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THE FORMATION OF C–Pd σ COMPLEXES FROM THE REACTION BETWEEN PALLADIUM(II) CHLORIDE AND ALLYLIC SULPHIDES

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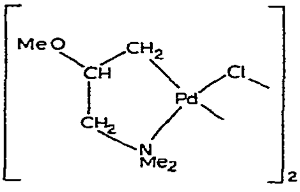
SUMMARY

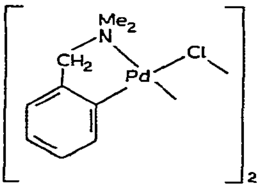
Allylic sulphides were found to react with palladium chloride in methanol in the presence of sodium carbonate at low temperature to give di-μ-chloro-bis(3-alkyl- or phenylmercapto-2-methoxypropyl)dipalladium(II). However, crotyl or cinnamyl sulphide did not give analogous complexes. Allylic sulphoxides were found to react with palladium chloride, but, from ethyl allyl sulphoxide alone the similar σ-complex was obtained in low yield. Benzyl phenyl sulphide gave exclusively bis(benzyl phenyl sulphide)dichloropalladium.

INTRODUCTION

Many organopalladium complexes with chelating ring including the co-ordinated N-atom have been prepared and characterized[1-7]. For example, treatment of allylamine or benzylamine with palladium chloride gives complex (I) or (II).



(I)

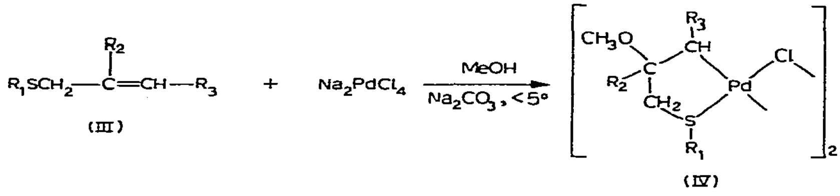


(II)

However, no analogous organopalladium complex with sulphur atom, which has a stronger co-ordination ability to palladium metal, was previously known. It was of interest, therefore, to examine the reaction of allylic sulphides or phenyl sulphide with palladium chloride, and we have found that several allylic sulphides undergo a similar oxypalladation reaction with sodium chloropalladate in methanol to give new carbon to palladium σ complexes. Phenyl sulphide, however, has been found to give only bis(phenyl sulphide)dichloropalladium.

RESULTS AND DISCUSSION

(1). *The reaction between allylic sulphides (III) and palladium chloride*



	R_1	R_2	R_3
a	t-Bu	Me	H
b	t-Bu	H	H
c	Ph	Me	H
d	Ph	H	H

	R_1	R_2	R_3
e	Et	Me	H
f	Et	H	H
g	Et	H	Me
h	Et	H	Ph

When tert-butyl methallyl sulphide (IIIa) was added to the methanolic solution of equimolar sodium chloropalladate at ice-bath temperature (below 5°), the colour of the solution changed from dark brown to brownish red, but no pure complex could be isolated at this stage. An equimolar amount of sodium carbonate was then added to the red solution, and the colour of the solution was found to change gradually to yellow, accompanied by the precipitation of a yellow complex, identified as bis{μ-chloro-[3-(tert-butylthio)-2-methoxy-2-methylpropyl]palladium(II)} (IVa). IR bands at 1462 and 1372 cm^{-1} were due to the t-butyl group, at 2815 and 1092 cm^{-1} to the methoxy group, at 338 cm^{-1} to the Pd–S bond, and at 288 cm^{-1} to the bridged Pd–Cl group. The NMR spectrum of (IVa) had three singlets at τ 6.69, 8.48 and 8.68 due to methoxy, tert-butyl and methyl groups, respectively, a broad AB-type quartet (J 11 Hz) at τ 7.38 assignable to $-CH_2S-$ group, and a broad singlet at τ 7.73 assigned to methylene group bound to palladium atom (relative intensity 3/9/3/2/2, for these assignments see later). These findings are fully consistent with structure (IVa).

Other allylic sulphides [(IIIb)–(IIIf)] similarly gave the corresponding complexes. The analytical data and physical properties of the products are listed in Table 1, and the NMR data in Table 2.

These reaction proceeded smoothly at ice-bath temperature to give complexes (IV) in high yield, but at room temperature or in the absence of the base (Na_2CO_3) no pure compound could be obtained. It is quite interesting that crotyl (IIIg) and cinnamyl sulphides (IIIh) did not give the analogous complexes, suggesting either that the oxypalladation reaction of an internal olefin is rather difficult or that the sec-C–Pd σ bond in the expected complexes from (IIIg) and (IIIh) is extremely unstable. Complexes (IV) obtained are relatively stable in air at refrigerator temperature, but are decomposed at room temperature with gradual darkening of the colour. The decomposition temperatures of the complexes (IV) (Table 1) indicates that methallyl derivatives [(IVa), (IVc) and (IVe)] are more stable than allyl homologues [(IVb), (IVd) and (IVf)], and that ethyl and tert-butyl derivatives [(IVa), (IVb), (IVe) and (IVf)] are more stable than the phenyl sulphide complexes [(IVc) and (IVd)].

TABLE 1

COMPLEXES PREPARED FROM ALLYLIC SULPHIDES

Complex	Yield (%)	Colour	M.p. (°C)	Analysis, found (calcd.) (%) C	H	Pd
(IVa)	88.7	Yellow	178–184[a]	33.85 (34.09)	5.79 (6.04)	33.32 (33.54)
(IVb)	75.2	Yellow	138–145[a]	31.57 (31.70)	5.43 (5.65)	34.81 (35.10)
(IVc)	75.9	Orange-red	172–174[a]	39.20 (39.19)	4.47 (4.48)	31.27 (31.55)
(IVd)	76.2	Red	84–106[a]	36.28 (37.18)	3.90 (4.06)	32.43 (32.93)
(IVe)	96.1	Yellow	170–171	29.04 (29.09)	5.08 (5.23)	36.20 (36.83)
(IVf)	93	Yellow	(Oil)	(26.20)	(4.76)	38.73 (38.68)

[a] Decomposed without melting.

TABLE 2

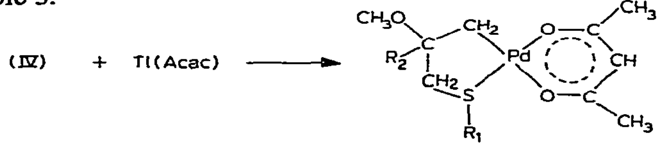
NMR SPECTRA OF COMPLEXES(IV)[a]

Complex	$\tau(R_1)$	$\tau(R_2)$	$\tau(OCH_3)$	$\tau(PdCH_2)$	$\tau(SCH_2)$
(IVa)	8.48 (s)	8.68 (s)	6.69 (s)	7.73 (bs)	7.38 (q)
(IVb)	8.46 (s)	[b]	6.70 (s)	[b]	[b]
(IVc)	1.9–3.0 (m)	8.78 (s)	6.75 (s)	7.58 (bs)	7.00 (q)
(IVd)	1.8–2.9 (m)	[b]	6.75 (s)	7.2–8.0 (m)	7.02 (bd)
(IVe)	8.57 (t), 7.2 (bm)	8.37 (s)	6.72 (s)	7.69 (bs)	[b]
(IVf)	8.54 (t), 7.2 (bm)	[b]	6.68 (s)	[b]	[b]

[a] Measured in $CDCl_3$ at room temperature, notation: s, singlet; bs, broad singlet; bd, broad doublet; t, triplet; q, quartet; m, multiplet; bm, broad multiplet. [b] Not assigned.

(IVa) was decomposed under atmospheric carbon monoxide in methanol, and the starting tert-butyl methallyl sulphide (IIIa) was regenerated, probably by reaction of (IVa) with the hydrogen chloride formed during the reaction. The expected carbon monoxide-insertion product (methyl ester) was not isolated.

(IV) were found to react with thallium acetylacetonate to give acetylacetonato derivatives (V), which were identified by their NMR spectra. The NMR data are listed in Table 3.



[(Vc), (Vd) and (Ve)]

In complexes (Vc) and (Vd), in contrast with the results for (Ve), the methyl resonance in the Acac group was found as two singlets at near τ 8 (chemical shift difference; 0.1 ppm). Similar behaviour is observed in the case of acetylacetonato-π-

TABLE 3

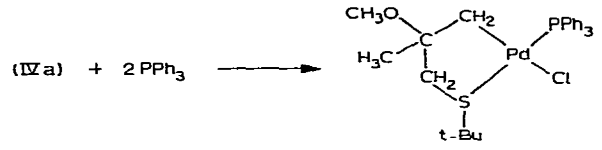
NMR SPECTRA OF COMPLEXES (V)[a]

Complex	$\tau(R_1)$	$\tau(R_2)$	$\tau(OCH_3)$	$\tau(PdCH_2)$	$\tau(SCH_2)$	Acac group	
						$\tau(CH_3)$	$\tau(CH)$
(Vc)	1.9–3.0 (m)	8.75 (s)	6.82 (s)	7.83 (bs)	7.01 (q)	8.15, 8.26	4.93
(Vd)	1.7–3.3 (m)	[b]	6.75 (s)	7.6 (m)	6.92 (d)	7.97, 8.06	4.79
(Ve)	8.61 (t), 7.2 (m)	8.73 (s)	6.78 (s)	7.68 (m)	7.2 (m)	8.18	4.93

[a] Measured in $CDCl_3$ at room temperature, for notation see Table 2. [b] Not assigned.

cinnamylpalladium (II), and both findings can be interpreted in terms of the anisotropic effect of the phenyl ring[8].

Treatment of complex (IVa) with one mol. of triphenylphosphine in benzene gave the monomeric complex (VIa).



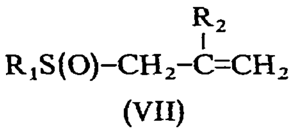
(VIa)

The NMR spectrum of (VIa) had three singlets at τ 7.05, 8.37, and 8.83 attributable to the methoxy, tert-butyl and methyl group, respectively, an AB-type quartet (J 11 Hz) at τ 7.34 due to $-SCH_2-$ which had a shape and chemical shift similar to those of (IVa), a doublet at τ 8.60 assignable to $Pd-CH_2-$, which had a higher chemical shift than in (IVa), and a multiplet due to a phenyl group bonded to the phosphorus atom (relative intensity 3/9/3/2/2/15). These assignments and the variations in the chemical shift for the several protons from (IVa) to (VIa) allow the structure of complex (IVa) to be elucidated, and show that the triphenylphosphine is situated *trans* to the sulphur atom.

(2). *The reaction of allylic sulphoxides with palladium(II) chloride*

Sulphoxide is a well known ambident ligand, and co-ordinates to the palladium atom through sulphur[9]. Thus allylic sulphoxides should form organopalladium complexes analogous to (IV). The reactions of several sulpoxides (VIIa)–(VIId) with sodium chloropalladate were performed in methanol in the presence of sodium carbonate. A colourless palladium complex, tentatively identified as bis{μ-chloro-[(3-ethylsulphoxido)-2-methoxypropyl]palladium(II)} (VIII), was obtained in 20% yield from the reaction between sodium chloropalladate and allyl ethyl sulphoxide (VIIa). However, the reproducibility of the reaction was poor, and the colour of the product (VIII) varied from white to pale yellow, depending upon the reaction conditions. (VIII) is soluble in water, sparingly soluble in methanol or other common organic solvents.

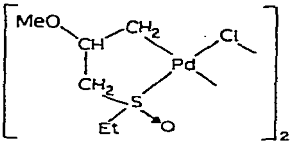
The infrared spectrum of (VIII) shows an absorption band at 2820 cm^{-1} due to the methoxy group, and a strong band at 1107 cm^{-1} assignable to the S-co-ordinat-



$$R_1S(O){-}CH_2{-}\overset{R_2}{\overset{|}{C}}{=}CH_2$$

(VII)

	a	b	c	d
R_1	Et	Et	Ph	t-Bu
R_2	H	Me	Me	H

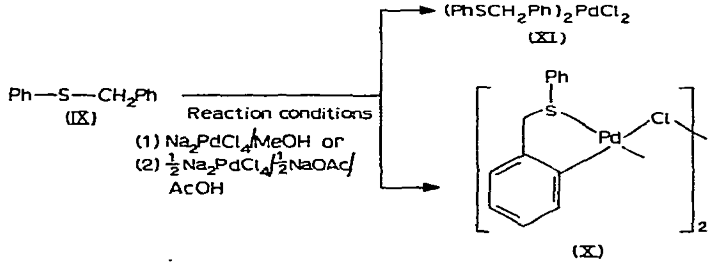


(VIII)

ed sulphoxide group, the frequency of which is near to that (1116 cm^{-1}) observed in $(DMSO)_2PdCl_2$[10], and is higher than that of free sulphoxides [ν(S–O) 1082 for (VIIa) and 1055 cm^{-1} for DMSO]. These observation and the elemental analysis (see Experimental section) are in good agreement with the tentative structure. The poor reproducibility and the low yield of complex (VIII) can be attributed to the weakness of the bond between the –S(O)– group and the Pd atom. Other sulphoxides did not give the corresponding complexes.

(3). *The reaction of benzyl phenyl sulphide with palladium chloride*

The results obtained in the reaction of allylic sulphides indicate that a sulphur atom has a complex-stabilizing effect similar to that of a nitrogen atom. Thus it is important to investigate whether the reaction of benzyl phenyl sulphide (IX) gives the benzyl amine-like organometallic complex (X) or the L_2PdCl_2-type complex (XI). We found that (IX) gave exclusively bis(benzyl phenyl sulphide)dichloropalladium (XI) under two different sets of conditions.



It then appears that S–Pd co-ordination is so strong that electrophilic substitution in the phenyl group by palladium ion is inhibited. and in this respect the sulphur atom is different from the nitrogen atom.

EXPERIMENTAL

Infrared spectra were run on a Nippon Bunko Model 403-G double beam grating spectrometer in KBr disk, callibrated by polystyrene. Nuclear magnetic resonance spectra (NMR) were measured in deuterochloroform with internal standard TMS using JEOL Optics C-60HL spectrometer.

Materials

Allylic sulphides were prepared by the modified Parham method[11]. Allylic sulphoxides were prepared by oxidation of the corresponding sulphides with 30% hydrogen peroxide in acetone[12] or acetic acid[13], or with sodium metaperiodate[14,15]. Their identities were checked before use by NMR and infrared spectra. Benzyl phenyl sulphide was obtained from the reaction of sodium thiophenoxide with benzyl chloride in ethanol, m.p. 31.7–32.5°.

The reaction of allylic sulphides with palladium chloride

General procedures are given. To a methanolic solution of sodium chloropalladate, prepared from 0.500 g (2.82 mmol) of palladium chloride, 0.340 g (5.80 mmol) of sodium chloride and methanol 20 ml, about 3 mmol of allylic sulphides was added dropwise at ice-bath temperature. Subsequently 140 mg of sodium carbonate (anhydrous; 1.56 mmol) was added, and the mixture was stirred for one and a half hours at ice-bath temperature. The resultant crystalline precipitate was filtered, washed with water and methanol, successively, and recrystallized from methanol.

When no precipitate appeared, the mixture was poured into water (100 ml), extracted with chloroform, and the solvent was evaporated at reduced pressure to give the required complex. From allyl ethyl sulphide, no crystals were obtained even after purifications by column chromatography.

Crotyl and cinnamyl ethyl sulphides gave only dark-brown products which could not be identified.

The reaction of complex (IVa) with carbon monoxide

To the suspension of (IVa) (1.402 g, 2.21 mmol) in methanol 20 ml, carbon monoxide was introduced at atmospheric pressure, and the mixture was kept at room temperature for 2 days under carbon monoxide. Metallic palladium was filtered off, and the solution was poured into water, extracted with ether and dried over anhydrous sodium sulfate. The metallic palladium was washed with ether in a Soxhlet extractor. Combined extracts were distilled to give small amount of oil, 43.2 mg, NMR spectrum of which showed the peaks at *8.71*(*s*). *8.20*(*s*), 7.50(m), *6.92*(*s*), 6.43(s), and *5.23*(*bs*); The main peaks (shown italicized) correspond with those of the starting sulphide (IIIa) or (IVa). The very low product recovers in this reaction can be attributed to the strong adsorption of sulphides on metallic palladium.

The preparation of complexes (V) and (VIa)

(V) and (VIa) were prepared by the procedure used for the synthesis of acetylacetonato and triphenylphosphine derivatives of π-allylic palladium complexes[16,17].

The reaction of benzyl phenyl sulphide with palladium chloride

(1). To a methanolic solution of 3.08 mmol of sodium chloropalladate, the equimolar amount of the sulphide was added at room temperature. The orange red complex separated at once was filtered off and analyzed; yield 0.707 g (43.6% based on palladium).

(2). Benzyl sulphide was treated with 0.5 equivalents of palladium chloride in the presence of sodium acetate (NaOAc/Pd 1/1) at room temperature. The precipitated complex was the same as above; yield 81%. Its infrared spectrum had the absorption bands at 340 and 318 cm^{-1}, assignable to ν(Pd–Cl) and ν(Pd–S), respectively.

The reaction of sulfoxide with sodium chloropalladate

The reactions were performed as for the sulphides, but under various conditions. No reproducible results were obtained. However, from allyl ethyl sulphoxide, a white complex (VIII) separated as a precipitate when the reaction mixture was kept in a refrigerator for a week, yield 20%, m.p. 150–160° (recrystallized from methanol). (Found: C, 24.62; H, 4.39. $C_{12}H_{26}Cl_2O_4Pd_2S_2$ calcd.: C, 24.75; H, 4.39%.)

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