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4-SUBSTITUTED BUT-2-ENYLPALLADIUM(II) COMPLEXES

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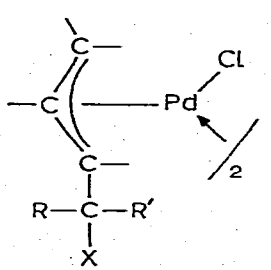
Summary

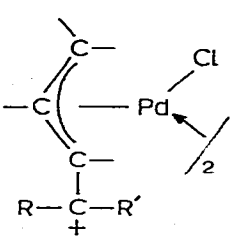
The chloro bridges in di-μ-chloro-4-methoxy- and di-μ-chloro-4-acetoxy-2-methyl-but-2-enylchloropalladium are split by Group V donor ligands Ph_3E (where E = P, As and Sb) to give $[(\eta^3\text{-}H_2CC(CH_3)CHCH_2X)\ PdCl \cdot EPh_3]$, (where X = OCH_3, $OCOCH_3$). These complexes are readily decomposed by dilute ethanolic hydrogen chloride yielding $[Ph_3E \cdot PdCl]_2$ and isoprene. The structures of the compounds are discussed in the light of their ^1H NMR spectra.

Introduction

4-Substituted but-2-enylpalladium complexes (I, X = Cl [1,2], OR [3], OCOR [4]) have been known for many years. Robinson and Shaw [3] showed that the 4-methoxy compounds (I, X = OCH_3) are readily converted into the 4-ethoxy-derivatives (I, X = OC_2H_5) by warming with 10^{-2} *M* hydrogen chloride in ethanol. As the ease of solvolysis was found to increase with increasing methyl substitution at C_4, it was suggested that the reaction proceeds via a carbonium ion intermediate (II), which can be stabilized in a similar way to the ferrocenyl carbonium ion (III) [5].



(I)



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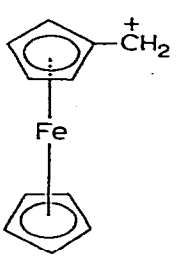


(III)

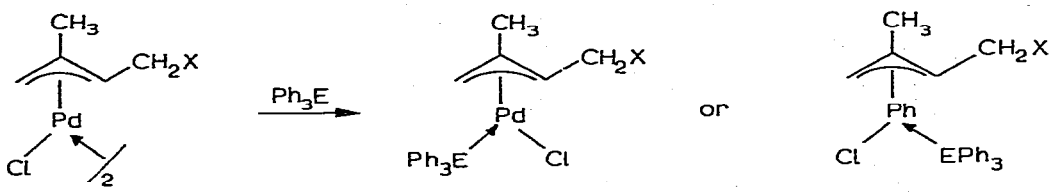
Lukas and Kramer [6] observed that cationic (diene)palladium complexes are formed by chloride abstraction from I (X = Cl), with SbF_5 at low tempera-

tures. PMR studies indicated that the organic ligand has an η^4-diene structure rather than the η^3-allyl structure (II).

More recently, a kinetic study [7] of the reaction between isoprene and $PdCl_4^{2-}$ has been published. This paper reports the preparation of some derivatives in which the chloro-bridges of I are split by Group V donor ligands, their PMR spectra and their decomposition by ethanolic hydrogen chloride.

Results and discussion

The chloro-bridges in (η^3-C_3H_5PdCl) are cleaved by triphenylphosphine, [8—10] and triphenylarsine [11—13]. Similarly, complexes I (X = OCH_3, $OCOCH_3$) react with Group V donor ligands Ph_3E (E = P, As, Sb) in a 1 : 1 ratio Ph_3E : Pd to yield crystalline air stable derivatives (V).



(I) (V) (VI)

Ia: X = OCH_3
Ib: X = $OCOCH_3$

Va: X = OCH_3, E = P
Vb: X = OCH_3, E = As
Vc: X = OCH_3, E = Sb
Vd: X = $OCOCH_3$, E = P
Ve: X = $OCOCH_3$, E = As
Vf: X = $OCOCH_3$, E = Sb

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Compound	Ligand	Colour	m.p. (°C)	Yield (%)	Found (calcd.) (%)		
					C	H	Other
Va	Ph_3P	White	133—5	85	57.81 (57.16)	5.30 (5.16)	Cl 6.86 (7.03)
Vb	Ph_3As	Yellow	136 dec.	80	52.69 (52.68)	4.69 (4.75)	
Vc	Ph_3Sb	Yellow	113	77	48.68 (48.52)	4.56 (4.38)	
Vd	Ph_3P	White	116—9 dec.	68	56.40 (56.42)	4.85 (4.93)	P 5.68 (5.82)
Ve	Ph_3As	Yellow	124—6 dec.	67	52.06 (52.20)	4.69 (4.56)	As 13.24 (13.03)
Vf	Ph_3Sb	Yellow	137	41	48.13 (48.27)	4.32 (4.22)	Sb 19.33 (19.57)

We assign structure V to these compounds rather than the isomeric form VI on the basis of PMR spectra, discussed below.

When Va, Vb and Vc (for numbering, see Table 1) are treated with 10^{-2} *M* ethanolic hydrogen chloride at room temperature, a brown precipitate of the bridged complex $[Ph_3E \cdot PdCl]_2$ is formed quantitatively over several hours, together with isoprene. Thus decomposition occurs under these conditions rather than the replacement of the methoxy group by ethoxy. The acetoxy complexes Vd, Ve, Vf react almost immediately to give $[Ph_3E \cdot PdCl]_2$, isoprene and ethyl acetate (formed by acid catalysed esterification of acetic acid).

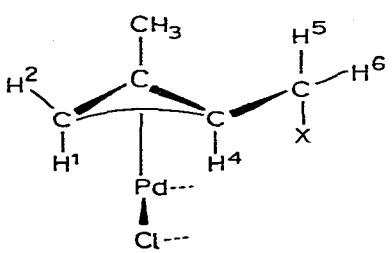
Compound I (X = Cl) does not yield the expected complex of type V with Ph_3E, but is decomposed to $[Ph_3E \cdot PdCl]_2$ and isoprene even in the absence of added acid.

Discussion

Addition of a Group V donor ligand therefore appears to destabilise 4-substituted but-2-enylpalladium complexes towards acid. As the 4-methoxy compounds are decomposed more slowly than the 4-acetoxy compounds, we suggest that the reaction involves protonation of the $-OCH_3$ or $OCOCH_3$ oxygen atom, followed by elimination of methanol or acetic acid respectively. In the 4-chloro-derivative, chloride ion is a sufficiently good leaving group to cause decomposition without addition of acid. The high *trans* effect of Ph_3P will also tend to labilise the allylic ligand and facilitate its replacement by Cl^-.

^{1}H NMR spectra

The 60 MHz spectra of compounds I (X = OCH_3 and X = $OCOCH_3$) have been reported [3,4]. In the spectrum of the acetoxy complex, two multiplets arise from protons 4, 5 and 6. At 100 MHz a typical *ABX* pattern emerges. The non-equivalence of H^5 and H^6 occurs because of the asymmetry of the allyl group: the palladium is on one side of the group.



In the spectrum of Ia, X = OCH_3, H^4, H^5 and H^6 all give a single resonance at both 60 MHz and 100 MHz. At 220 MHz, however, the band appears as a multiplet, indicating an *ABC* system with all protons having almost identical chemical shifts.

There are two possible geometrical isomers V and VI of the Ph_3E-substituted compounds. Previous work has shown that phosphine ligands tend to be bonded *trans* to the more substituted end of the π-enyl group as in V [9,14]. Moreover protons *trans* to the phosphine tend to be shielded and those *cis* to be de-

TABLE 2

^{1}H NMR CHEMICAL SHIFTS (δ) FOR 4-METHOXY- AND 4-ACETOXY BUT-2-ENYLPALLADIUM COMPLEXES

Complex	H^1	H^2	H^3	H^4	H^5,H^6	OCH_3	$OCOCH_3$	C_6H_5
Ia	2.85	3.81	2.22	3.62	3.62	3.40		
Va	2.60	2.71	1.96	4.16	4.16	3.46		7.4
Vb	2.74	3.34	2.01	4.10	4.10	3.41		7.5
Vc	2.78	3.76	2.04	3.93	3.93	3.33		7.4
Ib	2.82	3.79	2.11	3.53	4.26		2.02	
Vd	2.71	2.83	2.05	4.14	4.80		1.98	7.4
Ve	2.70	3.27	2.10	4.13	4.76		2.07	7.3
Vf	2.71	3.76	2.09	4.17	4.72		2.04	7.5

shielded. We observe deshielding of H^4, H^5 and H^6 and shielding of H^1 and H^2 in the spectra of compounds V relative to the chlorobridged dimers I. (See Table 2).

Changes in the NMR spectra with temperature have been noted for many phosphine and arsine derivatives of π-allylpalladium chloride [15]. At room temperature the spectrum of Ve consists of four broad bands arising from protons 1, 2, 4 and 5 and two narrow peaks from the methyl groups. On cooling to —40°C the broad lines gradually sharpen until the spectrum resembles that of the triphenylstibine complex Vf. The PMR spectrum of π-allyltriphenylarsine palladium chloride is also broad at room temperature, and this has been interpreted in terms of a change from an η^3-allyl complex at low temperatures to an η^1-σ-allyl complex, as well as loss of ligand [12]. The triphenylstibine and chlorobridged complexes Vf and Ib, have temperature independent NMR spectra between —60° and +70°C.

An unusual change occurs in the spectrum of the triphenylphosphine derivative of the acetoxy complex Vd, when the sample is cooled from room temperature to —40°C. Protons H^1 and H^2 give rise to two resonances at δ 2.71 and δ 2.83 at room temperature, but show only on signal at δ 2.85 at —40°C. No further change occurs down to —60°C. The closeness of the shifts of the anti and syn protons H^1 and H^2 indicates considerable asymmetry of the bonding of the allyl group to palladium, as has been found for [PdCl(2-methylallyl)-(PPh_3)] [16]. Perhaps as the temperature is lowered this asymmetry becomes even more pronounced in the case of Vd, so that H^1 and H^2 become essentially equivalent.

Experimental section

Di-μ-chloro-4-methoxy and di-μ-chloro-4-acetoxy-2-methyl but-2-enylchloropalladium were prepared by literature methods [3,4].

Compounds Va—Ve were prepared as follows: the ligand dissolved in the minimum of warm benzene was added with stirring to an equimolar quantity of the chloro-bridged complex in the minimum of benzene. After standing for one hour at 10°C, light petroleum (b.p. 40—60°C) was added. The precipitated complex was filtered, washed with light petroleum (b.p. 40—60°C) and then

with diethyl ether. The samples were purified by dissolving in benzene and reprecipitating with light petroleum. Analytical data are listed in Table 1.

^{1}H NMR spectra were measured at 100 MHz in deuterochloroform using a Varian HA 100 spectrometer. The 220 MHz spectrum of Ia was obtained at P.C.M.U., Harwell. Chemical shifts relative to TMS are listed in Table 2.

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