Complexes of Terpenes with Transition Metals. Part I. The Reactions of *cis*- and *trans*-Ocimene and of Myrcene with Palladium(II)

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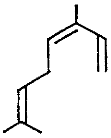
Treatment of *cis*- or *trans*-ocimene with disodium tetrachloropalladate in methanol gives the π-allylpalladium(II) complex of geranyl methyl ether. In acetone solution, *cis*-ocimene is inverted to *trans*-ocimene, cyclised to limonene, and dimerised to a palladium(II)-complex of a C_{20}-terpene dimer. Under similar conditions in methanol, myrcene is cyclised to bis{chloro-[1,α,β-*trihapto*-3-(1-methoxy-1-methylethyl)-1-vinylcyclopentane]palladium-(II)}but in acetone solution it gives the palladium(II)-complex of a C_{20}-dimer. The dimers appear to be derived from a head-to-head C_{10}–C_{10} diterpene.

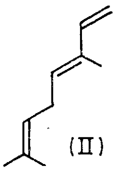
METAL complex formation is now a well established method for the initiation of a range of reactions by olefins and it appeared appropriate to examine the reactions of terpenoid olefins.

Initially we studied the value of palladium(II)-complex formation for the reaction of *cis*- (I) and *trans*-ocimene (II) with disodium tetrachloropalladate(II), in the presence or absence of nucleophilic reagents such as methanol or acetic acid.

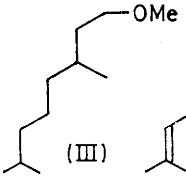
Both *cis*- and *trans*-ocimene reacted with disodium tetrachloropalladate(II) in methanol during several hours, the colour of the solution changing from red-brown to yellow; *trans*-ocimene reacted more rapidly. However, both isomers gave the same product, $C_{11}H_{19}OPdCl$, which has been characterised as the 2,3,4-*trihapto*-complex † (IV).



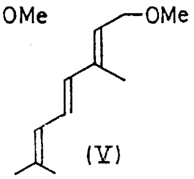
(I)



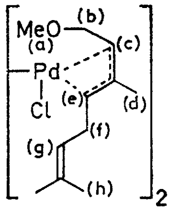
(II)



(III)



(V)



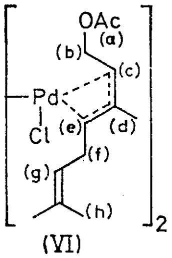
(IV)

τ
(a) 6·85 (s), (b) 6·36 (d),
(c) 6·28 (m), (d) 7·85(s),
(e) 6·58 (m), (f) 7·59,
(g) 4·75 (t), (h) 8·29, 8·33 (s)

This complex, when shaken in ethanol under hydrogen, deposited palladium to give methyl tetrahydrogeranyl ether (III). This established the gross carbon skeleton, and the detailed structure as (IV) follows from the n.m.r. data given. The assignment of the protons (c) and (e) of the π-allyl system and of the methyl group (d) are in accordance with simpler analogues;[1] the terminal $Me_2C{:}CH\cdot$ group is clearly not involved in complex formation since the n.m.r. signals for protons (g) and (h) appear as in the spectrum of geranyl acetate which shows signals at τ 4·78, 8·26, and 8·33.

In the mass spectrometer the complex (IV) gave a principal ion at *m/e* 166 ($C_{11}H_{18}O$) (loss of Pd and HCl). A reaction of this kind could also be reproduced chemically by treatment of the complex (IV) with pyridine in dioxan. Palladium was deposited and the organic residue could be isolated as a conjugated triene [$\lambda_{max.}$ 270 (ε 3·5 × 10^4), 278 (4 × 10^4), and 288 nm (3·4 × 10^4)]. This triene, which on hydrogenation gave methyl tetrahydrogeranyl ether (III), is regarded as (V), or less probably the 4,5-*cis*-isomer.

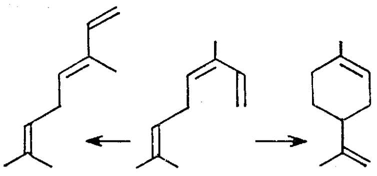
A geranyl acetate π-allyl complex (VI), analogous with (IV), was obtained from reaction of ocimene with disodium tetrachloropalladate(II) in acetic acid–sodium acetate, or from bis(benzonitrilechloro)palladium(II) in acetic acid. When shaken in hydrogen this complex (VI) formed tetrahydrogeranyl acetate, and the detailed formulation follows from the n.m.r. data quoted.



(VI)

τ
(a) 7·94 (s), (b) 5·68 (d),
(c) 6·3 (m), (d) 7·89 (s),
(e) 6·5 (m), (f) 7·6,
(g) 4·7 (t), (h) 8·28, 8·32 (s)

The reactions of *cis*- and *trans*-ocimene in methanol to form the same complex (IV), but at different rates, implies *cis* → *trans* stereomutation which may be acid- or palladium(II)-catalysed. *cis*-Ocimene, treated with disodium tetrachloropalladate(II) in acetone in presence of calcium carbonate as an acid buffer, was converted into a mixture, found by g.l.c. analysis to contain a high proportion of *trans*-ocimene as well as some limonene (VII). Thus there is evidence for the transformation (I) → (II) and (VII), apparently induced by co-ordination to palladium(II). The detailed mechanism



(II) (I) (VII)

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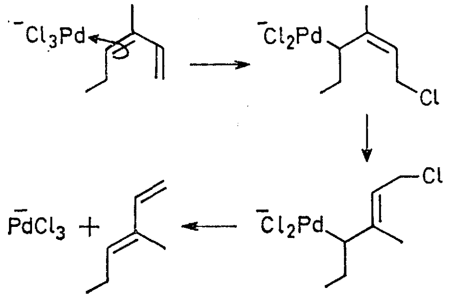
† The nomenclature in this paper for indicating the positions of co-ordination of the metal atom to the olefin is that suggested by F. A. Cotton (*J. Amer. Chem. Soc.*, 1968, **90**, 6230).

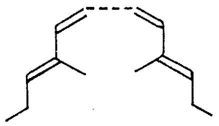
[1] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

of the *cis* → *trans* stereomutation has not been examined. The presence of calcium carbonate appears to exclude acid catalysis, but palladium(II)-catalysed addition and elimination of chloride ion is a possibility (Scheme).

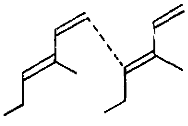
Oligomerisation of dienes and olefins by transition-metal catalysis is well known, and the formation of limonene (VII) above implies catalysis of olefin–olefin interaction by complex formation with palladium(II) in the case of *cis*-ocimene. An analogous cyclisation with *trans*-ocimene is not possible, but by reaction with a second molecule, complex formation with palladium(II) could, in principle, lead to the formation of an ocimene dimer. Close examination of the products of reaction of ocimene with disodium tetrachloropalladate(II) in acetone confirmed this inference. A yellow complex was isolated by chromatography. This, when shaken in hydrogen, released a hydrocarbon which in the mass spectrometer gave an ion at *m/e* 282 ($C_{20}H_{42}$), clearly derived from an acyclic ocimene dimer. The mass spectrum showed a fragment ion at *m/e* 267 (282 − 15), but no fragment due to loss of an ethyl residue, indicating the occurence of dimerisation as in (VIII) rather than alternatives such as (IX). The hydrogenation product was indistinguishable from 2,6,11,15-tetramethylhexadecane by g.l.c. and mass spectral comparison, and the evidence as a whole is consistent with formation of the dimer by head-to-head union of ocimene units. The parent palladium(II)-dimer complex showed π-allylic proton signals in the n.m.r. spectrum at τ 6·2 and 6·67, two vinyl protons at τ 4·9, a group of 15 protons at τ 8·33 and a higher field 3-H signal at τ 8·75.



SCHEME

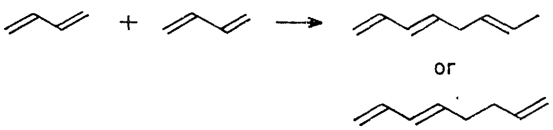


(VIII)



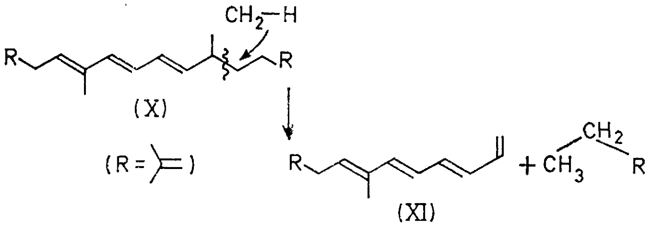
(IX)

In the mass spectrometer the palladium(II)-C_{20} complex failed to show the molecular ion, but gave a strong ion at *m/e* 188 ($C_{14}H_{20}$); these data are most consistent with a dimer formulated as (X) which would be expected to give a $C_{14}H_{20}$ fragment (XI). This formulation is in agreement also with the known dimerisation of butadiene which is found to occur with hydrogen migration,[2] [*e.g.*, reaction (1)]

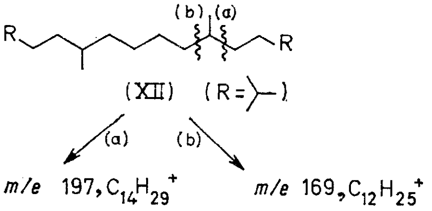


(1)

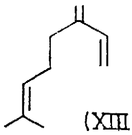
The head-to-head dimeric formulation (X) also accounts for the fragmentation of the perhydro-dimer to give ions at *m/e* 197 and 169, with bond fission to be expected at tertiary centres of the carbon chain, as in (XII).



(X) (XI)



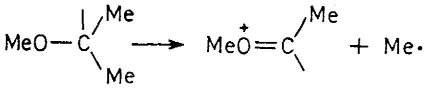
(XII)



(XIII)

On the basis of these results we examined the behaviour of myrcene (XIII). With disodium tetrachloropalladate(II) in methanol, myrcene gave a methoxy-complex, $[\{Pd(C_{10}H_{16}{\cdot}OMe)Cl\}_2]$ which, however, was clearly structurally different from the type of π-allyl derivative (IV). The presence of a π-allyl grouping could be deduced from the n.m.r. spectrum: doublets at τ 6·11 and 6·99, and a singlet due to the methoxy-group at τ 6·83. However, the remaining methyl groups appeared as a six-proton signal at τ 8·83, which suggested a unit $MeO{\cdot}CMe_2{\cdot}$, formed by methanol addition at the isopropylidene end of the myrcene chain. The complex showed a principal ion at *m/e* 166 ($C_{10}H_{15}OCH_3$), a strong ion at *m/e* 151 (166 − 15), and a significant fragment at *m/e* 73 $[Me_2C{=}OMe]^+$.

When shaken in hydrogen, the complex gave a product showing in the mass spectrum a principal ion at *m/e* 155 ($C_{10}H_{19}O$), corresponding to the ready fragmentation (2) from a parent ion $C_{11}H_{22}O$.



$$\mathrm{MeO{-}\overset{|}{C}Me_2} \longrightarrow \mathrm{Me\overset{+}{O}{=}CMe} + \mathrm{Me\cdot} \qquad (2)$$

This hydrogenation product proved to be similar to, but not identical with dihydro-α-terpinyl methyl ether (XIV). In particular, the hydrogenation product showed a three-proton triplet at τ 9·12 and a two-proton multiplet at τ 8·76. This implication of the

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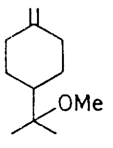
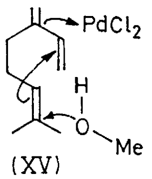
[2] *Cf.* H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem.*, 1965, **4**, 327; H. Takalashi, S. Tai, and M. Yamaguchi, *J. Org. Chem.*, 1965, **30**, 1661; R. G. Miller, J. J. Kealy, and A. L. Barney, *J. Amer. Chem. Soc.*, 1967, **89**, 3756.

presence of an ethyl group was confirmed by the appearance in the mass spectrum of ions at *m/e* 138, ($C_{10}H_{18}$) [($C_{11}H_{22}O$) − (MeOH)], and 109 (C_8H_{13}) [($C_{10}H_{18}$) − (C_2H_5)].

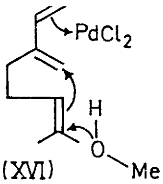
Cyclisation of myrcene may, in principle, take the course shown at (XV), leading to dihydro-α-terpinyl methyl ether (XIV) after hydrogenation, or as in (XVI), giving an ethyl-cyclopentane derivative (XVII). Comparison of the n.m.r. data for dihydro-α-terpinyl methyl ether (XIV) and the hydrogenated complex clearly indicates the presence of the cyclopentane structure (XVII).



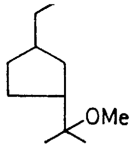
(XIV)



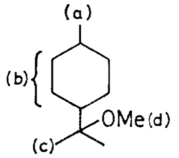
(XV)



(XVI)



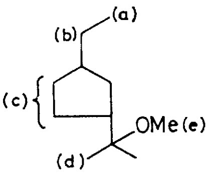
(XVII)



(XIV)

τ

(a) 9·5 (d), (b) 8·77 (m),
(c) 8·93 (s), (d) 6·93 (s)

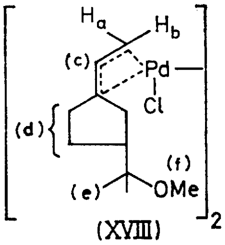


(XVII)

τ

(a) 9·12 (t), (b) 8·76 (m),
(c) 8·5 (m), (d) 8·9 (s),
(e) 6·9 (s)

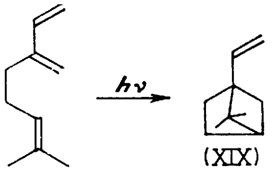
The palladium(II)-allyl complex from myrcene is therefore formulated as (XVIII), in agreement with the n.m.r. data. The mode of cyclisation represented by (XVIII) has a close analogy with the known[3] photocyclisation of myrcene to give (XIX).



(XVIII)

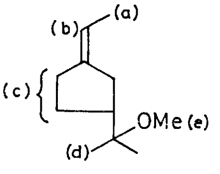
τ

(a) 6·11 (d, *J* 7·6 Hz)
(b) 6·99 (d, *J* 13 Hz)
(c) 4·75 (m)
(d) 8·0—8·3 (m)
(e) 8·83 (s)
(f) 6·83 (s)



(XIX)

The π-allyl complex (XVIII) was characterised also by formation of 1 : 1 derivatives with pyridine and with triphenylphosphine. With alcoholic potassium cyanide, (XVIII) gave a hydrocarbon which on the basis of the n.m.r. spectrum is formulated as (XX).

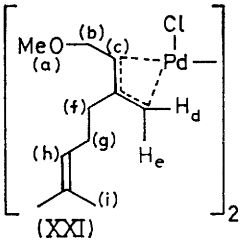


(XX)

τ

(a) 8·4 (d, *J* 6 Hz)
(b) 4·77, (c) 7·56—8·0
(d) 8·86 (s), (e) 6·78 (s)

Accompanying the derivative (XVIII) from the reaction of myrcene with methanol and disodium tetrachloropalladate(II), was a second complex isolated in small yield. This with hydrogen gave methyl tetrahydrogeranyl ether; the n.m.r. data indicated the formulation (XXI).

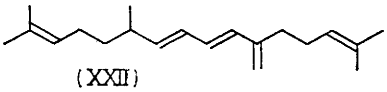


(XXI)

τ

(a) 6·6, (b) 6·39,
(c) 6·7, (d) 7·2,
(e) 6·2, (f, g) 7·67, 7·75,
(h) 4·8, (i) 8·3, 8·37

The possibility of dimerisation of myrcene by complex formation with palladium(II) in the absence of a nucleophilic solvent was examined by use of disodium tetrachloropalladate(II) in acetone with calcium carbonate as buffer. This reaction gave two complexes, R_F 0·79 and 0·15 on silica-gel plates with benzene–ethyl acetate (5 : 2). The complex with R_F 0·79, when shaken in hydrogen, gave a hydrocarbon, *m/e* 282 ($C_{20}H_{42}$), which was identical (mass spectrum and g.l.c. comparison) with 2,6,11,15-tetramethylhexadecane. This complex appears therefore to be derived from a myrcene dimer. In the n.m.r. spectrum the C_{20}-complex showed a total of 12 protons with signals at τ 8·32, 8·4, and 8·43 and a fifth methyl group appearing as a doublet at τ 8·75 (*J* 4 Hz). A two-proton singlet at τ 5·2 is attributed to a $>C=CH_2$ group, and the signals from two further vinyl protons appeared at τ 4·93. These data are consistent with a formulation (XXII) for the dimer, but the details of the structure are necessarily tentative, and on the available evidence the point of co-ordination cannot be specified.



(XXII)

The second complex, R_F 0·15, from reaction of myrcene in acetone, proved to be $C_{10}H_{17}OPdCl$, (XXIII), an analogue of (XVIII), the hydroxy-group being derived from the water of hydration of disodium tetrachloropalladate(II). The presence of the hydroxy-group was indicated by i.r. bands at 3460 and 1130 cm^{-1}; a six-proton singlet at τ 8·78 in the n.m.r. spectrum indicates the presence of the group $HO{\cdot}\overset{|}{C}Me_2$. The complex on

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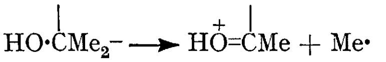
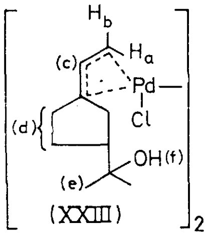
[3] R. H. S. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 1892.

hydrogenation gave a product which in the mass spectrometer gave a principal ion at *m/e* 141 ($C_9H_{17}O$) arising by the expected fragmentation (3). The complex itself gave ions at *m/e* 152 ($C_{10}H_{16}O$), 137 ($C_9H_{13}O$; loss of CH_3), and 134 ($C_{10}H_{14}$; loss of H_2O).



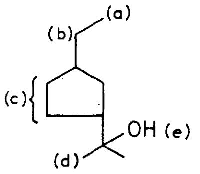
$$HO{\cdot}\overset{|}{C}Me_2{-} \longrightarrow H\overset{+}{O}{=}\overset{|}{C}Me + Me{\cdot} \qquad (3)$$

The formulation (XXIII) for this complex and (XXIV) for the hydrogenation product are in agreement with the n.m.r. data. With alcoholic potassium cyanide the complex (XXIII) gave a product characterised by ions at *m/e* 154 ($C_{10}H_{18}O$), 139 ($C_9H_{15}O$), 136 ($C_{10}H_{16}$), and 59 ($Me_2C{=}\overset{+}{O}H$). The formulation of structure (XXV) for this product corresponds with that for (XX) before, and with the n.m.r. data.



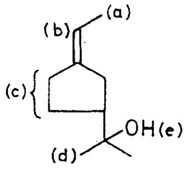
(XXIII)

τ (a) 6·97 (d), (b) 6·09 (d), (c) 4·7 (m), (d) 7·79—8·14, (e) 8·78 (s), (f) 7·64 (s)



(XXIV)

τ (a) 9·08 (t), (b) 8·84 (m), (c) 8·4 (m), (d) 8·74 (s), (e) 7·8 (s)



(XXV)

τ (a) 8·38 (d, *J* 6 Hz) (b) 4·76 (m), (c) 7·7, 7·8, (d) 8·79 (s), (e) 7·7

EXPERIMENTAL

Commercial samples of *cis*- and *trans*-ocimene and myrcene were purified by preparative g.l.c.

A solution of *cis*-ocimene (10 mmol) and disodium tetrachloropalladate(II) (2·7 mmol) in methanol (10 ml) was set aside for 15 h; the mixture was then filtered and the solvent evaporated off under reduced pressure at room temp. The organic residue, extracted into chloroform, was purified by t.l.c. on silica gel in benzene–ethyl acetate (5 : 1). A liquid product, R_F 0·9, contained *cis*- and *trans*-ocimene and other substances. A yellow product, R_F 0·5, gave *bis[chloro*-(2,3,4-trihapto-*geranyl methyl ether*)-*palladium*(II)] (IV), m.p. 136° (from ether–ethanol) [Found: C, 42·85; H, 6·25; Pd, 11·25. $(C_{11}H_{19}OPdCl)_2$ requires C, 42·65; H, 6·45; Pd, 11·45%]. $\lambda_{max.}$ (EtOH) 215 (ε 10^4) and 233 ($9{\cdot}5 \times 10^3$); $\nu_{max.}$ 1670, 1095, and 840 cm^{-1}; *m/e* 166, 151, 135, 121, 107, 98, and 45. This complex was shaken with hydrogen in ethanol to give methyl tetrahydrogeranyl ether, b.p. 105° at 15 mmHg, identified by g.l.c. comparison and n.m.r. spectra [τ 6·56 (2H, q, *J* 7 Hz), 6·71 (3H, s, OMe), 9·11 (9H, d, *J* 6 Hz), 8·72, and 8·85 (10H, m)] with an authentic sample prepared by hydrogenation of geranyl methyl ether prepared from geraniol, sodium hydride, and methyl iodide.

The reaction of *trans*-ocimene with disodium tetrachloropalladate(II) was carried out in a similar way.

3,7-*Dimethylocta*-2,4,6-*trienyl Methyl Ether*.—Complex (IV) (3 mmol) in dioxan (4 ml) with pyridine (15 mmol) was stirred for 3 h. Deposited palladium was filtered off and the filtrate was acidified (HCl) and extracted. The product was chromatographed on silica gel in light petroleum and gave a material, R_F 0·4, which was distilled; $\lambda_{max.}$ (EtOH) 270 (ε $3{\cdot}5 \times 10^4$), 278 (4×10^4), and 288 ($3{\cdot}4 \times 10^4$) nm. Hydrogenation (Pt–ethanol) gave methyl tetrahydrogeranyl ether (g.l.c. comparison).

Bis[chloro-(2,3,4-trihapto-*geranyl acetate)palladium*(II)], m.p. 130°, was obtained from *cis*-ocimene (5 mmol) and bis(benzonitrilechloro)palladium(II) (2 mmol) in acetic acid [Found: C, 43·5; H, 6·16; Cl, 10·2; Pd, 31·6. $(C_{12}H_{19}O_2PdCl)_2$ requires C, 42·8; H, 5·64; Cl, 10·55; Pd, 31·5%] (from ether); $\nu_{max.}$ 1735 and 1230 cm^{-1}. This product gave tetrahydrogeranyl acetate (g.l.c. comparison) when shaken in ethanol with hydrogen.

cis-*Ocimene with Disodium Tetrachloropalladate*(II) *in Acetone*.—(a) *cis*-Ocimene (5 mmol) and disodium tetrachloropalladate(II) (1·5 mmol) in acetone (15 ml) containing calcium carbonate (3 mmol) were stirred for 9 h. The product (g.l.c. comparison) was found to contain *cis*- and *trans*-ocimene, and limonene in roughly equal amounts.

(b) *cis*-Ocimene (12 mmol) and disodium tetrachloropalladate(II) (1·5 mmol) were set aside for 9 h in acetone (10 ml); the mixture was then filtered, and concentrated (*in vacuo*). The product was separated on silica gel (t.l.c.) first with light petroleum as eluant, which removed excess of organic material, R_F 0·73, and then with benzene–ethyl acetate (5 : 2) which gave a yellow product, R_F 0·8 (Found: C, 45·2; H, 5·8; Cl, 12·1; Pd, 32·9. Calc. for $C_{20}H_{32}Pd_2Cl_2$: C, 43·5; H, 5·8; Cl, 12·7; Pd, 38·0%), $\nu_{max.}$ 1670 and 1645 cm^{-1}; *m/e* 188, 173, 156, 142, 128, 119, 97, 69, 55, and 43. When shaken in hydrogen in ethanol this material gave a product with a mass spectrum (*m/e* 282, 267, 211, 197, 169, 141, 127, 113, 99, 85, 71, 57, and 43) identical with that of 2,6,11,15-tetramethylhexadecane prepared by reaction of sodium and tetrahydrogeranyl bromide; the two substances proved to be the same by g.l.c. comparison also.

Myrcene with Disodium Tetrachloropalladate(II) *in Methanol*.—Myrcene (8 mmol) and disodium tetrachloropalladate(II) (2 mmol) were set aside for 20 h in methanol (10 ml); the solution was then filtered and the solvent evaporated off under reduced pressure. T.l.c. of the organic residue on silica gel with benzene–ethyl acetate (5 : 1) as eluant gave a band, R_F 0·85, containing uncomplexed materials, and two yellow components, R_F 0·71 and 0·44. The material with R_F 0·71 proved to contain a number of components by t.l.c. on silica gel in benzene, but none in sufficient amount for further examination. The product with R_F 0·44 formed a yellow solid, m.p. 48—50° (from ether) [Found: C, 42·6; H, 6·1; Cl, 11·45. $(C_{11}H_{19}OPdCl)_2$ requires C, 42·65; H, 6·45; Cl, 11·45%]; $\lambda_{max.}$ 217 and 238 nm ($9{\cdot}5 \times 10^3$); $\nu_{max.}$ 1075 (CO) cm^{-1}; *m/e* 166, 151, 136, 134, 119, 73, and 59. This product is regarded as *bis-*{*chloro*-[1,α,β-trihapto-3-(1-*methoxy*-1-*methylethyl*)-1-*vinylcyclopentane*]*palladium*(II)}.

When shaken in ethanol under hydrogen this gave 1-ethyl-3-(1-methoxy-1-methylethyl)cyclopentane (XVII); *m/e* 155, 138, 109, 73, 67, and 59. Dihydro-α-terpinyl methyl ether prepared for comparison gave a similar mass spectrum, but with a significant ion at *m/e* 123 (C_9H_{15}) ($C_{11}H_{22}O - CH_4O - CH_3$), which did not appear in the mass spectrum of (XVII).

The *pyridine complex* from (XVIII) was prepared in chloroform and separated by t.l.c. on silica gel in benzene–ethyl acetate (5 : 1 (R_F 0·5); τ 1·16—2·71 (C_5H_5N), 6·83 (3H, s, OMe), 6·22 (d, *J* 7 Hz) and 6·95 (d, *J* 13 Hz) (π-allyl), 8·02—8·10 (5H, m, cyclopentane), and 8·86 (6H, s, $Me_2C{\cdot}O$).

The *triphenylphosphine derivative* of (XVIII) was characterised by its n.m.r. spectrum: τ 2·43—2·82 (15, m), 6·92 (3H, s), 8·88 (6H), and 6·84 (π-allyl).

1-*Ethylidene*-3-(1-*methoxy*-1-*methylethyl*)*cyclopentane*, obtained from (XVIII) and potassium cyanide in ethanol was purified by t.l.c. on silica gel in benzene (R_F 0·3). The n.m.r. data are given in the text.

Myrcene with Disodium Tetrachloropalladate(II) *in Methanol–Calcium Carbonate*.—This reaction gave, in addition to the complex (XVIII), a second yellow product, R_F 0·7 on silica gel in benzene–ethyl acetate (5 : 1), m.p. 95° (from ether–light petroleum). The quantity available did not permit combustion analysis. However, when this product was shaken with hydrogen in ethanol methyl tetrahydrogeranyl ether was obtained (g.l.c. comparison). The n.m.r. data are given in the text.

Myrcene with Disodium Tetrachloropalladate(II) *in Acetone*.—Myrcene (4·7 mmol), disodium tetrachloropalladate(II) (1·7 mmol), and calcium carbonate (10 mmol) were set aside for 24 h in acetone (15 ml). T.l.c. on silica gel with benzene–ethyl acetate (5 : 2) as eluant separated uncomplexed material, R_F 0·87, and two yellow products, R_F 0·79 and 0·15.

The product with R_F 0·79 after rechromatography was obtained as a yellow solid; *m/e* 272, 257, 229, 203, 189, 170, 161, 83, and 69 (Found: C, 55·6; H, 7·0. Calc. for $C_{20}H_{32}PdCl$: C, 58·0; H, 7·7%. Calc. for $C_{20}H_{32}PdCl_2$: C, 53·6; H, 7·1%); τ 4·93 (3H, m), 5·27 (2H, s), 6·1 (d, *J* 6 Hz), 6·96 (d, *J* 13 Hz), 7·95—8·12 (9H, m), 8·32, 8·40, 8·43 (12H), and 8·75 (3H, d, *J* 4 Hz).

When shaken with hydrogen in ethanol this substance gave a product, b.p. 160° at 5 mmHg. This perhydro-C_{20} hydrocarbon had a mass spectrum with peaks at *m/e* 282, 280, 267, 207, 169, 141, 127, 111, 109, 99, 85, 71, 69, 57, and 43, and an n.m.r. spectrum with signals at τ 8·75 (25H) and 9·11 (18H, d, *J* 5 Hz).

The product with R_F 0·15 was rechromatographed to give a yellow solid [Found: C, 40·9; H, 5·9. $(C_{10}H_{17}OPdCl)_2$ requires C, 40·6; H, 6·1%], regarded as *bis*{*chloro*-[1,α,β-trihapto-3-(1-*hydroxy*-1-*methylethyl*)-1-*vinylcyclopentane*]-*palladium*(II)} (XXIII); $\nu_{max.}$ 3450 and 1130 (OH) cm^{-1}; *m/e* 152, 137, 134, 94, and 79. The n.m.r. data are given in the text. When shaken with hydrogen in ethanol this complex gave a product, b.p. 110° at 11 mmHg; $\nu_{max.}$ 3400 and 1150 cm^{-1}; *m/e* 141, 123, 109, 95, 81, 67, 59, and 55 with metastable ions $141^+ \rightarrow 123^+$ and $123^+ \rightarrow 81^+$. This is regarded as 1-ethyl-3-(2-hydroxy-2-methylethyl)-cyclopentane (XXIV).

The complex (XXIII) was also obtained in excellent yield by reaction of myrcene and disodium tetrachloropalladate(II) in acetone–water (3 : 5).

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