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NOTE

THE REACTIONS OF ALKENEPALLADIUM CHLORIDE COMPLEXES WITH ALCOHOLS

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The reaction of di-μ-chloro-dichlorobis(ethylene)dipalladium with isopropanol in the presence of disodium hydrogen phosphate has been reported to give diisopropyl acetal and small amounts of isopropyl vinyl ether[1]. With ethanol, the same complex yields diethyl acetal[2]. The synthesis of vinyl ethers by reactions in which palladium salts act as catalysts has been claimed in two recent patents[3,4]. We report here the results of a systematic study of the reactions of various alcohols with the π complexes of palladium chloride with ethylene, propylene and butene.

RESULTS

All reactions were carried out by adding 10 g of the complex to 20 ml of the anhydrous alcohol under strictly anaerobic conditions. The mixtures were stirred at room temperature and analyzed by quantitative GLC. Reaction products were

TABLE 1

REACTION OF DI-μ-CHLORO-DICHLOROBIS(ETHYLENE)DIPALLADIUM WITH VARIOUS ALCOHOLS

Alcohol	Reaction time (h)	Major products (%)[a]	Minor products (%)[a]
CH_3OH	4	$CH_3CH(OCH_3)_2$ (44.7) $CH_2(OCH_3)_2$ (23.7)	CH_3Cl (1)
C_2H_5OH	4	CH_3CHO (45.2) $CH_3CH(OC_2H_5)_2$ (34.8)	C_2H_5Cl (1) $(C_2H_5)_2O$ (3.3)
C_2H_5OH[b]	4	CH_3CHO (43.7) $^{14}CH_3CH(OC_2H_5)_2$ (35.6)[c]	C_2H_5Cl (~1) $(C_2H_5)_2O$ (2.8)
iso-C_3H_7OH	6	iso-C_3H_7Cl (67.5) $(CH_3)_2CO$ (10.5)	(iso-$C_3H_7)_2O$ (~1)
tert-C_4H_9OH	18	tert-C_4H_9Cl (20.0)	CH_3CHO (16.4) $(CH_3)_2C{=}CH_2$ (25.4) H_2O (8.2)
iso-C_3H_7OH[d]	18	CH_3CH(O-iso-$C_3H_7)_2$ (17)	$\left.\begin{matrix}CH_3CHO\\(CH_3)_2CO\end{matrix}\right\}$ (~0.4)

[a] All percentages are mole % based on starting olefin complex. [b] ^{14}C-labelled ethylene–$PdCl_2$ used. [c] >85% ^{14}C-activity in acetal. [d] 11.36 g (0.08 mole) of anhydrous Na_2HPO_4 added.

isolated and identified by NMR and IR spectroscopy. The results of the reactions of di-μ-chloro-dichlorobis(ethylene)dipalladium with various alcohols are summarized in Table 1.

In all cases in Table 1 gas was evolved and this was shown by mass spectrometry to be ethylene. The black residue was filtered and shown by X-ray spectroscopy to be palladium metal.

The reaction with ethanol was repeated diluting the system 20 times with tetradecane. The same amount of acetal was formed in 4 h but almost no acetaldehyde was detected. The same reaction, except that tetradecane was replaced by toluene, was carried out at 0° and 10°. There was an extremely large drop in rate (the same product yields were obtained in about 200 h) but the product distribution remained unchanged. No ethyl vinyl ether was detected in the products and it was shown that ethyl vinyl ether is converted rapidly to acetal when added to the reactions initially.

The results for the reactions of di-μ-chloro-dichlorobis(propylene)dipalladium are summarized in Table 2. Gas was evolved from all reactions and was shown by mass spectrometry to be propylene. The black precipitates were identified as palladium metal by X-ray crystallography.

Table 3 shows the products formed when di-μ-dichlorobis(butene)dipalladium is used. These reactions were extremely slow and no gas was apparently evolved. However, considerable quantities of butene (isomer not identified) were detected in the reaction solution by GLC.

Since (see below) most of the reaction products from the interaction of alcohols with olefin–$PdCl_2$ π complexes can be explained in terms of the decomposition of

TABLE 2

REACTION OF DI-μ-CHLORO-DICHLOROBIS(PROPYLENE)DIPALLADIUM WITH VARIOUS ALCOHOLS

Alcohol	Reaction time (h)	Major products (%)[a]	Minor products (%)[a]
C_2H_5OH	4	C_2H_5Cl (34.5)	$CH_3CH(OC_2H_5)_2$ (16.4) $(C_2H_5)_2O$ (4.1)
iso-C_3H_7OH	6	iso-C_3H_7Cl (47.2) $(CH_3)_2CO$ (12.7)	(iso-$C_3H_7)_2O$ (0.1)
iso-C_3H_7OH[b]	6	iso-C_3H_7Cl (24.4) $(CH_3)_2CO$ (8.2)	(iso-$C_3H_7)_2O$ (0.1)

[a] All percentages are mole % based on starting olefin complex. [b] 11.36 g (0.08 mole) of anhydrous Na_2HPO_4 added.

TABLE 3

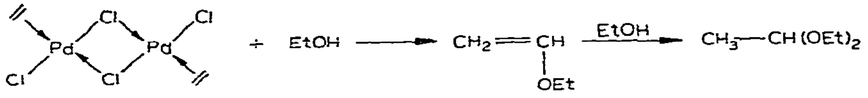
REACTION OF DI-μ-CHLORO-DICHLOROBIS(BUTENE)DIPALLADIUM WITH VARIOUS ALCOHOLS

Alcohol	Reaction time (days)	Major products (%)	Minor products (%)
C_2H_5OH	2.5	C_2H_5Cl (21.7)	$(C_2H_5)_2O$ (5.33) $CH_3CH(OC_2H_5)_2$ (2.68)
iso-C_3H_7OH	2.5	iso-C_3H_7Cl (35.4) $(CH_3)_2CO$ (8.9)	(iso-$C_3H_7)_2O$ (0.1)

alcohol–$PdCl_2$ complexes, the alcohol merely displacing the olefin which takes no further part in the reaction, similar results might be expected from the reaction of an alcohol with $PdCl_2$ itself rather than with the complex. Consequently, 8.65 g (0.049 mole) of $PdCl_2$ was stirred at room temperature in 30 ml of ethanol for 4 h. No products of any kind were detected by GLC. This probably is due only to the insolubility of the $PdCl_2$ in the reaction medium. Therefore, 9.66 g (0.146 mole) of lithium acetate was added to increase the solubility of the palladium salt. After 4 h the reaction mixture now contained 0.32 g CH_3CHO (29.8% based on $PdCl_2$) and 0.242 g $CH_3CH(OC_2H_5)_2$ (8.4% based on $PdCl_2$).

DISCUSSION

When di-μ-chloro-dichlorobis(ethylene)dipalladium reacts with alcohols, only methanol and ethanol yield products in which the ethylene is incorporated. In the case of ethanol, the product acetal could be derived from two routes, one involving ethylene and one not:



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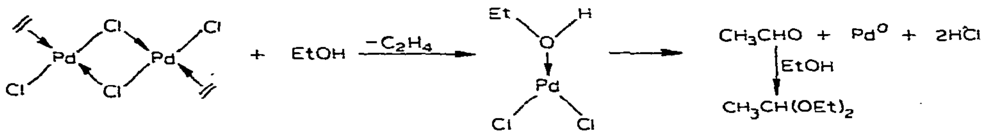
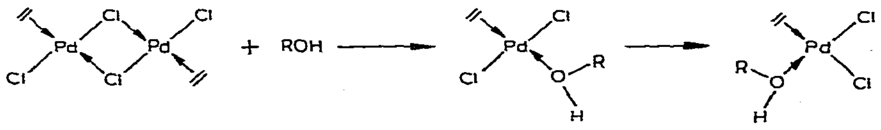


However, the reaction using ^{14}C labelled ethylene (Table 1) shows conclusively that only about 15% of the acetal is derived from acetaldehyde. The two major products must therefore be produced by two distinct reaction paths. Apparently these two paths have different kinetic orders since dilution decreases the yield of acetaldehyde but does not affect the amount of acetal formed.

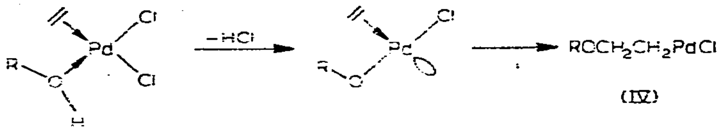
Essentially the same scheme explains the products formed from methanol where we can postulate formation of dimethyl acetal by attack of methanol on ethylene and dimethyl formal by reaction of methanol with formaldehyde derived from oxidation of the alcohol. The relatively high yield of dimethyl formal, as compared to the amount of diethyl acetal formed from acetaldehyde in the ethanol reaction, is presumably due to the greater reactivity of formaldehyde and its consequent greater ability to complete with complexed olefin for the alcohol.

The formation of acetal can be looked at in two ways. The first step is most probably breaking of the dimer bridge followed by isomerization of the complex:



(I) (II) (III)

Complex (III) may then eliminate HCl and undergo *cis* ligand insertion:

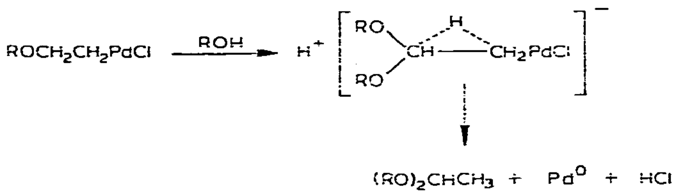

(IV)

Two routes are possible for the formation of acetal from (IV):

(*a*) $ROCH_2CH_2PdCl \longrightarrow ROCH{=}CH_2 + Pd^\circ + HCl$

$$ROCH{=}CH_2 \xrightarrow[ROH]{PdCl_2} (RO)_2CHCH_3$$

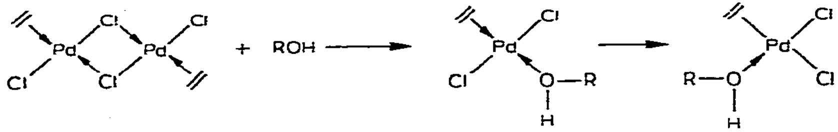
(*b*)

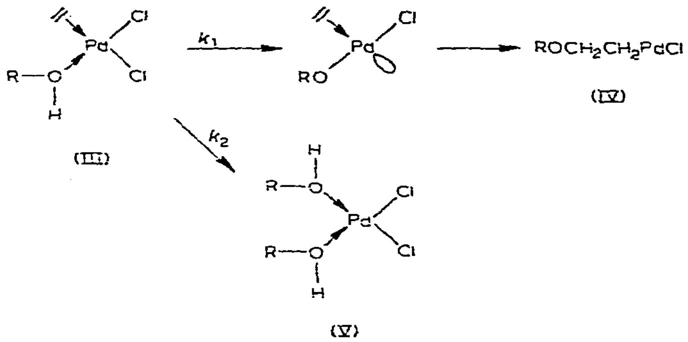


If the second step is rapid compared with the first in mechanism (*a*) then it is not possible from product distributions to distinguish between (*a*) and (*b*). This distinction is important because if (*a*) is the major reaction pathway, it is conceivable that conditions could be found whereby the vinyl ether would be the major isolated product, but if (*b*) is the major pathway no substantial quantity of vinyl ether could ever be formed.

We have shown that, under the reaction conditions, vinyl ether is converted very rapidly to the acetal. The observation of Stern and Spector[1] that small amounts of isopropyl vinyl ether are formed under their reaction conditions would favor pathway (*a*). However, even here, there is reason to believe that the ether may have come from reaction (*a*) and the acetal by route (*b*). Moiseev was unable to isolate any vinyl ether from the reaction of methanol with di-μ-chloro-dichlorobis(ethylene)-dipalladium and showed, furthermore, that when the reaction was run in CH_3OD no deuterium could be detected in the acetal[5]. For methanol, therefore, the reaction almost has to occur by pathway (*b*). Moiseev's results present an interesting analogy with Smidt's observation that when ethylene is reacted with D_2O in the presence of $PdCl_2$, no deuterium is found in the acetaldehyde produced[6].

When alcohols higher than ethanol are used (in the absence of a base such as Na_2HPO_4) the olefin is merely displaced from the complex and no products resulting from attack of alcohol on the olefin are observed. We believe that two competing reactions can take place:

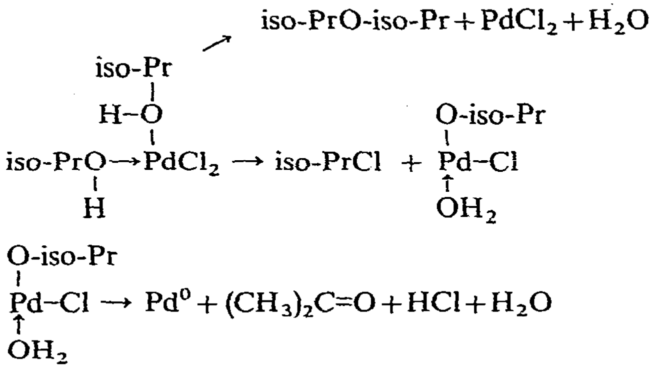




(III) (IV) (V)

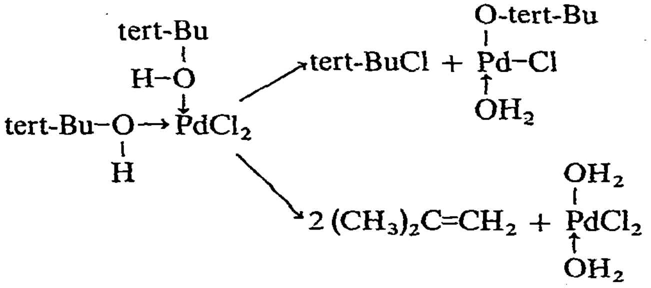
and when $R = CH_3$, C_2H_5, $k_1 \gg k_2$ and when $R = (CH_3)_2CH$, $(CH_3)_3C$, $k_2 \gg k_1$. The formation of acetal in the presence of Na_2HPO_4 when $R = (CH_3)_2CH$, reported by Stern and Spector[1] and confirmed by us, can be explained by this material assisting in the removal of the proton from the alcohol in compound (III) and thus increasing k_1 relative to k_2.

The products obtained from the uncatalyzed reactions with iso-C_3H_7OH and tert-C_4H_9OH can be rationalized by the reaction schemes:



$$\begin{array}{l}\nearrow \text{iso-PrO-iso-Pr} + \text{PdCl}_2 + \text{H}_2\text{O}\\ \begin{array}{c}\text{iso-Pr}\\ |\\ \text{H-O}\\ |\\ \text{iso-PrO}\rightarrow\text{PdCl}_2\\ |\\ \text{H}\end{array} \rightarrow \text{iso-PrCl} + \begin{array}{c}\text{O-iso-Pr}\\ |\\ \text{Pd-Cl}\\ \uparrow\\ \text{OH}_2\end{array}\end{array}$$

$$\begin{array}{c}\text{O-iso-Pr}\\ |\\ \text{Pd-Cl}\\ \uparrow\\ \text{OH}_2\end{array} \rightarrow \text{Pd}^0 + (\text{CH}_3)_2\text{C=O} + \text{HCl} + \text{H}_2\text{O}$$



$$\begin{array}{c}\text{tert-Bu}\\ |\\ \text{H-O}\\ \downarrow\\ \text{tert-Bu-O}\rightarrow\text{PdCl}_2\\ |\\ \text{H}\end{array} \begin{array}{l}\nearrow \text{tert-BuCl} + \begin{array}{c}\text{O-tert-Bu}\\ |\\ \text{Pd-Cl}\\ \uparrow\\ \text{OH}_2\end{array}\\ \searrow 2\,(\text{CH}_3)_2\text{C=CH}_2 + \begin{array}{c}\text{OH}_2\\ |\\ \text{PdCl}_2\\ \uparrow\\ \text{OH}_2\end{array}\end{array}$$

In the latter case, it is difficult to explain the observation that the palladium ultimately is reduced to free metal unless one makes the rather unsatisfactory assumption that HOCl is eliminated somewhere in the reaction path. This is also true for the formation of bis(π-allylpalladium chloride) from $PdCl_2$ and allyl alcohol which, formally at least, also requires the loss of HOCl.

For complexes of propylene and butene, it appears that $k_2 > k_1$ irrespective of the alcohol used and, consequently, products arising from *cis*-ligand insertion on the olefin are present only in minor amounts, if at all.

EXPERIMENTAL

The alkene–$PdCl_2$ complexes were prepared by the direct reaction of the olefin and the palladium salt as described previously[7]. Elemental analyses (by Galbraith Laboratories, Knoxville, Tenn.) were in excellent agreement with theory. The following values for a propylene complex were typical: (Found: C, 16.41; H, 2.71; Cl, 32.26; Pd, 48.65. $C_3H_6Cl_2Pd$ calcd.: C, 16.37; H, 2.74; Cl, 32.47; Pd, 48.42%.)

Reaction solutions were filtered and were chromatographed on a Perkin–Elmer Column R (Polypropylene glycol, Ucon oil LB550-X). Samples of each component were trapped and their identity determined by comparing their NMR and IR spectra with authentic samples. The yield of each component was computed from the area of its GLC peak using standard procedures.

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