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PLATINUM(II) AND PALLADIUM(II) COMPLEXES FORMED FROM 1-HEXEN-5-ONE (ALLYLACETONE)

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SUMMARY

1-Hexen-5-one, (I), reacts with $Pt_2X_4(C_2H_4)_2$ to give *cis*-$PtX_2[CH_2{=}CHCH_2CH_2C(O)Me]$, which shows no tendency towards ligand isomerisation. Isomerisation of (I) occurs on reaction with sodium chloropalladate(II), and is accompanied by the formation of a π-allyl complex, $\{[MeCH{=}CH{=}CHC(O)Me]PdCl\}_2$, which undergoes the normal bridge-cleavage reactions with pyridine and triphenylphosphine. NMR and IR data are given to support the structures proposed.

INTRODUCTION

The reaction of 4-methyl-3-penten-2-one, (II) with sodium chloroplatinate(II)[1] or $Pt_2Cl_4(C_2H_4)_2$[2] has been shown to result in isomerisation of the olefin and formation of *cis*-$PtCl_2[CH_2{=}CMeCH_2C(O)Me]$ whereas the reaction of (II) with sodium chloropalladate(II) gave a π-allyl complex $\{[CH_2{=}CMe{=}CHC(O)Me]PdCl\}_2$[3,4]. We now describe the coordinative behaviour of the related ligand 1-hexen-5-one, (I), towards platinum(II) and palladium(II).

RESULTS AND DISCUSSION

The reaction of (I) with $Pt_2X_4(C_2H_4)_2$ (X = Cl, Br) gives a crystalline, mononuclear complex, $PtX_2(C_6H_{10}O)$. [The related reaction of (I) with dry sodium chloroplatinate(II) gave an intractable red oil.] The nature of the ligand, $C_6H_{10}O$, was determined by reaction of the complex with tri-n-butylphosphine. This results in a quantitative displacement of the ligand which has NMR and IR spectra identical to (I). Although the complex was too insoluble for NMR measurements, IR spectra indicate that both the carbonyl and olefin groups are coordinated to platinum since the two strong bands due to ν(C=O) and ν(C=C) in the free ligand are both shifted to lower frequency in the complex (see Table 1).

The Raman spectrum of $PtCl_2(C_6H_{10}O)$ shows two intense bands due to ν(Pt–Cl) which are absent in the corresponding bromo complex and is thus consistent with a *cis*-configuration. Bands, which are almost coincident with the Raman bands, are also observed in the far-IR spectra (see Table 1), thus lending support to these

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound	*M.p.* (°C)	*Analysis found (calcd.) (%)*				*Mol.wt.*[a] *found (calcd.)*	*IR bands* (cm^{-1})			*Raman bands* (cm^{-1}) (Pt–X)[b]
		C	*H*	*N*	*Hal*		$\nu(C{=}O)$	$\nu(C{=}C)$	$\nu(Pt$–$X)$[b]	
CH_2=$CHCH_2CH_2C(O)Me$							1721	1645		
$MeCH$=$CHCH_2C(O)Me$							1699	1641		
$MeCH_2CH$=$CHC(O)Me$							1676	1627		
cis-$[PtCl_2(I)]$[c]	170–174	19.8 (19.8)	2.8 (2.75)		19.35 (19.5)	395 (364)	1620	1510	364, 325	362 323
cis-$[PtBr_2(I)]$[c]	146–150	16.2 (15.9)	2.3 (2.2)		35.9 (35.3)	434 (453)	1615	1510	253 213	255 214
$[Pd_2Cl_2(A)_2]$[d]	175–185 (dec.)	30.6 (30.2)	3.8 (3.8)		14.0 (14.9)	464 (477)	1685		261 252	
$[PdBr_2(A)_2]$[d]	215–225 (dec.)	25.0 (25.4)	3.3 (3.2)		27.8 (28.2)	533 (566)	1680		188 169	
$[PdCl(A)Py]$[d]	194–198 (dec.)	41.1 (41.6)	4.3 (4.4)	4.3 (4.4)	11.5 (11.2)	333 (317.5)	1687		287	
$[PdBr(A)Py]$[d]	175–185 (dec.)	36.0 (36.5)	3.95 (3.9)	3.75 (3.9)	22.3 (22.1)	383 (362)	1687		208 or 191[e]	
$[PdCl(A)(PPh_3)]$[d]	⩾200 (dec.)	57.5 (57.5)	4.6 (4.8)			515 (500.5)	1689		260	

[a] Molecular weights measured osmometrically at ca. 35° in ca. 1–10×10^{-3} *M* solutions in chloroform. [b] X = Cl or Br. [c] I = CH_2=$CHCH_2CH_2C(O)Me$. [d] A = $MeCH$=CH=$CHC(O)Me$. [e] Assignment not clear.

assignments*. These frequencies are considerably higher than is usually found for square-planar platinum(II) complexes and is a reflection of the low *trans*-influence of an olefin and a ketonic carbonyl when coordinated to platinum(II)[5].

Thus $PtX_2(C_6H_{10}O)$ is formulated as shown in Fig. 1, and unlike (II), (I) does not isomerise on coordination to platinum(II). This is presumably a reflection of the greater stereochemical strain which would result by coordination of (II) without rearrangement compared to coordination of (I). Furthermore, no isomerisation of the ligand occurred on heating (ca. 110°) a toluene solution of $PtX_2(C_6H_{10}O)$ for 2 h. Apart from slight decomposition to platinum metal, unchanged complex could be recovered almost quantitatively.

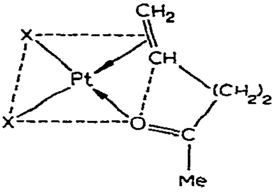

Fig. 1.

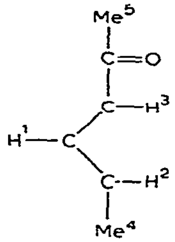

Fig. 2.

The reaction of (I) with sodium chloropalladate(II) or $PdCl_2(PhCN)_2$ gives a dimeric π-allyl complex, $Pd_2Cl_2(C_6H_9O)_2$. The far-IR spectra of the chloro and bromo analogues are very similar to those previously reported[6] for dimeric halo-bridged π-allyl–palladium complexes, (see Table 1), and support for this formulation comes from the products obtained by bridge-cleavage reactions, *e.g.*:

$$Pd_2Cl_2(C_6H_9O)_2 + 2\,L \rightarrow 2\,PdCl(C_6H_9O)L$$
$$L = PPh_3 \text{ or } Py$$

The product containing triphenylphosphine was too insoluble for NMR determinations but it was possible to obtain an NMR spectrum of the pyridine adduct which shows unambiguously that the C_6H_9O unit must be present as shown in Fig. 2. The resonances due to H^{1-5} (see Fig. 2.) occur at τ 4.1 (1) dd, 5.7 (1) dq, 6.3 (1) d, 8.55 (3) d, 7.8 (3) s**, respectively and both the coupling constants (J_{12}, J_{13} 11 Hz; J_{24} 6 Hz) and chemical shifts are very similar to those found for other palladium π-allyl complexes[4,6,7].

The band due to ν(C=O) in $PdCl(C_6H_9O)Py$ occurs at lower frequency than is found in (I) (see Table 1), due to conjugation of the olefin and carbonyl groups. Bands in similar positions are found for $PdCl(C_6H_9O)(PPh_3)$ and $Pd_2X_2(C_6H_9O)_2$ and it seems probable that these complexes also contain the C_6H_9O ligand as shown in Fig. 2. This formulation for $Pd_2Cl_2(C_6H_9O)_2$ has previously been suggested but no chemical or spectroscopic evidence was presented[8].

Olefin isomerisation by palladium catalysts is well known[9] and examination of the filtrate from the preparation of $Pd_2Cl_2(C_6H_9O)_2$ indicated the presence of all

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* Comparison of the Raman and far IR spectra of *cis*-$PtX_2(CH_2{=}CMeCH_2C(O)Me)$ suggests that ν(Pt–X) should be reassigned to X = Cl: IR 367, 325 cm^{-1}; Raman 365, 323 cm^{-1}. X = Br; IR, 238, 208 cm^{-1}; Raman 239, 215 cm^{-1}.

** Intensities are given in brackets: s, singlet; d, doublet; q, quartet.

three isomers of hexen-5-one (see Table 1). It proved impossible to obtain a complete separation of these isomers by TLC but both IR and UV spectra of the enriched fractions are consistent with the presence of these isomers. Thus the isolation of palladium complexes containing only the π-allyl group shown in Fig. 2. can be attributed to the increased stability afforded by conjugation of the π-allyl and carbonyl groups.

EXPERIMENTAL

Molecular weight determinations were made using an Hitachi–Perkin–Elmer 115 molecular weight apparatus. NMR spectra were recorded on a Perkin–Elmer R10 60MHz spectrometer at 33.5° in deuteriochloroform solution. IR spectra (4000–400 cm^{-1}) were recorded as nujol mulls on a Perkin–Elmer 457 spectrometer and (400–100 cm^{-1}) as polythene discs on an RIIC Fourier (FS720) spectrometer fitted with a transform FTS 100-7 computer. Raman spectra were obtained on crystalline samples using a Coderg spectrometer with an OIP 181B He/Ne laser emitting at 180 mW at 6328 Å. Electronic spectra were measured on a Unicam SP800 spectrometer using matched 1 cm silica cells. TLC was carried out by elution with dichloromethane of a 0.9 mm support of Kieselgel GF254 containing a fluorescent indicator. Microanalyses were carried out by Mr. G. Powell of this laboratory.

1-Hexen-5-one was supplied by Koch–Light Ltd. and used without further purification (VPC showed purity $>99\%$ using a 20% SE30 Chromosorb W column).

cis-Dichloro(1-hexen-5-one)platinum(II), $PtCl_2(CH_2{=}CHCH_2CH_2C(O)Me)$

This complex was prepared by either of the two following methods.

(*a*). The ligand (I) (0.3 g, 0.00306 mol) was added to a solution of $Pt_2Cl_4(C_2H_4)_2$ (0.9 g, 0.00153 mol) in benzene (50 ml). This solution was refluxed (3 h) and then allowed to cool to room temperature. Concentration gave the product (ca. 70%). Recrystallisation from dichloromethane gave pale yellow crystals.

(*b*). The ligand (I) (1.25 g, 0.0128 mol) was added to solid $Pt_2Cl_4(C_2H_4)_2$ (1.5 g, 0.00255 mol). Immediate effervescence occurred and after shaking for 5 min the excess ligand was removed *in vacuo*. The residue was recrystallised as above to give a ca. 70–80% yield of the product.

The corresponding bromide complex was prepared by method (*b*) using $Pt_2Br_4(C_2H_4)_2$.

Di-μ,μ'-chlorobis(1-methyl-4-acetylallyl)dipalladium(II), $\{[MeCH{=}CH{=}CHC(O)Me]PdCl\}_2$

This complex was prepared by either of the two following methods.

(*a*). A benzene solution of *cis*-$[PdCl_2(PhCN)_2]$ (0.5 g, 0.00138 mol) and the ligand (I) (0.14 g, 0.00143 mol) was boiled for 3 h. Concentration to dryness followed by recrystallisation from dichloromethane gave the product as pale yellow crystals ca. 60%).

(*b*). A slurry of sodium chloropalladate (0.35 g) in excess ligand, (I) (1.5 ml) was boiled vigorously for ca. 0.5 min. The excess ligand was removed *in vacuo* and the residue recrystallised from dichloromethane to give the product (50%).

The corresponding bromide was prepared by addition of a 10% excess of lithium bromide to a solution of the chloro complex in acetone solution. The solution was evaporated to dryness and the residue recrystallised from dichloromethane to give the product as yellow crystals.

Isomerisation of (I) by sodium chloropalladate

The filtrate from (*b*) above was shown in GLC to contain 5% of a product which IR and UV spectra suggest to be the two other isomers of hexen-5-one. An increased yield (15%) of these two isomers was obtained by boiling the reaction mixture for 1 h. Attempts to obtain these isomers pure were unsuccessful but the product after almost complete removal (< 1%) of (I) by TLC has bands in the IR spectrum at 1699, 1676, 1641 and 1627 cm^{-1} which have been assigned as shown in Table 1. The UV spectrum of this fraction showed a shoulder at ca. 275 and a very intense band at 226 nm. These bands are consistent with a low intensity $\pi \rightarrow \pi^*$ transition in the carbonyl group of $MeCH{=}CHCH_2C(O)Me$ and a high intensity $\pi \rightarrow \pi^*$ transition in the α,β-conjugated olefin of $MeCH_2CH{=}CHC(O)Me$[10].

Brdige-cleavage reactions of $\{[MeCH{=}CH{=}CHC(O)Me]PdX\}_2$ ($X = Cl, Br$)

To the palladium dimer (1 mol) in dichloromethane solution was added either triphenylphosphine or pyridine (2 mol). Concentration of the resulting solution gave the product which was recrystallised from dichloromethane. The properties of the compounds prepared in this way are shown in Table 1.

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REFERENCES

1 R. D. Gillard, B. T. Heaton and M. F. Pilbrow, *J. Chem. Soc. A*, (1970) 353.
2 M. F. Pilbrow, unpublished observations.
3 G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, 4 (1962) 986.
4 C. W. Fong and W. Kitching, *Aust. J. Chem.*, 22 (1969) 477.
5 R. McWeeney, R. Mason and A. D. C. Towl, *Discuss. Faraday Soc.*, 47 (1969) 20.
6 M. S. Lupin and B. L. Shaw, *J. Chem. Soc. A*, (1966) 1410.
7 K. Vrieze, H. C. Volger and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 3 (1969) 109.
8 J. Tsuji and S. Imamura, *Bull. Chem. Soc. Jap.*, 40 (1967) 197.
9 F. R. Hartley, *Chem. Rev.*, 69 (1969) 799.
10 C. N. R. Rao, *Ultra-Violet and Visible Spectroscopy*, Butterworths, London, 1967, p. 40.