Rhodium, Palladium, and Platinum Complexes formed from 2,2,4-Trimethylpent-3-en-1-ol

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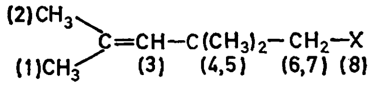
2,2,4-Trimethylpent-3-en-1-ol ($Me_2C{:}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$) reacts with palladium(II) chloride to give π-enyl complexes, *i.e.* $\{[(CH_2{\cdot}CMe{\cdot}CH){\cdot}CMe_2{\cdot}CH_2{\cdot}OAc]PdCl\}_2$ in aqueous acetic acid and $\{[(CH_2{\cdot}CMe{\cdot}CH){\cdot}CMe_2{\cdot}CH_2{\cdot}OH]PdCl\}_2$ in dimethylformamide. No interaction between the palladium and acetate or hydroxy-functions is observed. Reaction with $[Rh(CO)_2Cl]_2$ in benzene gives the olefin complex $[(Me_2C{:}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH)Rh(CO)Cl]_2$ in which the hydroxy-function is also co-ordinated to the metal. With platinum(II) chloride in dimethylformamide the alcohol yields an olefin complex $[Me_2C{:}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}O{\cdot}PtCl]_2$ which contains a Pt–O covalent bond. N.m.r. and i.r. data are given to support the structures proposed.

2,2,4-TRIMETHYLPENT-3-EN-1-OL (Ib) and the corresponding acetate (Ia) are possible precursors of acyclic π-enyl systems. Our original intention was to prepare the chloro-analogue of (Ib) and then the corresponding Grignard reagent; chlorination, however, resulted in a rearrangement to give 5-chloro-2,5-dimethylhex-2-ene $(CH_3)_2C{:}CH{\cdot}CH_2{\cdot}C(CH_3)_2Cl$ which eliminates hydrogen chloride to give diene derivatives.[1] We studied there-



(I) a; X = OAc
b; X = OH

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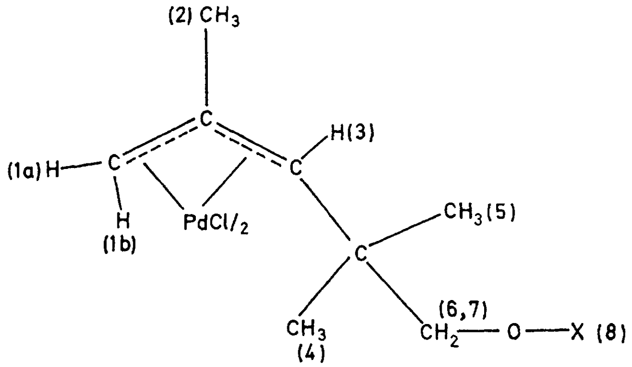
[1] C. F. Wilcox and D. L. Nealy, *J. Org. Chem.*, 1963, **28**, 3454.

fore the reactions of the alcohol with transition-metal species, and here report complexes of rhodium, palladium, and platinum.

RESULTS AND DISCUSSION

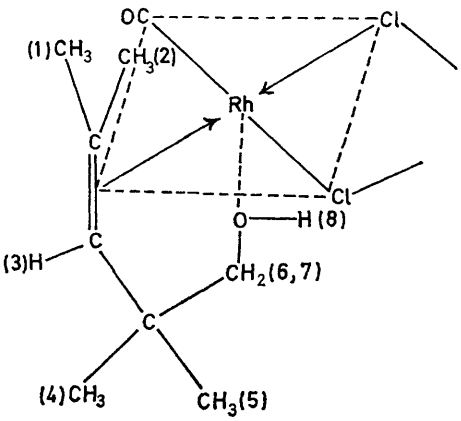
2,2,4-Trimethylpent-3-en-1-ol (Ib) reacts with palladium dichloride in 50% aqueous acetic acid at 90° to give yellow crystals which we formulate as the dimeric π-enyl complex (IIa) in which acetylation of the hydroxy-group by the solvent has occurred. This result was confirmed by isolation of the same product from the reaction of the acetate (Ia) and palladium dichloride under analogous conditions. The dimeric nature of this complex is given support by the reaction with triphenylphosphine which cleaves the halogen bridge to give the monomeric phosphine adduct (III). The formation of π-enyl palladium complexes by proton abstraction from an olefinic ligand is well known,[2] and the 60 MHz ^{1}H n.m.r. spectral assignments (see Table) are consistent with the structures proposed. The failure to observe inequivalence between the methylene protons (6,7-H) in complexes (IIa) and (IV), and also the methyl protons (4,5-H) in complex (IV) presumably indicates that any inequivalence is too small to detect. The absence of any marked interaction between the carbonyl group and metal centre is indicated by the similarity in carbonyl frequencies for free (1745 cm^{-1}) and complexed (*ca.* 1735 cm^{-1}) olefinic ligand.



(IIa) X = OAc
(IV) X = OH

We have prepared a palladium π-enyl derivative (IV) of the alcohol (Ib) in which the hydroxy-group is retained by using dimethylformamide (DMF) as solvent.[3] There appears to be no interaction between the hydroxy-group and palladium since co-ordination to a metal would be expected to decrease the hydroxy stretching frequency, whereas it actually increases by 80 cm^{-1} on complex formation. The intermolecular hydrogen bonding of the free liquid alcohol is reduced by co-ordination to a metal *via* a functional group other than hydroxy, and the stretching frequency of the latter is thus increased.

In contrast, we find that (Ib) reacts with $[Rh(CO)_2Cl]_2$ in benzene to give a stable, crystalline, diamagnetic product in which a strong interaction between the hydroxy-group and the metal occurs. Analytical and i.r. data support the dimeric structure $[(ol)Rh(CO)Cl]_2$, (V) (*M* in benzene 520, calc. 589). A single carbonyl absorption is observed at 2000 cm^{-1}, and ν(Rh–Cl) absorptions at 300s and 250w cm^{-1} are consistent with bridging chlorine *trans* to CO.[4] A similar complex with ethylene has been reported.[5] The hydroxy stretching frequency is lowered by 210 cm^{-1} on co-ordination, a shift which is not altered on dilution, indicating an intramolecular effect. In addition a large chemical shift downfield for the hydroxy-proton (bonded τ 3·76, free ligand τ 7·58) is observed in accordance with a pronounced interaction between the oxygen and metal centre. A rhodium(I) complex of allyl alcohol $[(ol)_2RhCl]_2$ is known,[6] but no mention was made of an analogous metal–hydroxy-interaction, although a similar but much weaker effect has been observed in the copper complex $[(ol)CuCl]_2$.[7]



(V)

A third type of interaction occurs on reaction of the alcohol (Ib) with platinum dichloride in DMF under the same conditions which yielded a π-enyl complex with palladium. The yellow micro-crystalline product exhibits no hydroxy i.r. absorption and the hydroxy-proton is absent from the n.m.r. spectrum. Analysis corresponds to the formula $[PtCl(C_8H_{15}O)]_n$ and a parent ion at 712 mass units (^{194}Pt) in the mass spectrum supports a dimeric structure ($n = 2$). We formulate the complex as the alkoxy-derivative (VI). The n.m.r.

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[2] R. Hüttel and J. Kratzer, *Angew. Chem.*, 1959, **71**, 456. R. Hüttel and H. Christ, *Chem. Ber.*, 1963, **96**, 3101; G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, 1962, **1**, 896; J. Tsuji, S. Imamura, and J. Kiji, *J. Amer. Chem. Soc.*, 1964, **86**, 4491; M. Donati and F. Conti, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 343; A. D. Ketley and J. Braatz, *Chem. Comm.*, 1968, 169.

[3] D. Morelli, R. Ugo, F. Conti, and M. Donati, *Chem. Comm.*, 1967, 801.

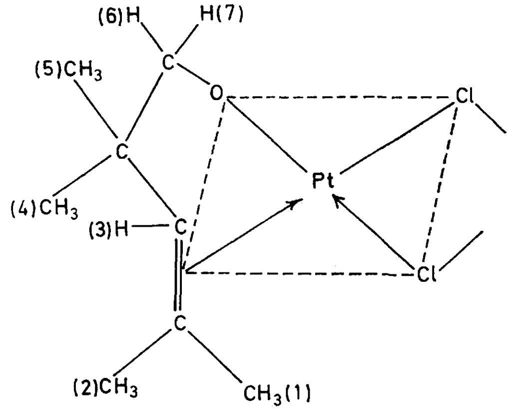
[4] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

[5] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 211.

[6] J. K. Nicholson and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 282.

[7] T. Ogura, N. Furuno, and S. Kawaguchi, *Bull. Chem. Soc. Japan*, 1967, **40**, 1171.

spectral data (see Table) shows that the methyl groups CH_3^1 and CH_3^2 are non-equivalent (τ 8·00, 9·48) in constrast to the rhodium derivative (τ 8·36, 8·38). In addition the *gem* methylene protons (6,7-H) are non-equivalent (τ 5·80, 6·92) and appear as doublets ($J_{6,7}$ = 11 Hz). No evidence of ^{195}Pt–H coupling was observed; the intervening oxygen atom in (VI) would explain the absence of Pt-coupling on 6,7-H but it is not known why 3-H is immune. The i.r. spectrum exhibits strong bands at 622, 578, 500, and 455 cm^{-1} (not present in the free ligand) which may be attributed to Pt–O vibrations.[8,9] A complex series of bands appear in the ν(Pt–Cl) region (353s, 346s, 332m, 310s, and 274s cm^{-1}) which may also include further Pt–O absorptions. Addition of *p*-toluidine to the dimer results in splitting of the bridge to give the monomeric amine adduct (*M* in benzene 412, calc. 466) which was not soluble enough for detailed n.m.r. studies. Mass spectral analysis of this adduct indicated initially only *p*-toluidine as parent ion; further heating generated the dimeric precursor. The far-i.r. spectrum shows two bands in the ν(Pt–Cl) region at 325s and 307m cm^{-1}. The 274 cm^{-1} absorption in (VI) is presumably due to bridging Pt–Cl,[10,11] since it disappears on splitting of the bridge. However it is difficult to make definitive assignments in view of the complexity observed.



(VI)

The formation of an alkoxy-platinum complex may be regarded as an extension of the effect found in a series of allyl alcohol complexes (ol)(amine)$PtCl_2$ in which a strong intramolecular interaction between hydroxy hydrogen and chlorine groups was established.[12] Further enhancement of such hydrogen bonding and consequent loss of hydrogen chloride could result in an analogous C–O–Pt bond.

^{1}H n.m.r. and i.r. data for free ligands and metal complexes [a]

	Compound	1-H		2-H	3-H	4-H	5-H	6-H	7-H	8-H	ν(C=O)	ν(OH)
(Ia)	R^{1}OCOMe [b]		8·30m		4·95m	8·95s		6·20s		8·05s	1745	
(IIa)	[(R^{2}OCOMe)PdCl]$_2$ [c]	a 6·30s	b 7·28s	7·75s	6·50s	8·70s	8·72s	5·92s		7·90s	1738	
(III)	(R^{2}OCOMe)(Ph$_3$P)PdCl [c]	7·42s	7·52s	7·92s	5·90s	8·45s	8·57s	5·70s	5·75s	7·92s	1733	
(Ib)	R^{1}OH [b]		8·30m		4·95sep	8·95s		6·65s		7·85s		3370
(IV)	[(R^{2}OH)PdCl]$_2$ [d]	a[e] 6·30d	b 7·25s	7·77s	6·53d [e]	8·77s		6·30 [e]		7·67s		3450
(V)	[(R^{1}OH)(CO)RhCl]$_2$	8·36s		8·38s	6·42s	8·57s	9·35s	6·46d	6·56d	3·76br [g]		3160
(VI)	[(R^{1}O)PtCl]$_2$ [f]	8·00s		9·48s	5·72s	8·65s	8·75s	5·80d [h]	6·92d [h]			

[a] τ Values in p.p.m. Me_4Si internal reference = 10·00; i.r. in cm^{-1}. [b] 60 MHz in CCl_4, R^1 = $Me_2C{=}CH{\cdot}CMe_2{\cdot}CH_2$–. [c] 60 MHz in $CDCl_3$; R^2 = $(CH_2{\cdot}CMe{\cdot}CH){\cdot}CMe_2{\cdot}CH_2$–. [d] 220 MHz in $CDCl_3$. [e] 6,7-H resonance (probably two singlets from inequivalent protons) overlaps with 1a-H; 1a-H coupled to 3-H, J[H(1a)–H(3)] < 1·0 Hz. [f] 220 MHz in C_6D_6. [g] 100 MHz in C_6D_6 using C.1204 spectrum accumulator. [h] J[H(6)–H(7)] 11·0 Hz.

EXPERIMENTAL

Molecular weight determinations (in benzene solution) were made using a modified Menzies–Wright ebulliometer. N.m.r. spectra at 60 MHz were recorded on a Perkin-Elmer R10 spectrometer at 33·5°, and at 220 MHz on a Varian HR 220 spectrometer at 13° using internal tetramethylsilane as standard. I.r. spectra (500—200 cm^{-1}) were recorded as Nujol mulls on a Grubb Parsons DM4 spectrometer, and (4000—400 cm^{-1}) on a Grubb Parsons Spectromaster as KBr discs or Nujol mulls. Electron-impact mass spectra were obtained on a conventional AEI MS9 high-resolution mass spectrometer. M.p.s were determined using a Kofler block apparatus. Rhodium, palladium, and platinum chlorides were obtained from Johnson, Matthey Limited. $[Rh(CO)_2Cl]_2$ was prepared by the literature method.[13] 2,2,4-Trimethylpent-3-en-1-yl acetate was prepared according to the method of Blake and Hamman,[14] and 2,2,4-trimethylpent-3-en-1-ol by alkaline hydrolysis of the acetate (15% aqueous sodium hydroxide in methanol) at reflux. Ether extraction and subsequent distillation afforded the alcohol (75%) b.p. 64—66°/15 mmHg, n_D^{25} 1·4530 (lit.[1] b.p. 89—90°/60 mmHg, n_D^{25} 1·4546).

Di-μ-chloro-di(2,2,4-*trimethylpent*-3-*en*-1-*ylacetate*)*dipalladium*(II), (Ia).—2,2,4-Trimethylpent-3-en-1-ylacetate (1·9 g, 11·3 mmol) and palladium chloride (2·0 g, 11·3 mmol) were heated in 50% aqueous acetic acid (100 ml) at 90° for 5 h

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[8] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 1967, **6**, 433.

[9] G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1733.

[10] D. M. Adams, *Proc. Chem. Soc.*, 1961, 335.

[11] A. D. Allen and T. Theophanides, *Canad. J. Chem.*, 1964, **42**, 1551.

[12] J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *J. Chem. Soc.*, 1963, 5170.

[13] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 212.

[14] U.S.P. 2,889,354/1959.

under nitrogen. Filtration and subsequent evaporation of the filtrate afforded a red-brown gum which was dissolved in ethyl acetate and chromatographed on neutral alumina to give a yellow oil (1·8 g). Addition of benzene–pentane precipitated pale yellow crystals (1·0 g 29% yield), m.p. 132—136° (decomp.) (Found: C, 38·6; H, 5·9; Cl, 11·0; Pd, 34·3. $C_{40}H_{68}Cl_4O_8Pd_2$ requires C, 38·6; H, 5·5; Cl, 11·4; Pd, 34·2%).

The same complex was also obtained (20% yield) from 2,2,4-trimethylpent-3-en-1-ol and palladium chloride under identical conditions.

Chloro(2,2,4-*trimethylpent*-3-*en*-1-*ylacetate*)*triphenylphosphinepalladium*(II), (III).—The dimer (IIa) (0·6 g, 0·97 mmol) and triphenylphosphine (0·5 g, 1·93 mmol) were heated to 50° in benzene (10 ml) for 1 h. Filtration, evaporation of solvent and recrystallisation from methylene dichloride–pentane afforded pale yellow crystals (0·9 g, 82% yield), m.p. 206—207° (decomp.) (Found: C, 58·5; H, 5·7; P, 5·8. $C_{28}H_{32}ClO_2PPd$ requires C, 58·7; H, 5·6; P, 5·4%).

Di-μ-*chloro-di*(2,2,4-*trimethylpent*-3-*en*-1-*ol*)*dipalladium*(II), (IV).—2,2,4-Trimethylpent-3-en-1-ol (3·0 g, 23·4 mmol) and palladium chloride (4·0 g, 22·6 mmol) were stirred in redistilled dimethylformamide (30 ml) at room temperature for 18 h under nitrogen. Filtration and subsequent evaporation of the filtrate gave a red-brown oil. Addition of toluene precipitated $[(DMF)_2H]_2[Pd_2Cl_6]$[5] (4·6 g). The toluene-soluble fraction was chromatographed on neutral alumina, and elution with ethyl acetate–toluene (1 : 1) gave a yellow solid which was recrystallised from diethyl ether–hexane (1·3 g, 20% yield), m.p. 140—142° (decomp.) (Found: C, 35·9; H, 5·6; Cl, 12·9. $C_{16}H_{30}O_2Cl_2Pd_2$ requires C, 35·7; H, 5·6; Cl, 13·2%).

Di-μ-*chloro-di*(*carbonyl*)*di*(2,2,4-*trimethylpent*-3-*en*-1-*ol*)*dirhodium*(I), (V).—The alcohol (Ib) (2·0 g, 15·6 mmol) and di-μ-chloro-tetra(carbonyl)dirhodium(I) (0·5 g, 2·58 mmol) were dissolved in benzene (30 ml) and heated at reflux for 3 h under nitrogen. Concentration of the resultant orange-yellow solution precipitated the product as yellow crystals (0·7 g, 93% yield), m.p. 145—147° (Found: C, 37·1; H, 5·7; Cl, 12·3. $C_{18}H_{32}Cl_2O_4Rh_2$ requires C, 36·7; H, 5·5; Cl, 12·1%).

Di-μ-*chloro-di*-1,3,4-*trihapto*-2,2,4-*trimethylpent*-3-*en*-1-*olatodiylplatinum*(II),[15] (VI).—Platinum dichloride (4·0 g, 15·1 mmol) was stirred in dry dimethylformamide (30 ml) under nitrogen for 30 min. The alcohol (Ib) (1·9 g, 15·1 mmol) was added and the mixture stirred at room temperature for 17 h. Filtration and evaporation afforded a black oil which was extracted with toluene and chromatographed on neutral alumina to give, on addition of hexane, yellow microcrystals (1·9 g, 36% yield), m.p. 140—141° (Found: C, 27·2; H, 4·3; Cl, 9·9; Pt, 53·0. $C_{16}H_{30}Cl_2O_2Pt_2$ requires C, 26·9; H, 4·2; Cl, 10·0; Pt, 54·5%).

Reaction with p-*Toluidine*.—Bridge splitting was achieved by reaction of (VI) (0·4 g, 0·56 mmol) and *p*-toluidine (0·1 g, 1·12 mmol) in toluene (30 ml) at room temperature for 2 h which precipitated the *p*-toluidine adduct as yellow crystals (0·4 g, 70% yield), decomp. 150° (Found: C, 38·4, 38·9; H, 5·1; Cl, 8·0; N, 3·2. $C_{15}H_{24}ClNOPt$ requires C, 40·2; H, 5·4; Cl, 7·8; N, 3·1%).

[1/947 *Received, June* 10*th*, 1971]

[15] F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6230.