

Some Insertion Reactions of Platinum Hydrido-complexes with Olefins : Hydrolysis of Platinum–Carbon σ -Bonds

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The insertion of olefins into the Pt–H bond of *trans*-PtH(NO₃)(PEt₃)₂ occurs *via* preliminary substitution of nitrate by olefin, and the intermediate *trans*-[PtH(C₂H₄)(PEt₃)₂]BPh₄ has been isolated. Butadiene and allene give π -allylic complexes and cyclo-octa-1,5-diene and norbornadiene give enyl-systems. Whereas PhN:CH·CH:·CHPh gives [PtH(PhN:CH·CH:CHPh)(PEt₃)₂]BPh₄ with no insertion, CH₂:CHCOMe gives [Pt(CH₂·CH₂·COMe)(PEt₃)₂]BPh₄, the Pt–C σ -bond of which is readily hydrolysed to give [Pt₂(OH)₂(PEt₃)₄]²⁺ and ethyl methyl ketone.

We have reported preliminary results¹ showing that the facility with which PtHX(PEt₃)₂ inserts olefins depends markedly on the nature of X; the reactions being favoured for good leaving groups such as nitrate. We suggested that the initial step is the substitution of

group X by the olefin to give cationic hydrido-olefin intermediates (certainly under conditions favouring salt formation) and we were able to isolate one such

¹ A. J. Deeming, B. F. G. Johnson and J. Lewis, *Chem. Comm.*, 1970, 598.

species, $[\text{PtH}(\text{C}_2\text{H}_4)(\text{PEt}_3)_2]\text{BPh}_4$. Clark and Kurosawa² recently reported related results confirming our original proposal. These conclusions contrast with the original suggestion,³ for reactions in non-polar solvents such as cyclohexane, that a neutral five-co-ordinate adduct is an intermediate in the reaction of ethylene with $\text{PtHCl}(\text{PEt}_3)_2$ giving an ethyl complex directly. Although adducts such as $\text{PtH}(\text{C}_2\text{H}_4)\text{X}(\text{PEt}_3)_2$ could be involved in the substitution reaction to give $[\text{PtH}(\text{C}_2\text{H}_4)(\text{PEt}_3)_2]^+$, under present experimental conditions they do not appear to lead directly to insertion.

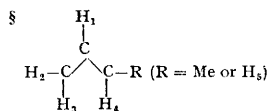
have shown, the chloride can be removed from the complexes PtHClL_2 ($\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}, \text{or PPhMe}_2$) by precipitation as AgCl to give the cationic complexes $[\text{PtH}(\text{acetone})\text{L}_2]^+$ which readily give ethyl complexes on reaction with ethylene at room temperature and at atmospheric pressure. We isolated an intermediate from one such reaction by bubbling ethylene into a solution of $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ and sodium tetraphenylborate in methanol which gave an immediate precipitate of $[\text{PtH}(\text{C}_2\text{H}_4)(\text{PEt}_3)_2]\text{BPh}_4$. Ethylene insertion occurs at rather more forcing conditions for the PEt_3 complex

Analytical, i.r. (measured in cm^{-1}), and n.m.r. data (in CDCl_3 soln) †

Complex *	C ‡	H	P (or As)	N (or F)	Some significant i.r. absorptions			Assignment	τ	Assignment §	Other comments
					CHCl_3	Nujol	Assignment				
$[\text{PtH}(\text{C}_2\text{H}_4)\text{P}_2]\text{BPh}_4$	58.25(58.55)	6.85(7.1)	8.2(7.95)		2196	2206	$\nu(\text{Pt-H})$	6.96 17.20	C_2H_4 Pt-H	$J(\text{Pt-H}) = 35.8$ $J(\text{Pt-H}) = 908$; $J(\text{P-H}) = 12.0$	
$[\text{PtH}(\text{CO})\text{P}_2]\text{BPh}_4$ ^a	57.1(57.0)	6.6(6.6)			2166	2170	$\nu(\text{Pt-H})$	14.66	Pt-H	$J(\text{Pt-H}) = 983$; $J(\text{P-H}) = 13.0$	
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)\text{P}_2]\text{BPh}_4$	58.95(59.15)	6.5(7.0)	7.7(7.85)		2063	2054	$\nu(\text{CO})$	5.55 6.17 7.77	H_1 H_2, H_5 H_3, H_4	$J(\text{H}_{2,3}\text{-H}_1) = 7.0$ $J(\text{H}_{3,4}\text{-H}_1) = 12.8$; $J(\text{Pt-H}_{3,4}) = 21$; $J(\text{H}_{3,4}\text{-P}) = 8.2$	
$[\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{P}_2]\text{BPh}_4$	67.1(66.6)	8.25(7.9)						5.02 6.07 7.38	H_1 H_2, H_5 H_3, H_4	$J(\text{H}_{2,3}\text{-H}_1) = 7.5$ $J(\text{H}_{3,4}\text{-H}_1) = 14$; $J(\text{H}_{3,4}\text{-P}) = 9.5$	
$[\text{Pt}(\pi\text{-C}_4\text{H}_7)\text{P}_2]\text{BPh}_4$ $[\text{Pt}(\pi\text{-C}_4\text{H}_7)\text{P}_2]\text{PF}_6$	59.45(59.6) 30.4(30.45)	7.55(7.15) 5.85(5.9)	7.9(7.7) 14.9(14.7)	18.4(18.05)				5.35 6.4 7.8	H_1 H_2, H_4 H_5	Assignments assisted by previous assignments on related compounds. Me signal obscured by PEt_3 signals	
$[\text{Pd}(\pi\text{-C}_4\text{H}_7)\text{P}_2]\text{BPh}_4$	67.25(67.0)	7.95(8.0)	8.9(8.65)					5.30 6.5 7.8	H_1 H_2, H_4 H_5	$J(\text{H}_1\text{-H}_2) = 7.5$; $J(\text{H}_1\text{-H}_4) = 13$ $J(\text{H}_5\text{-P}) = 10$	
$[\text{Pt}(\pi\text{-C}_4\text{H}_7)\text{As}_2]\text{BPh}_4$	54.0(53.75)	6.45(6.45)	17.15(16.75)					5.16 5.6—6.4 7.7	H_1 H_2, H_4 H_5	$J(\text{H}_1\text{-H}_2) = 13$	
$[\text{Pt}(\text{C}_6\text{H}_5)\text{P}_2]\text{BPh}_4$ $[\text{Pt}(\text{C}_6\text{H}_5)\text{P}_2]\text{BPh}_4$ $[\text{PtH}(\text{PhN}:\text{CH}:\text{CH}:\text{CHPh})\text{P}_2]\text{BPh}_4$ ^b	61.3(61.45) 59.95(61.2) 63.9(63.9)	7.4(7.4) 7.05(7.05) 6.7(6.75)	7.45(7.2) 7.05(7.35) 6.4(6.45)	1.4(1.45)	2195	3200	$\nu(\text{Pt-H})$	27.90	Pt-H	$J(\text{Pt-H}) = 1119$; $J(\text{P-H}) = 14.8$; $J(\text{H-H}) = 3.5$	
$[\text{Pt}(\text{CH}_2\text{=C}^a\text{CH}_2\text{=C}^b\text{COCH}_3\text{e})\text{P}_2]\text{BPh}_4$ ^c	58.35(58.5)	6.9(7.0)			1558	1563	$\nu(\text{C:N})$	7.35	H^a	Complex multiplets due to the phenyl and olefin hydrogens	
					1615	1613	$\nu(\text{CO})$	8.14	H^c		
$\text{Pt}_2(\text{OH})_2\text{P}_4(\text{BF}_4)_2$ ^d	27.5(26.95)	5.9(5.85)	11.7(11.6)	14.5(14.2)		3450	$\nu(\text{OH})$	6.48	OH	Multiplet Singlet H^b signal probably lies under the CH_3 signal of the PEt_3 ligand Recorded in SO_2 solution. Half-height width of absorption variable (8—24 Hz) depending on the particular solution.	

^a $\nu(\text{Pt-H})$, 2167; $\nu(\text{CO})$, 2064 reported for $[\text{PtH}(\text{CO})\text{P}_2]\text{ClO}_4$. ^b An absorption at 1576 cm^{-1} is probably due to tetraphenylborate. ^c Treatment of a chloroform solution with PEt_3 gave a non-co-ordinated ketonic species with $\nu(\text{CO})$ at 1704 cm^{-1} . ^d $\nu(\text{OD})$ for the corresponding OD-complex in chloroform, 2546 cm^{-1} .

* $\text{P} = \text{PEt}_3, \text{As} = \text{AsEt}_3$. † Resonances due to $\text{PEt}_3, \text{AsEt}_3$, or BPh_4 are as expected and not included in the Table. ‡ Found % with required values in parentheses.



Here we report our results on reactions of $\text{PtHX}(\text{PEt}_3)_2$ with ethylene, conjugated or non-conjugated dienes or the heterodienes, methyl vinyl ketone, and the cinnamaldehyde anil $\text{PhN}:\text{CH}:\text{CH}:\text{CHPh}$.

Reactions of Platinum Hydrides with Ethylene.—The reaction of $\text{PtHCl}(\text{PEt}_3)_2$ with ethylene in cyclohexane (80 atm, 95°C) leads to a 25% conversion into $\text{PtEtCl}(\text{PEt}_3)_2$ and this reaction is reversed by heating the ethyl complex *in vacuo* at 180°C .⁴ Higher pressures (192 atm, 80°C) and the use of tetrahydrofuran as solvent gave complete reaction.³ Insertion can occur under milder conditions since, as Clark and Kurosawa²

than for those described above,² and therefore the cationic hydrido-ethylene complex could be isolated at room temperature. The complex is only moderately stable in solution, slowly giving $\text{PtPh}_2(\text{PEt}_3)_2$ ⁵ by reaction with the BPh_4^- anion. The complex $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ similarly gives this phenyl complex on slow reaction with NaBPh_4 in methanol.

The n.m.r. spectrum of the complex $\text{trans-}[\text{PtH}(\text{C}_2\text{H}_4)(\text{PEt}_3)_2]\text{BPh}_4$ (see Table) illustrates the *trans*-configuration since the hydrido-ligand is coupled to two equivalent ^{31}P nuclei (12.0 Hz). Thus not only is the ethylene *trans* to the strongly *trans*-labilising

² H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.

³ J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. (A)*, 1968, 190.

⁴ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

⁵ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

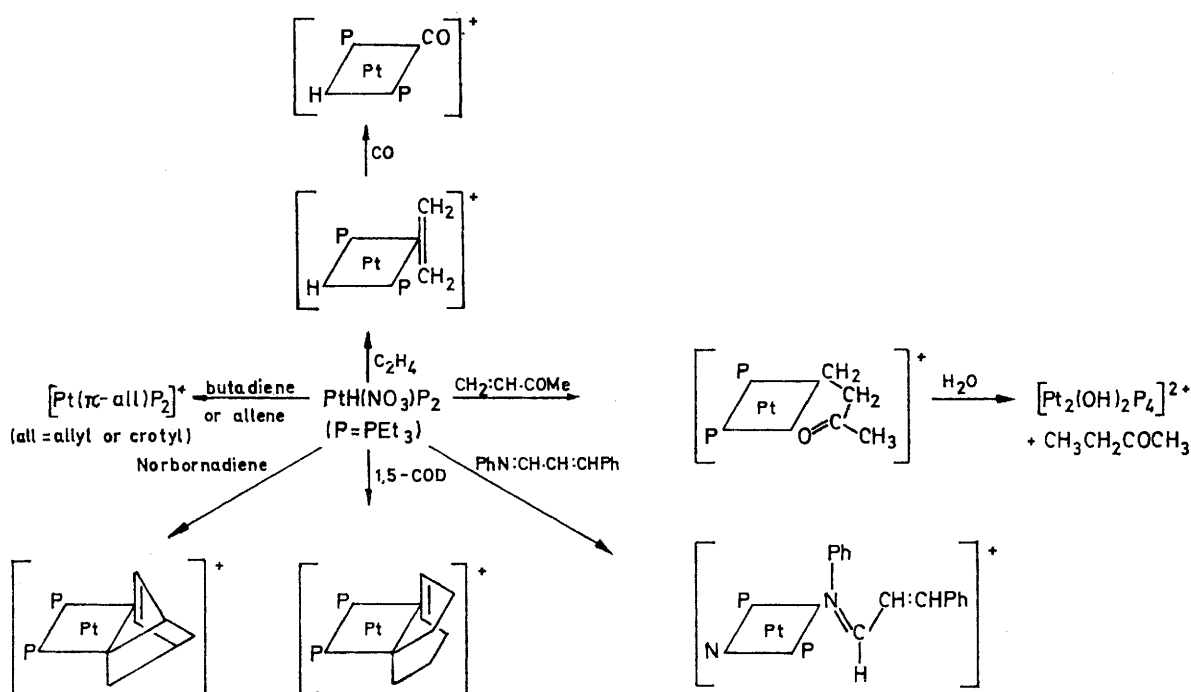
hydride but also the cationic nature of the complex should reduce the π -basicity of the platinum to the olefin. Both factors are expected to make the complex unstable and yet it is sufficiently stable to be stored indefinitely under nitrogen at 0 °C. The stability may be due to the *trans*-arrangement since the subsequent ethylene insertion reaction requires either a *trans*-*cis* isomerisation or co-ordination of another ethylene molecule. In these ways the hydride and the olefin can take up *cis*-positions in the co-ordination sphere. The ethylene is very readily displaced by CO to give $[\text{PtH}(\text{CO})(\text{PEt}_3)_2]\text{BPh}_4$, previously prepared with other counter anions,⁶ or by chloride to give $\text{PtHCl}(\text{PEt}_3)_2$.

Reactions of Platinum Hydrides with Dienes.— $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ reacts rapidly with various dienes in

arrangement of the methyl groups, which is presumably thermodynamically most stable. We have no direct evidence for the structures of the cyclo-octenyl or norbornenyl complexes but assume that these are as in the Scheme.

Reactions of Platinum Hydrides with Heterodienes.—Because of the ease and generality with which the insertion into the Pt-H bond by dienes was shown to occur we examined the related reactions with the heterodienes $\text{PhN}:\text{CH}:\text{CH}:\text{CHPh}$ and $\text{CH}_2:\text{CHCOMe}$. If insertion occurred we wished to establish to which atom the hydride had added and whether or not π -allylic groups containing heteroatoms had been formed.

The cinnamaldehyde anil $\text{PhN}:\text{CH}:\text{CH}:\text{CHPh}$ reacts readily with $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ to give a cationic complex,



methanol to give complexes of type $[\text{Pt}(\text{enyl})(\text{PEt}_3)_2]^+$ where enyl = π -allyl (from allene), π -crotyl (from butadiene), cyclo-octa-4-enyl (from cyclo-octa-1,5-diene), or norbornenyl (from norbornadiene). Similar but much slower reactions occur for $\text{PtHCl}(\text{PEt}_3)_2$. No cationic hydrido-olefin complexes were detected in these reactions presumably because the insertions occurred much more rapidly than for ethylene. Nevertheless we believe that such intermediates are formed because of the effect of the anionic ligand on the rate of the reaction.

The nature of the π -allylic complex $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PEt}_3)_2]^+$ and the π -crotyl $[\text{Pt}(\pi\text{-C}_4\text{H}_7)(\text{PEt}_3)_2]^+$ were confirmed by the close similarity of their i.r. and n.m.r. spectra with those of the analogous palladium complexes prepared by the reaction of PEt_3 with $[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2$ or $[(\pi\text{-C}_4\text{H}_7)\text{PdCl}]_2$ using a known procedure.⁷ The n.m.r. data are recorded in the Table. These show that the platinum and palladium π -crotyl complexes both have the *anti*-

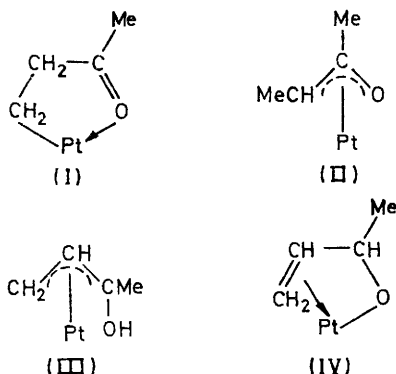
which was precipitated as the tetraphenylborate salt and shown to be *trans*- $[\text{PtH}(\text{PhN}:\text{CH}:\text{CH}:\text{CHPh})(\text{PEt}_3)_2]\text{BPh}_4$. The lack of insertion was confirmed by the i.r. spectrum, $\nu(\text{Pt-H}) = 2195 \text{ cm}^{-1}$, and the hydride n.m.r. signal. As well as the expected nuclear spin-spin coupling of the hydride with the ^{31}P and the ^{195}Pt nuclei there was a further coupling of 3.5 Hz presumably to a vinylic hydrogen of the N-containing ligand. Co-ordination through the nitrogen and the lack of co-ordination through the carbon-carbon double bond are apparent in the small changes in the n.m.r. and i.r. spectra of the ligand on co-ordination. Insertion also fails to occur under more vigorous treatment. Reaction of $\text{PtHCl}(\text{PEt}_3)_2$ and $\text{PhN}:\text{CH}:\text{CH}:\text{CHPh}$ in refluxing solvent (2 h in methanol or $7\frac{1}{2}$ h in 2-methoxyethanol)

⁶ H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 3360.

⁷ J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1968, 774.

followed by addition of NaBPh_4 gave a good yield of $[\text{PtH}(\text{PhN}:\text{CH}:\text{CH}:\text{CPh})(\text{PEt}_3)_2]\text{BPh}_4$ in each case. It is possible that the configuration of the ligand is as shown in the Scheme and it is this *trans*-arrangement about the N:C bond which prevents co-ordination of the C:C to the platinum and hence insertion.

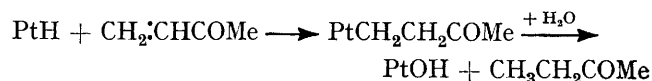
This behaviour contrasts markedly with that of the $\alpha\beta$ -unsaturated ketone, $\text{CH}_2:\text{CHCOMe}$, which reacts readily with $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ and NaBPh_4 in methanol to give a precipitate immediately of the 2-acetyethyl complex $[\text{Pt}(\text{CH}_2\text{CH}_2\text{COMe})(\text{PEt}_3)_2]\text{BPh}_4$. We believe that in this case the initial interaction with the metal takes place through the olefinic group rather than the hetero-atom and insertion can readily occur. Of the four possible types of bonding (I)—(IV) shown we



believe that the linkage between the $\text{C}_4\text{H}_7\text{O}$ group and the platinum is as shown in (I). The value of $\nu(\text{CO})$ at 1615 cm^{-1} is only 109 cm^{-1} below that of the methyl vinyl ketone while structures (II)—(IV) would require a much greater reduction than this. A frequency of 1600 cm^{-1} has been reported for a ketone co-ordinated to platinum(II) in a chelate system.^{8,9} The n.m.r. spectrum of our complex is also completely consistent with bonding type (I) (see Table). This bonding also occurs in intermediates formed in the hydrogenation of $\alpha\beta$ -unsaturated ketones catalysed by $\text{IrHCl}_2(\text{Me}_2\text{SO})_3$.¹⁰ Further the reaction of $\text{Mn}(\text{CO})_5$ with (*o*-vinylphenyl)diphenylphosphine has been shown to give two isomeric compounds, $\text{Mn}(\text{CO})_3(\text{Ph}_2\text{PC}_6\text{H}_4\text{C}_4\text{H}_6\text{O})$, which have been studied by X-ray structural analysis.¹¹ One isomer with $\nu(\text{CO})$ at 1644 cm^{-1} contains metal-ligand bonding entirely analogous to (I), while the other isomer has bonding as in (II) with no i.r. band assignable to $\nu(\text{C}=\text{O})$. These results support our structural assignment.

Hydrolysis of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{COMe})(\text{PEt}_3)_2]\text{BPh}_4$.—Our attempts to prepare this complex with other counter anions were unsuccessful owing to the ready hydrolysis of the Pt-C σ -bond. For example, the complex $[\text{PtH}(\text{solvent})(\text{PEt}_3)_2]\text{BF}_4$, formed in methanol by treat-

ment of $\text{PtHCl}(\text{PEt}_3)_2$ with AgBF_4 , was treated with methyl vinyl ketone to give a cationic complex which proved to be $[\text{Pt}_2(\text{OH})_2(\text{PEt}_3)_4](\text{BF}_4)_2$. It was possible that an intermediate complex containing a Pt-C bond had been formed and so to confirm this we treated $[\text{Pt}(\text{CH}_2\text{CH}_2\text{COMe})(\text{PEt}_3)_2]\text{BPh}_4$ with AgBF_4 in methanol. A precipitate of AgBPh_4 was obtained and the solvent distilled from the mixture was shown to contain ethyl methyl ketone. This was isolated as its 2,4-dinitrophenylhydrazone derivative (52% based on the platinum complex) and the involatile material remaining after distillation yielded $[\text{Pt}_2(\text{OH})_2(\text{PEt}_3)_4](\text{BF}_4)_2$ (57% yield). Thus the platinum-carbon bond is readily hydrolysed and the overall reaction may be represented as follows:



Hydrolysis of platinum-carbon σ -bonds is known to occur in acidic solution,^{12,13} but in this case the hydrolysis must take place at low hydrogen ion concentrations since the hydroxo-product is itself very reactive towards protonic acids.¹⁴

We have evidence that the hydroxo-complex exists as the hydroxo-bridged dimer in the solid state and as a solvated monomer in methanol solution¹⁴ and we will report our results on this and on related hydroxo-complexes elsewhere. Hydroxo-complexes of this type have been reported recently.^{15,16}

EXPERIMENTAL

The complex *trans*- $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ was prepared as previously described.⁴

Hydrido(ethylene)bis(triethylphosphine)platinum(II) Tetraphenylborate.—Ethylene was bubbled for 1 min through a solution of $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ (0.33 g) and sodium tetraphenylborate (0.23 g) in methanol (5 ml). The product was precipitated as white crystals (0.34 g), m.p. $78\text{--}80^\circ$ (decomp. with evolution of gas). Ethylene (1.03 mol per mol of platinum complex) was absorbed during the reaction.

Displacement of Ethylene from $[\text{PtH}(\text{C}_2\text{H}_4)(\text{PEt}_3)_2]\text{BPh}_4$ by Carbon Monoxide.—A suspension of the hydrido-ethylene complex (0.031 g) and NaBPh_4 (0.036 g) in methanol (20 ml) was treated with carbon monoxide at atmospheric pressure for 20 min. Evaporation of the solution gave $[\text{PtH}(\text{CO})(\text{PEt}_3)_2]\text{BPh}_4$ as white crystals (0.016 g); this was shown to be identical to a sample prepared by treating a solution of $\text{PtHCl}(\text{PEt}_3)_2$ and NaBPh_4 in methanol with carbon monoxide.

Action of Allene on $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$.—Allene was bubbled for 5 min through a solution of $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ (0.27 g) and NaBPh_4 (0.35 g) in methanol (10 ml). The precipitate (0.28 g) was recrystallised from dichloromethane-methanol to give (π -allyl)bis(triethylphosphine)platinum(II) tetraphenylborate as white crystals, m.p. $150\text{--}160^\circ$ (decomp.) Related reactions with butadiene gave the following

¹³ U. Belluco, M. Giustiniani, and M. Graziani, *J. Amer. Chem. Soc.*, 1967, **89**, 6494.

¹⁴ A. J. Deeming and P. Howes, unpublished results.

¹⁵ S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc. (A)*, 1971, 3441.

¹⁶ G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Canad. J. Chem.*, 1972, **50**, 3694.

⁸ G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, 1962, **1**, 896.
⁹ R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. (A)*, 1970, 353.

¹⁰ M. McPartlin and R. Mason, *J. Chem. Soc. (A)*, 1970, 2206.

¹¹ M. A. Bennett, G. B. Robertson, R. Watt, and P. O. Whimp, *Chem. Comm.*, 1971, 752.

¹² U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaola, *Inorg. Chem.*, 1967, **6**, 718.

compounds: (π -crotyl)bis(triethylphosphine)platinum(II) tetraphenylborate as white crystals (78% yield), m.p. 148—150°; (π -crotyl)bis(triethylphosphine)platinum(II) hexafluorophosphate as white prisms (50% yield), m.p. 219—222° (decomp.); (π -crotyl)bis(triethylarsine)platinum(II) tetraphenylborate as very pale yellow crystals (68% yield), m.p. 132—133°.

(π -Allyl)bis(triethylphosphine)palladium(II) Tetraphenylborate.—Triethylphosphine (0.3 g) in methanol (3 ml) was added to a suspension of [(π -allyl)PdCl]₂ (0.23 g) in water (10 ml) and the suspension was shaken for 45 min. After removal of a small quantity of dark deposit a solution of NaBPh₄ (0.5 g) in methanol (30 ml) was added to precipitate the product as colourless crystals (82% yield), m.p. 108—110°. The π -crotylpalladium complex prepared similarly gave colourless crystals (54% yield), m.p. ca. 120° (decomp.). The i.r. spectra of these complexes in the region 4000—625 cm⁻¹ were almost identical with those of the corresponding platinum complexes.

(Cyclo-oct-4-enyl)bis(triethylphosphine)platinum(II) Tetraphenylborate.—Cyclo-octa-1,5-diene (0.3 ml) was added to a solution of PtH(NO₃)(PEt₃)₂ (0.57 g) and NaBPh₄ (0.30 g) in methanol (15 ml). The white precipitate, which formed within a few minutes, was recrystallised from dichloromethane-methanol to give the product as white crystals (0.80 g), m.p. 165—166° (decomp.). A similar experiment with PtHCl(PEt₃)₂ gave the same compound but only over several hours.

(Norbornenyl)bis(triethylphosphine)platinum(II) Tetraphenylborate.—This complex was prepared similarly from PtH(NO₃)(PEt₃)₂, the product separating as an oil

which slowly crystallised as buff crystals (39%), decomp. above 80°. Lack of stability prevented further purification.

Reaction of PtH(NO₃)(PEt₃)₂ with PhN:CH:CH:CHPh.—A solution of PhN:CH:CH:CHPh (0.10 g) in methanol (10 ml) was added to a solution of PtH(NO₃)(PEt₃)₂ (0.17 g) and NaBPh₄ (0.19 g) in methanol (5 ml). The yellow precipitate (0.24 g) was recrystallised from dichloromethane-methanol to give [PtH(PhN:CH:CH:CHPh)(PEt₃)₂]BPh₄ as pale yellow needles (0.20 g), m.p. 119—121°.

Reaction of PtH(NO₃)(PEt₃)₂ with Methyl Vinyl Ketone.—Methyl vinyl ketone (1 ml) was added to a solution of PtH(NO₃)(PEt₃)₂ (0.37 g) and NaBPh₄ (0.35 g) in methanol (6 ml). The white crystalline precipitate was washed with methanol and shown to be (2-acetyethyl)bis(triethylphosphine)platinum(II) tetraphenylborate (0.40 g), m.p. 140—142°.

Hydrolysis of [Pt(CH₂:CH₂:COMe)(PEt₃)₂]BPh₄.—A suspension of the 2-acetyethyl complex (0.484 g) and silver tetrafluoroborate (0.129 g) in methanol (10 ml) was shaken for 2 h. The solvent was distilled and collected at -78°. Addition of 2,4-dinitrophenylhydrazine reagent gave the 2,4-DNP derivative of ethyl methyl ketone (orange crystals, 0.076 g) which was characterised by comparison of the i.r. and n.m.r. spectra and m.p. with those of an authentic sample. A methanolic extract of the involatile material from the reaction yielded di- μ -hydroxo-tetrakis(triethylphosphine)diplatinum(II) tetrafluoroborate as white crystals (0.176 g), m.p. 233—238° (decomp.). The corresponding di- μ -deuteroxo-complex was precipitated from an acetone solution upon addition of D₂O.

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