0 mmol) in chloroform (20 cm³). The mixture was stirred in the dark at room temperature, the silver halide was filtered off, and the residue washed with chloroform. The solvent was removed and the residue extracted with chloroform. To this solution, a solution of $\text{Na}(\text{OCHO})$ (5.5 mmol) in methanol (20 cm³) was added. The mixture was stirred for 6 h, then the solvent was removed and the residue extracted with dichloromethane. On adding methanol and cooling, a white precipitate was obtained. Yield 70%.

The compound $\text{trans}[\text{PtX}(\text{R})(\text{PPh}_3)_2]$ (0.2 mmol) was dissolved in CH_2Cl_2 (10 cm³) and a solution of NaBH_4 (1.2 mmol) in ethanol was added dropwise at 0°C . After stirring for 2 h the solvent was removed, and the residue extracted with CH_2Cl_2 . On adding methanol to a solution a white solid was formed. Yield 60%.

cis- and trans- $[\text{PtH}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2]$. A solution of AgClO_4 (0.48 mmol) in methanol was added to a solution of *cis-* or *trans*- $[\text{PtCl}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2]$ (0.48 mmol) in CH_2Cl_2 under a nitrogen atmosphere. The mixture was stirred for 1 h (*cis* isomer) or 24 h (*trans* isomer). The AgCl was filtered off and the solution was cooled (0°C for the *trans* isomer; -40°C for the *cis* isomer) and solid NaBH_4 (1.92 mmol) was added. The mixture was stirred for 1 h, the solvent removed, and the solids obtained were recrystallized from CH_2Cl_2 -methanol. Yield 40–45%.

$[\text{PtH}(\text{Ph})(\text{dppe})]$. A solution of NaBH_4 (1.55 mmol) in ethanol was added to a solution of $[\text{PtCl}(\text{Ph})(\text{dppe})]$ (0.28 mmol) in CH_2Cl_2 at -40°C , under nitrogen. The mixture was stirred for 40 min, and the solvent removed. Dichloromethane (5 cm³) was added, the solution was filtered, and methanol (15 cm³) was added. The volume of the solution was reduced to 10 cm³ whereupon a white solid was formed. Yield 30%.

$[\text{Pt}(\text{MeO}_2\text{CC}=\text{CHCO}_2\text{Me})\text{R}(\text{PPh}_3)_2]$. To a solution of $\text{trans}[\text{PtH}(\text{R})(\text{PPh}_3)_2]$ (0.18 mmol) ($\text{R} = \text{C}_6\text{H}_4\text{Cl-}p, \text{C}_6\text{H}_4\text{Me-}p, \text{ or } \text{C}_6\text{H}_4\text{Me-}o$) in benzene (20 cm³), $\text{MeO}_2\text{CC}=\text{CHCO}_2\text{Me}$ (0.18 mmol) was added and the mixture was refluxed for 30 min and then reduced to half volume. On adding hexane, a white solid crystallized. When $\text{R} = \text{C}_6\text{H}_4\text{Me-}o$, a slight excess of acetylene was used (0.225 mmol) and the reaction time was 2 h. The products were recrystallized from benzene-hexane. Yield 70–75%.

$\text{R} = \text{C}_6\text{H}_4\text{Cl-}p$, m.p. 158–160 °C (decomp.) (Found: C, 59.7; H, 4.2; Cl, 3.3. Calc.: C, 59.15; H, 4.20; Cl, 3.65%). N.m.r. in CDCl_3 : ^1H (SiMe₄), $\delta(\text{CO}_2\text{CH}_3)$ 3.2(s)—3.6(s) p.p.m.; ^{31}P [$\text{P}(\text{OMe})_3$], $\delta(\text{P}) - 122.0$ p.p.m., $J(\text{P-Pt}) = 3168$ Hz. $\text{R} = \text{C}_6\text{H}_4\text{Me-}p$, m.p. 140–142 °C (decomp.) (Found: C, 61.9; H, 4.7. Calc.: C, 61.70; H, 4.60%). N.m.r. in CDCl_3 : ^1H (SiMe₄), $\delta(\text{CO}_2\text{CH}_3)$ 3.2(s)—3.6(s) and $\delta(\text{CH}_3)$ 1.8(s) p.p.m.; ^{31}P [$\text{P}(\text{OMe})_3$], $\delta(\text{P}) - 121.9$ p.p.m., $J(\text{P-Pt}) = 3211$ Hz. $\text{R} = \text{C}_6\text{H}_4\text{Me-}o$, m.p. 143–145 °C (decomp.) (Found: C, 61.7; H, 4.6. Calc.: C, 61.70; H, 4.60%). N.m.r. in CDCl_3 : ^1H (SiMe₄), $\delta(\text{CO}_2\text{CH}_3)$ 2.9(s)—3.6(s) and $\delta(\text{CH}_3)$ 1.7(s) p.p.m.; ^{31}P [$\text{P}(\text{OMe})_3$], $\delta(\text{P}) - 123.9$ p.p.m., $J(\text{P-Pt}) = 3231$ Hz.

Thermal Decompositions.—The compound $[\text{PtH}(\text{R})(\text{PPh}_3)_2]$ (0.1–0.12 mmol) was dissolved in xylene (15 cm³) or suspended in *n*-decane (15 cm³). The mixture was refluxed under a nitrogen atmosphere. After a period of time the mixture was filtered and the solution analysed by ^{31}P n.m.r. spectroscopy and gas chromatography.

Reactions with CO at High Pressure.—The compound $[\text{PtH}(\text{R})(\text{PPh}_3)_2]$ (0.1–0.12 mmol) was dissolved in CHCl_3 (2 cm³). The mixture was placed in a pressure reactor and 50 atm

CO were introduced. After 12 h, the resulting solutions were analysed by gas chromatography and ^{31}P n.m.r. spectroscopy.

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