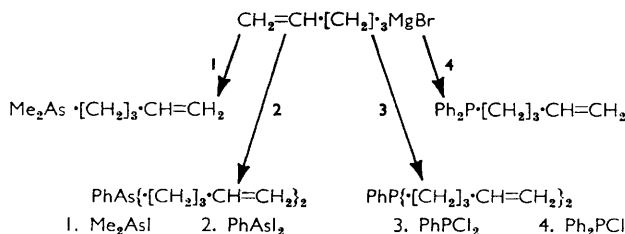**872.** *Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. Part I. Complexes of Ligands containing the Pent-4-enyl Group.*

By M. A. BENNETT, H. W. KOUWENHOVEN, J. LEWIS, and R. S. NYHOLM.

Chelate complexes of general formula $LPtX_2$ (X = Cl, Br, and I) are formed by tertiary phosphines and arsines containing the pent-4-enyl group, having the general formula $CH_2=CH \cdot [CH_2]_3 \cdot P(As)R_2$. In them both the olefinic double bond and the phosphorus or arsenic atom are co-ordinated to platinum(II). The co-ordinated double bond is readily displaced by other monodentate ligands such as tertiary arsines, *p*-toluidine, and thiocyanate ion. The molecular weights of the chelate complexes $LPtX_2$ in chloroform increase with increasing concentration. The complex $LPdCl_2$ (L = pent-4-enyldiphenylphosphine) is dimeric, and the double bond is not co-ordinated to the metal. In the complexes of the pent-4-enyl ligands with mercury(II) halides, the double bond is again not co-ordinated to the metal. Possible reasons for the reluctance of the pent-4-enyl ligands to form chelate complexes are discussed.

ALTHOUGH complexes of transition metals with mono- and di-olefins, and with tertiary phosphines and arsines, are well known, little study has been made of complexes which have both a double bond *and* a phosphorus or arsenic atom of a chelate group co-ordinated to the metal. We report here the complexes formed with platinum(II), palladium(II), and mercury(II) by some tertiary phosphines and arsines containing the pent-4-enyl group, $CH_2=CH \cdot [CH_2]_2 \cdot CH_2 \cdot$ hereafter denoted by C_5H_9. These ligands are prepared by reaction of the appropriate halogeno-alkyl- or -aryl-phosphine or -arsine with the Grignard reagent of pent-4-enyl bromide, as shown.

$$CH_2=CH \cdot [CH_2] \cdot_3 MgBr$$

$$Me_2As \cdot [CH_2]_3 \cdot CH=CH_2 \qquad 2 \qquad 3 \qquad Ph_2P \cdot [CH_2]_3 \cdot CH=CH_2$$

$$PhAs\{\cdot [CH_2]_3 \cdot CH=CH_2\}_2 \qquad PhP\{\cdot [CH_2]_3 \cdot CH=CH_2\}_2$$

1. Me_2AsI 2. $PhAsI_2$ 3. $PhPCl_2$ 4. Ph_2PCl

Complexes of Platinum(II).—Pent-4-enyldimethylarsine, $C_5H_9Me_2As$, reacts [1] with acidified tetrachloroplatinate(II) solution to give a monomeric complex $C_5H_9Me_2AsPtCl_2$. The corresponding bromo- and iodo-compounds can be prepared by adding lithium bromide and iodide respectively to the reaction mixture. This method fails with the other pentenyl ligands, and a more satisfactory procedure is the dropwise addition of the ligand in chloroform solution to a well-stirred suspension of excess of anhydrous platinum(II) chloride or bromide in refluxing chloroform. The complexes of the general formula $LPtX_2$ (L = pent-4-enyl ligand; X = Cl or Br) are isolated from the chloroform solution; the corresponding iodides (X = I) are obtained by treating the chlorides or bromides with sodium

[1] Kouwenhoven, Lewis, and Nyholm, *Proc. Chem. Soc.*, **1961**, 220.

iodide in acetone. The colours of the complexes vary from colourless (chlorides), very pale yellow (bromides), to yellow (iodides). They are generally insoluble or only slightly soluble in petrol, ether, benzene, alcohol, and carbon tetrachloride, fairly soluble in acetone, and readily soluble in chloroform and methylene chloride. The iodides are much less soluble than the chlorides and bromides in all solvents.

The complexes are diamagnetic, non-conducting in nitrobenzene, and essentially monomeric in acetone and chloroform, although there appears to be some association in chloroform. The infrared spectra of the complexes $LPtX_2$ ($L = C_5H_9Me_2As$ or $C_5H_9Ph_2P$; $X = Cl$, Br, or I) show a reduction in the C=C stretching frequency from *ca.* 1640 cm.$^{-1}$ in the free ligands and their methiodides to *ca.* 1505 cm.$^{-1}$ in the complexes (Table 1), a shift which is characteristic of an olefinic double bond co-ordinated to platinum(II).[2] The same shift is observed in the anion $[C_5H_9OH,PtCl_3]^-$, isolated as its $[Coen_2Cl_2]^+$ salt, obtained from pent-4-en-1-ol and the $[PtCl_4]^{2-}$ ion. We therefore formulate these complexes as chelate, square planar compounds of platinum(II), with both the double bond and the phosphorus or arsenic co-ordinated to the metal (I). The complexes $LPtCl_2$ ($L = (C_5H_9)_2PhP$ or $(C_5H_9)_2PhAs$) show bands in their infrared spectra at *ca.* 1640 and 1505 cm.$^{-1}$, indicating that only one of the two available double bonds is co-ordinated to the metal (II).

1, PhMe$_2$As; 2, *p*-toluidine; 3, C$_5$H$_9$Me$_2$As; 4, Ph$_2$MeAs; 5, NaI; 6, NaCNS
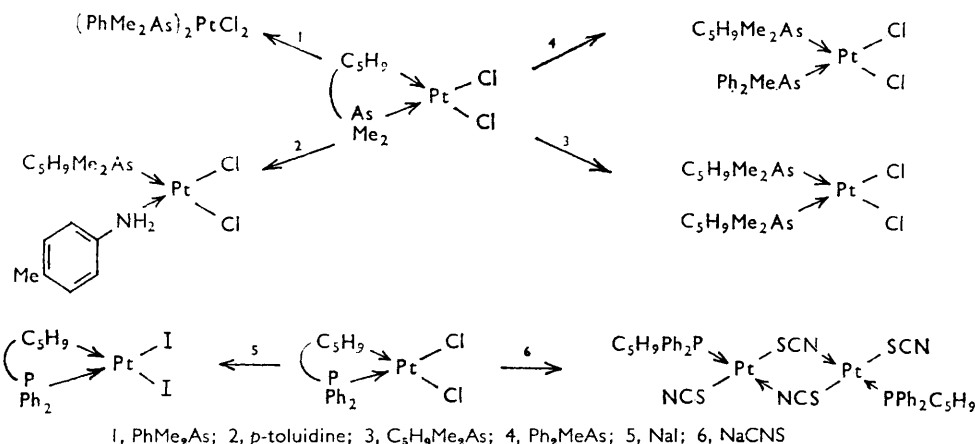
The co-ordinated double bond in the chelate complexes is readily replaced by other ligands (see annexed Chart). Diphenylmethylarsine reacts with $C_5H_9Me_2AsPtCl_2$ at room temperature giving the mixed tertiary arsine complex $(C_5H_9Me_2As)(Ph_2MeAs)PtCl_2$, in which the C=C stretching frequency of the olefinic tertiary arsine is restored to 1640 cm.$^{-1}$. Under the same conditions, phenyldimethylarsine replaces the entire olefinic ligand, giving $(PhMe_2As)_2PtCl_2$. *p*-Toluidine also replaces the co-ordinated double bond in $C_5H_9Me_2AsPtCl_2$ giving a mixed tertiary arsine–amine complex, but the chelate complex is re-formed on prolonged heating. $C_5H_9Me_2AsPtCl_2$ also reacts readily with excess of $C_5H_9Me_2As$ giving the bis(tertiary arsine) complex; similarly $C_5H_9Ph_2PPtCl_2$ with excess of $C_5H_9Ph_2P$, gives the bis(tertiary phosphine) complex. In both of these complexes, the C=C stretching frequency moves back to 1640 cm.$^{-1}$. Reaction of $C_5H_9Me_2As$ with a large excess of $[PtCl_4]^{2-}$ in the presence of nitrite ion affords only the dinitrobis(tertiary arsine) complex $(C_5H_9Me_2As)_2Pt(NO_2)_2$, there being no evidence for a dinitro-chelate complex. Sodium thiocyanate replaces the co-ordinated double bond of $C_5H_9Ph_2PPtCl_2$ giving a dimeric complex $[C_5H_9Ph_2PPt(SCN)_2]_2$, whose infrared spectrum shows a band at *ca.* 1640 cm.$^{-1}$ due to the unco-ordinated C=C stretching frequency, and bands at 2115 and 2170 cm.$^{-1}$ assignable to terminal and bridging thiocyanate C–N stretching frequencies, respectively.[3]

[2] Chatt and Duncanson, *J.*, 1953, 2939.
[3] Chatt and Duncanson, *Nature*, 1956, **178**, 997.

We formulate this as shown in the Chart; it is analogous to known tertiary phosphine–thiocyanate complexes of platinum(II).[3]   There is no evidence for a bisthiocyanate chelate complex with the olefinic phosphine.

The configuration of the platinum complexes has been determined by measuring the infrared spectra in the range 450—200 cm.$^{-1}$ to locate the metal–halogen stretching frequencies.   The results are in Table 1.   Coates and Parkin [4] have shown that *trans*-L_2PtCl_2 complexes (L = tertiary phosphine or arsine) show one strong Pt–Cl stretching frequency at *ca.* 330 cm.$^{-1}$, whereas *cis*-isomers show two or three less intense bands in the region 315—280 cm.$^{-1}$.   The chelate chloro-complexes of the olefinic tertiary phosphines and arsines show two or three strong bands in the region 325—280 cm.$^{-1}$ which are absent from the spectra of the corresponding bromides, and are assigned as Pt–Cl stretching frequencies.   This indicates mutually *cis*-chlorine atoms and supports the proposed structure for the complexes (I).   The compounds in which the co-ordinated double bond is replaced by a tertiary phosphine or arsine also show three bands in the 315—280 cm.$^{-1}$ region, so that they also probably have the *cis*-configuration, at least in the solid state.

The molecular weights of the chelate platinum(II) complexes in chloroform, and of *cis*-$(C_5H_9Ph_2P)_2PtCl_2$ in benzene, increase approximately linearly with concentration of complex.

(I)   (II)

The results are in Table 2.   The effect seems to be diminished in acetone, although limited solubility in this solvent makes comparison difficult.   Jensen [5] has shown that *cis*-L_2PtCl_2 complexes (L = dialkyl suphide), which have dipole moments of 9—10 D, show similar behaviour in benzene, and his results for *cis*-$(Pr^n{}_2S)_2PtCl_2$ in benzene over a range of concentrations are given in Table 2 for comparison.   It has been suggested [5] that association of polar *cis*-L_2PtCl_2 molecules causes the observed increase of molecular weight, which is not shown by *trans*-L_2PtCl_2 complexes.   We find that $C_5H_9Ph_2PPtI_2$ shows a higher degree of association in chloroform than its chloro- or bromo-analogue at the same molarity, although *cis*-L_2PtI_2 complexes generally have lower dipole moments than their chloro-analogues.[5,6]   This problem is under investigation.

Complexes of Mercury(II) *and Palladium*(II).—The mercury(II) complexes of the pentenyl ligands are non-chelate complexes of general formula $[LHgX_2]_2$ and occasionally L_2HgX_2 (X = Cl, Br, I; L = pentenyl ligand), the double bond being unco-ordinated in all cases shown by the infrared spectrum (Table 1).   They are formulated as shown in (III) and (IV), with tetrahedral co-ordination about mercury(II).

(III)   (IV)   (V)
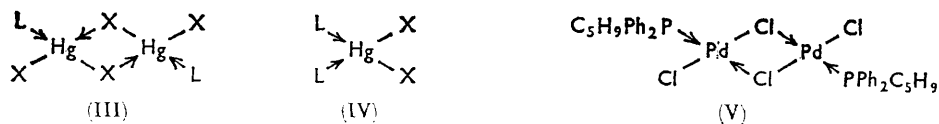
We have been unable to prepare chelate complexes of palladium(II) with the pentenyl ligands analogous to those of platinum(II).   The orange-red dimeric complex $[C_5H_9Ph_2PPdCl_2]_2$ obtained from dichlorobis(benzonitrile)palladium(II) and the olefinic tertiary phosphine shows an unco-ordinated double bond frequency in its infrared spectrum

[4] Coates and Parkin, *J.*, 1963, 421.
[5] Jensen, *Z. anorg. Chem.*, 1935, **225**, 97.
[6] Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.

TABLE 1.

C=C and M–Cl stretching frequencies (cm.$^{-1}$).

Ligand (L)	Compound	C=C	M–Cl
$C_5H_9Me_2As$	LMe$^+$I$^-$	1640m	—
,,	LPtCl$_2$	1506m	312—303s, br; 294s; 273s
,,	LPtBr$_2$	1504m	—
,,	LPtI$_2$	1506m	—
,,	L$_2$PtCl$_2$	1640m	312s; 294s; 270(ms, br)
,,	L$_2$Pt(NO$_2$)$_2$	1640m	—
,,	(Ph$_2$MeAs)LPtCl$_2$	1640m	312s; 296m; 248w; 277w, sh; 275m
,,	(*p*-tol)LPtCl$_2$	1639m	Not measured
$C_5H_9Ph_2P$	LMe$^+$I$^-$	1640w	—
,,	LPtCl$_2$,CHCl$_3$	*a*	322m; 284vs; 278vs
,,	LPtCl$_2$,C$_6$H$_6$	1506w	324ms; 285vs; 278vs
,,	LPtBr$_2$	1505vw	—
,,	LPtBr$_2$,CHCl$_3$	1506vw	—
,,	LPtI$_2$,CHCl$_3$	*a*	—
,,	[LPt(SCN)$_2$]$_2$	1640vw	—
,,	L$_2$PtCl$_2$	1639w	312s; 288s; 278s
,,	[LPdCl$_2$]$_2$	1640w	Not measured
,,	[LHgCl$_2$]$_2$	1639w	,,
,,	L$_2$HgBr$_2$	1639w	—
,,	L$_2$HgI$_2$	1639w	—
,,	[LHgBr$_2$]$_2$	1645m	
,,	[LHgI$_2$]$_2$	1639m	
$(C_5H_9)_2PhAs$	LPtCl$_2$,0·5C$_6$H$_6$	1640m; 1505m	329s; 248vs; 280m, sh
	LPtCl$_2$	1639vw; 1505vw	Not measured
	[LHgCl$_2$]$_2$	1640m	,,
$(C_5H_9)_2PhP$	LPtCl$_2$,0·7C$_6$H$_6$	1640m; 1505w	,,
	LPtCl$_2$,0·5 (ether)	1640w; 1505w	326ms; 286s; 278m, sh
	[LHgCl$_2$]$_2$	1640m	Not measured
C_5H_9OH	[LPtCl$_3$]$^-$	1504vw	,,

a Band too weak to be located.

Abbreviations: s, strong; vs, very strong; ms, medium strong; m, medium; w, weak; br, broad; sh, shoulder.

TABLE 2.

Molecular weight data for platinum(II) complexes.^{a}

Complex	M (calc.)	Solvent	Molarity	M (obs.)
C$_5$H$_9$Me$_2$AsPtCl$_2$	440	CHCl$_3$	0·0181	505
		,,	0·0256	519
		,,	0·0316	548
		,,	0·0400	561
		Acetone	0·0111	421
		,,	0·0165	437
C$_5$H$_9$Me$_2$AsPtBr$_2$	529	CHCl$_3$	0·0094	515
		,,	0·0132	541
		,,	0·0158	574
		,,	0·0276	628
C$_5$H$_9$Me$_2$AsPtI$_2$	623	,,	0·0037	625
$(C_5H_9)_2$PhAsPtCl$_2$,0·5C$_6$H$_6$	595	Acetone	0·0070	572
		,,	0·0310	625
C$_5$H$_9$Ph$_2$PPtCl$_2$,CHCl$_3$	639	CHCl$_3$	0·0210	669
		,,	0·0308	705
		,,	0·0849	854
C$_5$H$_9$Ph$_2$PPtBr$_2$,CHCl$_3$	728·5	,,	0·0149	761
		,,	0·0197	779
C$_5$H$_9$Ph$_2$PPtI$_2$,CHCl$_3$	821·5	,,	0·0069	846
		,,	0·0152	956
cis-(C$_5$H$_9$Ph$_2$P)$_2$PtCl$_2$................	775	C$_6$H$_6$	0·0132	835
		,,	0·0162	892
cis-(Pr$^n_2$S)$_2$PtCl$_2$ *b*	502·5	,,	0·0188	516
		,,	0·0346	523
		,,	0·0568	629
		,,	0·0810	678
		,,	0·1190	734

a Determined osmometrically; accurate to within $\pm 5\%$. *b* From Ref. 5, determined cryoscopically in benzene.

(Table 1), and is undoubtedly similar to the well-known halogen-bridged complexes of palladium (V). The corresponding complexes with the other pentenyl ligands formed oils which could not be purified.

Discussion.—Chatt [7] has observed that $[C_2H_4PtCl_3]^-$ reacts with Pr^n_3P to give an impure compound thought to contain *trans*-$[(C_2H_4)(Pr_3P)PtCl_2]$, and that this readily loses the olefin at room temperature.* In general, if L is a ligand of moderate to high *trans*-effect, complexes of the type *trans*-$[(olefin)LPtCl_2]$ decompose readily to $[LPtCl_2]_2$.[8] Our results show that even when L and the olefinic double bond are joined in a chelate group, and therefore mutually *cis*, the co-ordinated double bond is readily displaced, so that the *trans*-effect of L is probably not the most important factor. We may compare the reaction of $[C_2H_4PtCl_3]^-$ or $[C_2H_4PtCl_2]_2$ with *p*-toluidine, with that of $C_5H_9Me_2AsPtCl_2$ and the same ligand. In the former, the chlorine atom *trans* to the double bond is substituted, giving *trans*-$[(C_2H_4)(p\text{-toluidine})PtCl_2]$, exemplifying the high *trans*-effect of co-ordinated ethylene;[9] in the latter case, the co-ordinated double bond is replaced. The difference cannot be due to any weakening of the platinum–olefin bond in the second case, because the shift in the C=C stretching frequency on co-ordination is almost identical in $[C_2H_4PtCl_3]^-$, $[C_5H_9OHPtCl_3]^-$, and $C_5H_9Me_2AsPtCl_2$. An important factor contributing to the difference in behaviour may be the great stability of $LL'PtCl_2$ complexes (L = tertiary phosphine, tertiary arsine; L' = tertiary phosphine, tertiary arsine, primary or secondary amine).

It seems likely that the steric restrictions are not sufficiently stringent to make the pentenyl ligands good chelate groups for any transition element other than platinum(II). The pentenyl group in the square planar chelate complexes has to be oriented so that the co-ordinated double bond is at right-angles to the plane of the metal and the other ligands,[10] and the flexible aliphatic chain can adopt various other conformations with the double bond unco-ordinated. It may be noted that the aliphatic tritertiary arsine $MeAs(CH_2CH_2CH_2AsMe_2)_2$ does not stabilise high co-ordination numbers and unusual oxidation states so readily as the aromatic ditertiary arsine $o\text{-}C_6H_4(AsMe_2)_2$,[11] and that the aliphatic tertiary arsine-thiol $Me_2As(CH_2)_3SH$ does not readily form chelate complexes.[12] We [13] have found that *o*-allylphenyldimethylarsine, in which the double bond is more sterically constrained than in the pentenyl ligands, forms chelate complexes with both Pd^{II} and Pt^{II}, which will be described subsequently.

EXPERIMENTAL

Pent-4-en-1-ol was prepared in two steps from tetrahydrofurfuryl alcohol [14] and was converted into a pent-4-enyl bromide by phosphorus tribromide.[15]

Pent-4-enyldimethylarsine.—A Grignard reagent from pent-4-enyl bromide (21·2 g.) and magnesium turnings (3·5 g.) in sodium-dried ether (60 ml.) was treated at 0° with dimethyl-iodoarsine (33 g.) in sodium-dried benzene (100 ml.) with stirring under nitrogen for 1 hr. The mixture was stirred under nitrogen for a further hour, decomposed with ammonium chloride solution, and siphoned under nitrogen into a separating funnel. The organic layer was separated, dried ($MgSO_4$), and distilled under nitrogen, giving the *arsine* (7 g.) as a colourless, air-sensitive liquid, b. p. 148°/747 mm., which was stored under nitrogen. It contained organic

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* *Added in proof:* Complexes of this type have recently been made by reaction of olefins with halogeno-bridged, tertiary phosphine complexes of platinum(II) (Chatt, Johnson, and Shaw, *J.*, 1964, 1662), and have been assigned a *cis*-configuration.

[7] Chatt, *J.*, 1951, 652.
[8] Chatt and Venanzi, *J.*, 1955, 2787.
[9] Chatt, *Ann. Reports*, 1946, **43**, 120.
[10] Wunderlich and Mellor, *Acta Cryst.*, 1954, **7**, 130; Alderman, Owston, and Rowe, *ibid.*, 1960, **13**, 149.
[11] Barclay, Nyholm, and Parish, *J.*, 1961, 4433.
[12] Chiswell and Livingstone, *J. Inorg. Nucl. Chem.*, 1961, **23**, 37.
[13] Bennett, Erskine, Lewis, and Nyholm, unpublished work.
[14] *Organic Syntheses*, Vol. 25, p. 84, John Wiley and Sons, New York.
[15] La Forge, Green, and Gersdoff, *J. Amer. Chem. Soc.*, 1949, **70**, 3708.

contaminants, and was used as such for reactions. It was characterised as the *methiodide*, white crystals, m .p. 153°, from ethanolic solutions of the arsine and methyl iodide, recrystallised from ethanol (Found: C, 30·5; H, 5·6. $C_8H_{18}AsI$ requires C, 30·4; H, 5·7%).

The mercuric bromide *complex* from ethanolic solutions of mercuric bromide and the tertiary arsine in 1 : 1 mole ratio was recrystallised from acetone as white crystals, m. p. 95° (Found: C, 15·8; H, 2·9%. *M* (cryoscopic in 0·3% w/v nitrobenzene), 1200. $C_7H_{15}AsBr_2Hg$ requires C, 15·7; H, 2·8%. *M*, 535). The mercuric iodide *complex* was similarly obtained from mercuric iodide and the ligand; it formed pale green crystals, m. p. 93°, from acetone (Found: C, 13·4; H, 2·4%. *M* (cryoscopic in 0·3% w/v nitrobenzene), 1400. $C_7H_{15}AsI_2Hg$ requires C, 13·4; H, 2·4%. *M*, 629).

Other Ligands.—These were prepared in the same way. Pent-4-enyl bromide (15·1 g.), magnesium (2·4 g.), and phenyldi-iodoarsine (20·3 g.) gave *dipent-4-enylphenylarsine* (7 g.) as a slightly yellow oil, b. p. 128—130°/1 mm. (Found: C, 64·5; H, 7·7. $C_{16}H_{23}As$ requires C, 66·2; H, 8·0%). This was not purified further, and was used directly. The methiodide was an oil which could not be crystallised. The 1 : 1-mercuric chloride *complex* formed white crystals, m. p. 92°, from 80% aqueous ethanol (Found: C, 34·0; H, 4·0%. *M* (osmometric in benzene), 1050 (0·92% w/v); 1049 (1·82% w/v). $C_{16}H_{23}AsCl_2Hg$ requires C, 34·2; H, 4·1%. *M*, 562). Pent-4-enyl bromide (15·1 g.), magnesium (2·4 g.), and phenyldichlorophosphine (8·95 g.) gave *dipent-4-enylphenylphosphine* (5 g.) as a colourless oil, b. p. 98—101°/0·2 mm. (Found: C, 79·0; H, 9·4; P, 12·6. $C_{16}H_{23}P$ requires C, 77·5; H, 9·3; P, 13·1%). The 1 : 1 mercuric chloride *complex* formed fine white needles, m. p. 86—87°, from ethanol (Found: C, 37·3; H, 4·9. $C_{16}H_{23}PCl_2Hg$ requires C, 37·1; H, 4·5%).

Pent-4-enyl bromide (7·55 g.), magnesium (1·2 g.), and diphenylchlorophosphine (11 g.) gave *pent-4-enyldiphenylphosphine* (6·6 g.) as a colourless oil, b. p. 118—121°/0·15 mm. (Found: C, 80·1; H, 7·9; P, 12·0. $C_{17}H_{19}P$ requires C, 80·3; H, 7·5; P, 12·2%). The methiodide, crystallised slowly from 80% aqueous ethanol, formed slightly yellow crystals, m. p. 105° (Found: C, 55·2; H, 6·0. $C_{18}H_{22}IP$ requires C, 54·6; H, 5·6%). Other derivatives prepared were the 1 : 1 mercuric chloride *complex*, m. p. 134° from 95% ethanol (Found: C, 38·8; H, 3·3; P, 6·2. $C_{17}H_{19}Cl_2HgP$ requires C, 38·8; H, 3·6; P, 5·9%); the 1 : 2 mercuric bromide *complex*, m. p. 143°, from ethanol (Found: C, 46·9; H, 4·3; P, 8·0%. *M* (osmometric in benzene), 796 (0·90% w/v); 843 (1·41% w/v). $C_{34}H_{38}Br_2HgP_2$ requires C, 47·0; H, 4·4; P, 7·1%. *M*, 869); the 1 : 2 mercuric iodide *complex*, m. p. 148°, from ethanol (Found: C, 42·5; H, 4·1. $C_{34}H_{38}HgI_2P_2$ requires C, 42·4; H, 4·0%).

Dichloropent-4-enyldimethylarsineplatinum(II).—*Method A.* Sodium tetrachloroplatinate(II) tetrahydrate (0·9 g., 0·002 mole) in 1 : 1 water–ethanol acidified with a few drops of 3N-HCl was treated with the arsine (0·4 g., 0·002 mole) in ethanol (20 ml.). The initially formed yellow precipitate (probably a salt of the type [Pt(arsine)$_4$][PtCl$_4$]) redissolved on shaking. The solution was set aside for 24 hr., and the white precipitate filtered off. Two recrystallisations from 1 : 1 chloroform–carbon tetrachloride gave colourless crystals of the chelate *complex* (0·4 g.), m. p. 196° (decomp.) (Found: C, 19·2; H, 3·4; Cl, 15·9; Pt, 44·0. $C_7H_{15}AsCl_2Pt$ requires C, 19·1; H, 3·4; Cl, 16·1; Pt, 44·4%).

Similarly prepared, with the addition of lithium bromide (1 g., 0·01 mole) to the original reaction mixture, was the pale yellow crystalline bromo-chelate *complex*, m. p. 197° (decomp.) (Found: C, 16·4; H, 2·9; Br, 30·2; Pt, 37·7. $C_7H_{15}AsBr_2Pt$ requires C, 15·9; H, 2·8; Br, 30·5; Pt, 36·9%). Addition of sodium iodide in place of lithium bromide gave yellow crystals of the iodo-chelate *complex*, m. p. 137° (decomp.) (Found: C, 13·6; H, 2·3; Pt, 31·7. $C_7H_{15}AsI_2Pt$ requires C, 13·5; H, 2·4; Pt, 31·3%). Both were recrystallised several times from 1 : 1 chloroform–carbon tetrachloride.

Addition of sodium nitrite (2 g., 0·03 mole) in the original preparation gave a pale yellow solution with no precipitate after 24 hr. The solution was evaporated (15 mm.) to *ca.* 10 ml., and the white precipitate filtered off. Recrystallisation from 50% aqueous methanol gave white crystals of *dinitrobis(pent-4-enyldimethylarsine)platinum*(II), m. p. 94° (Found: C, 26·8; H, 4·7; Pt, 30·1%. *M* (osmometric in benzene), 569 (0·73% w/v); 586 (1·67% w/v). $C_{14}H_{30}As_2N_2O_4Pt$ requires C, 26·4; H, 4·8; Pt, 30·7%; *M*, 635). It is readily soluble in most solvents except petrol and water.

Method B. A well-stirred suspension of anhydrous platinum(II) chloride (1 g., 0·004 mole) in refluxing chloroform (50 ml.) was treated dropwise with the arsine (0·5 g., 0·003 mole) in chloroform (15 ml.) during 2 hr. The solution was filtered, solvent was removed (15 mm.)

to *ca.* 5 ml. volume, and the product precipitated by adding carbon tetrachloride (40 ml.). It was recrystallised from 1 : 1 chloroform–carbon tetrachloride to give the chelate chloro-complex (0·48 g.), identical with that obtained by Method A (Found: C, 19·3; H, 3·5%).

Similarly, by use of anhydrous platinum(II) bromide (1·5 g., 0·004 mole), the identical chelate bromo-complex was obtained (Found: C, 16·4; H, 2·6; Br, 29·9%).

The following chelate complexes were obtained similarly by Method B; the solvent used for recrystallisation is given in parentheses (petrol is light petroleum, b. p. 60—80°). *Dichloro(dipent-4-enylphenylarsine)platinum*(II) from platinum(II) chloride (1 g., 0·003 mole) and the arsine (0·5 g., 0·002 mole), yellow crystals (0·6 g.) solvated with benzene, m. p. 98—100° (1 : 2 benzene–petrol) (Found: C, 38·7; H, 4·4; Cl, 12·2; Pt, 32·3. $C_{16}H_{23}AsCl_2Pt,0\cdot5C_6H_6$ requires C, 38·3; H, 4·4; Cl, 11·9; Pt, 32·8%). The unsolvated *complex* was obtained from ether, m. p. 98° (Found: C, 35·2; H, 4·1; Cl, 12·7. $C_{16}H_{23}AsCl_2Pt$ requires: C, 34·6; H, 4·2; Cl, 12·7%). *Dichloro(dipent-4-enylphenylphosphine)platinum*(II), pale yellow crystals solvated with benzene, m. p. 109° (1 : 2 benzene–petrol) (Found: C, 42·3; H, 4·6. $C_{16}H_{23}Cl_2PPt,0\cdot7C_6H_6$ requires C, 42·8; H, 4·8%). Ether in place of benzene gave an ether *solvate*, m. p. 100° (Found: C, 38·9; H, 4·9; Cl, 13·6. $C_{16}H_{23}Cl_2PPt,0\cdot5C_4H_{10}O$ requires C, 39·3; H, 5·1; Cl, 12·9%). *Dichloro(pent-4-enyldiphenylphosphine)platinum*(II), fine white crystals of the chloroform *solvate*, m. p. 200° (1 : 1 chloroform–carbon tetrachloride) (Found: C, 33·8; H, 3·5; Cl, 28·8; Pt, 30·3. $C_{17}H_{19}Cl_2PPt,CHCl_3$ requires C, 33·8; H, 3·2; Cl, 27·7; Pt, 30·5%). Colourless plates of the benzene *solvate*, m. p. 200°, were obtained from boiling benzene (Found: C, 46·2; H, 4·2; Cl, 13·0; Pt, 33·0. $C_{17}H_{19}Cl_2PPt,C_6H_6$ requires C, 46·2; H, 4·2; Cl, 11·9; Pt, 32·6%). After heating at 90°/0·1 mm. for 4 hr., both solvates gave the colourless unsolvated, chelate *complex*, m. p. 200° (Found: C, 39·4; H, 3·6. $C_{17}H_{19}Cl_2PPt$ requires C, 39·0; H, 3·7%). The corresponding bromo-chelate *complex* formed pale yellow crystals, m. p. 200° (decomp.) (1 : 1 chloroform–carbon tetrachloride) (Found: C, 30·6; H, 2·7; Pt, 27·1. $C_{17}H_{19}Br_2PPt,CHCl_3$ requires: C, 30·1; H, 2·8; Pt, 27·1%). Recrystallisation from benzene gave a complex containing some benzene as shown by the infrared spectrum, but the analytical data were close to those for the unsolvated *complex* (Found: C, 34·9; H, 3·6; Br, 26·6; Pt, 33·0. $C_{18}H_{19}Br_2PPt$ requires C, 34·1; H, 3·2; Br, 25·0; Pt, 32·6%).

Reaction of the Chelate Complexes with Ligands.—(*a*) *Iodide ion.* $C_5H_9Me_2AsPtCl_2$ (0·1 g., 0·0002 mole) in acetone (30 ml.) was treated wih sodium iodide (0·3 g., 0·002 mole). The red solution was refluxed (30 min.), the precipitate of NaCl filtered off, and the filtrate evaporated to dryness (15 mm.). The reddish-orange residue was crystallised several times from 1 : 1 chloroform–carbon tetrachloride giving $C_5H_9Me_2AsI_2Pt$ identical with that obtained by Method A (Found: C, 14·1; H, 2·5%).

Similarly from $C_5H_9PPh_2PtCl_2,CHCl_3$ (0·1 g., 0·0002 mole), sodium iodide (0·3 g., 0·002 mole) and acetone (30 ml.), yellow crystals of *di-iodo(pent-4-enyldiphenylphosphine)platinum*(II) as the solvate, decomp. 215° (reddens at 95°) from 1 : 1 chloroform–carbon tetrachloride (Found: C, 25·9; H, 2·4; Pt, 23·7. $C_{17}H_{19}I_2PPt,CHCl_3$ requires C, 26·3; H, 2·4; Pt, 23·7%).

(*b*) *Thiocyanate ion.* From $C_5H_9Ph_2PPtCl_2,CHCl_3$ (0·29 g., 0·0004 mole), sodium thiocyanate (1 g., 0·012 mole), and acetone (30 ml.) pale yellow crystals of *dithiocyanatobis(pent-4-enyldiphenylphosphine)-μμ'-dithiocyanatodiplatinum*(II) (0·2 g.) (benzene–petrol), m. p. 105—110° (Found: C, 39·3; H, 3·3; N, 5·0%. *M* (osmometric in chloroform), 1066 (0·92% w/v); 1100 (1·13% w/v). $C_{19}H_{19}N_2PPtS_2$ requires C, 40·3; H, 3·4; N, 4·95%; *M*, 566). It is readily soluble in chloroform and acetone, soluble in benzene on heating, and insoluble in ether and carbon tetrachloride.

(*c*) *p-Toluidine.* From $C_5H_9Me_2AsPtCl_2$ (0·27 g., 0·0006 mole), *p*-toluidine (0·5 g., 0·005 mole), and chloroform (15 ml.), refluxed for 30 min., were obtained yellow needles of *dichloropent-4-enyldimethylarsine-p-toluidine platinum*(II) (0·15 g.) (1 : 5 chloroform–petrol), m. p. 98° (Found: C, 30·4; H, 4·7; Cl, 13·4; N, 2·7. $C_{14}H_{24}AsCl_2NPt$ requires C, 30·7; H, 4·4; Cl, 13·0; N, 2·6%). The complex partially decomposes on heating in chloroform, re-forming the original chelate, hence recrystallisation must be done quickly.

(*d*) *4-Pentenyldimethylarsine.* From $C_5H_9Me_2AsPtCl_2$ (0·18 g., 0·0004 mole), the arsine (0·2 g., 0·001 mole), and benzene (10 ml.), refluxed for 30 min., was obtained pale yellow *dichlorobis(pent-4-enyldimethylarsine)platinum*(II) (0·1 g.) (ether), m. p. 55° (Found: C, 28·5; H, 5·4; Pt, 31·2. $C_{14}H_{30}As_2Cl_2Pt$ requires: C, 27·4; H, 4·9; Pt, 31·8%). It is readily soluble in all organic solvents except petrol, and readily forms an oil on attempted crystallisation.

(*e*) *Pent-4-enyldiphenylphosphine.* From $C_5H_9Ph_2PPtCl_2,CHCl_3$ and $C_5H_9Ph_2P$ as in (*d*),

pale yellow crystals of *dichlorobis(pent-4-enyldiphenylphosphine)platinum*(II) (methanol during 2 days), m. p. 98—100° (turns deep yellow at 77°) (Found: C, 50·8; H, 5·3; Cl, 9·7; Pt, 27·0. $C_{34}H_{38}Cl_2P_2Pt$ requires C, 52·7; H, 4·95; Cl, 9·2; Pt, 25·2%). Repeated recrystallisations failed to improve these figures. The complex is readily soluble in all organic solvents except petrol.

(*f*) *Diphenylmethylarsine.* From $C_5H_9Me_2AsPtCl_2$ (0·16 g., 0·0004 mole), diphenylmethylarsine (0·2 g., 0·001 mole), and chloroform (15 ml.), were obtained colourless crystals of *dichloropent-4-enyldimethylarsinediphenylmethylarsineplatinum*(II) (0·09 g.) (1 : 1 benzene–light petroleum, b. p. 80—100°), m. p. 162° (Found: C, 36·1; H, 4·3; Cl, 9·8; Pt, 28·4. $C_{20}H_{28}As_2Cl_2Pt$ requires C, 35·2; H, 4·1; Cl, 10·4; Pt, 28·5%).

(*g*) *Phenyldimethylarsine.* As in (*f*), colourless crystals of *dichlorobis(phenyldimethylarsine)-platinum*(II) (1 : 2 dichloromethane–petrol), m. p. 160° (Found: C, 30·7; H, 4·0; Pt, 30·9. $C_{16}H_{22}As_2Cl_2Pt$ requires C, 30·5; H, 3·5; Pt, 30·9%). The infrared spectrum shows no C=C stretching frequency at either 1640 or 1505 cm.$^{-1}$.

Dichlorobis(pent-4-enyldiphenylphosphine)-μμ'-dichlorodipalladium(II).—A solution of $(C_6H_5CN)_2PdCl_2$ [16] (0·42 g., 0·0012 mole) in benzene (50 ml.) was stirred and treated dropwise in the cold with the phosphine (0·28 g., 0·0011 mole) in benzene (20 ml.) during 30 min. The mixture was stirred for a further hour and the red solution filtered from a small amount of brown amorphous material. Solvent was removed (15 mm.) to *ca.* 5 ml., the solution again filtered, and light petroleum, b. p. 80—100° (30 ml.), added to precipitate an oily orange-red solid which crystallised on standing overnight at 0°. This procedure was repeated three times to give orange crystals of the *complex* (0·2 g.), which decomposed to Pd metal at 120—150° (Found: C, 47·7; H, 4·9; Pd, 25·4%. *M* (osmometric in chloroform) 814 (0·86% w/v); 848 (1·17% w/v). $C_{17}H_{19}Cl_2PPd$ requires C, 47·3; H, 4·4; Pd, 24·7%; *M*, 432). It is easily soluble in benzene, chloroform, and acetone, slightly soluble in carbon tetrachloride and ether on warming. It decomposes in hot methanol, ethanol, and benzonitrile giving a brown solid which gave indefinite analytical data.

Trichloropent-4-en-1-ol platinate(II) *anion.*—This was prepared in the form of its *trans*-dichlorobis(ethylenediamine) cobalt(III) salt as *green crystals* by the method of Pfeiffer and Hoyer [17] (Found: C, 16·1; H, 4·3; N, 9·0. $C_9H_{26}Cl_5N_4OPt$ requires C, 17·0; H, 4·1; N, 8·8%).

Infrared Spectra.—These were recorded in Nujol and hexachlorobutadiene mulls on a Grubb-Parsons GS2A spectrometer in the region 4000—500 cm.$^{-1}$. The low frequency spectra (450—200 cm.$^{-1}$) were measured at 25° in Nujol mulls held between polythene discs on a Grubb-Parsons double-beam grating spectrophotometer, type DM2, serial number 28.

Analyses.—For the arsine complexes, platinum was determined by direct ignition to the metal after moistening with concentrated sulphuric acid. The phosphine complexes were decomposed with successive small portions of concentrated sulphuric acid and heated to fuming for 5—10 min. after each addition. The residue was extracted with hot water, filtered on ashless filter paper, and ignited to the metal.

Molecular Weights.—These were determined using a Mechrolab vapour pressure osmometer.

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