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THE REACTIONS OF METALLIC MERCURY WITH π-ALLYL COMPOUNDS OF Ni, Pd AND Pt

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SUMMARY

The reaction of metallic mercury with π-allyl compounds of nickel, palladium and platinum has been discussed. Nickel complexes do not react with mercury but palladium and platinum derivatives give the corresponding allylmercury halides. A reaction mechanism for π-allylpalladium chloride, for example, has been suggested, that involves the cleavage of the μ-halide bridges in the (π-C_3H_5PdCl) molecule and π-σ-perturbation in the π-allyl ligand, causing *cis*-migration of the σ-bonded allyl group from palladium to the mercury atom.

INTRODUCTION

The reactions of the π-allyl transition-metal compounds of the nickel sub-group with nucleophilic reagents are the most characteristic of their few reactions. A detailed investigation was carried out for the π-allylpalladium halides because they are readily available and are comparatively stable. Tsuji *et al.* have shown[2] that in the reaction with carbon monoxide, for example, the motive force of the above processes is a cleavage of the μ-halide bridge in the dimer molecule of the π-allyl complex. A reaction has recently been reported of π-allylpalladium chloride with enamines and sodium malonic ester, leading to C-allylation into a point of highest electronic density, in the nucleophilic molecule[3]. Although di-π-allyl compounds (particularly nickel derivatives) can be used as catalysts in the specific cyclo-oligomerization of butadiene[4], there is still a lack of information on their reactivity. Of the di-π-allyl derivatives of nickel, palladium and platinum, only the former was shown to react with carbon monoxide[4] giving nickel carbonyl and diallyl derivatives, unlike the π-allyl halide complexes.

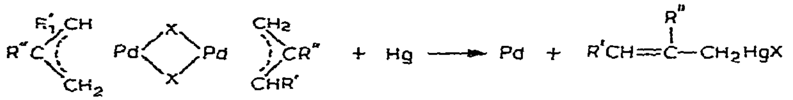
We have found[5] that allylpalladium chloride reacts rapidly with metallic mercury in benzene solution giving both allylmercury chloride and metallic palladium. In the present paper we have studied the reaction of mercury with π-allyl halides and with the di-π-allyl compounds of nickel, palladium and platinum. We have also studied, taking allylpalladium halides as example, the effect of substituents in the π-allyl group on the reaction with metallic mercury. The reaction mechanism suggested shows that this reaction can be regarded in the same way as other nucleophilic reactions of these π-allylmetal compounds.

RESULTS

The reaction was usually carried out by shaking the benzene solution of the respective π-allyl compound with excess metallic mercury; the solution was completely decolourised after several minutes. In the case of the di-π-allyl compounds, the diallylmercury generated was converted into allylmercury chloride by passing hydrogen chloride through the flask.

1. *Substituted π-allylpalladium halides*

The reaction of substituted π-allylpalladium compounds with metallic mercury is described by the following scheme:


(1)

With excess mercury, the reaction with π-allylpalladium chloride proceeds almost instantaneously. The substituents investigated produce no significant effect on the reaction rate. It is of interest to note that only the reaction with 1-acetyl-2-methyl-π-allylpalladium chloride was inhibited; the solution completely lost its colour after 20–30 min.

The quantitative yields obtained for substituted allylmercury compounds are given in Table 1.

TABLE 1

REACTION OF π-ALLYLPALLADIUM HALIDES WITH METALLIC MERCURY

No.	R′	R″	X	M.p. (°C)	Yield (%)	Analysis (%) Found C	H	Hal.	Hg	Calcd. C	H	Hal.	Hg
1	H	H	Cl	110–111	100								
2	H	H	Br	124–5	100								
3	H	H	I	134–5	100								
4	CH_3	H	Cl	76–7	100	16.60	2.64	12.67	68.11	16.49	2.42	12.21	68.87
5	CH_3	H	Br	90–91	94	14.36	2.10	23.92	59.78	14.32	2.10	23.81	59.98
6	C_6H_5	H	Cl	122–3	73	30.27	2.56	10.33	56.72	30.60	2.59	10.04	56.78
7	H	C_6H_5	Cl	56–7	67	30.41	2.57	10.96	55.77	30.60	2.59	10.04	56.78
8	H	neo-C_5H_{11}	Cl	64–65	72	27.71	4.35	10.83	57.05	27.59	4.34	10.18	57.88
9	CH_3CO	CH_3	Cl	67–8	64	21.53	2.84	10.84	59.63	21.63	2.72	10.64	60.20
10	H	H	$OCOCH_3$	109–110	97	19.54	2.83			19.60	2.66		
11	$ClCH_2$	H	Cl										
12	H	Cl	Cl										

A different mechanism is followed for compounds containing halogen in the π-allyl group. On shaking metallic mercury with a benzene solution of 1-chloromethyl-π-allylpalladium chloride (XI) the mixture decolourised, but a powdery solid which contained carbon and mercury and was insoluble in organic solvents was precipitated with metallic palladium. This substance is probably an organomercury polymer. Another halide-containing compound, 1-chloro-π-allylpalladium chloride (XII), reacted with metallic mercury in the normal way: the benzene solution of XII lost its colour, metallic palladium precipitated and after removal of the solvent a white crystalline solid was obtained. However, we failed to analyse the latter, since it spontaneously decomposed, giving mercuric chloride and allene.

2. *The behaviour of allylpalladium complexes containing other ligands, with metallic mercury*

In order to determine the effect of a ligand combinated with the palladium atom in its π-allyl complex, the reactions of metallic mercury with the following types of π-allylpalladium complexes were investigated:

$(\pi\text{-}C_3H_5PdX)_2$ (I, X=Cl; II, X=Br; III, X=I; X, X=$OCOCH_3$)
$(\pi\text{-}C_3H_5PdL)^+Cl^-$ (XIII, L = en; XIV, L = *o*-phen)
$\pi\text{-}C_3H_5PdQ$ (XVI, Q=$\pi\text{-}C_3H_5$; XVII, Q=$\pi\text{-}C_5H_5$; XVIII, Q=Acac)
$C_3H_5PdClPPh_3$ (XV).

The compounds with bridged bonds (I, II, III, X), as well as di-π-allylpalladium (XVI) react rapidly with metallic mercury according to eqn. (1). However, we could find no difference in the rates of reactions of these compounds for various bridged groups. Organomercury compounds prepared from the complexes I–III and X, show a considerable decrease in stability in the series: $C_3H_5HgCl \gg C_3H_5HgBr > C_3H_5HgI \gg C_3H_5HgOCOCH_3$. The latter compound decomposes on keeping at about 0°.

π-Allylpalladium acetylacetonate (XVIII) reacts with metallic mercury much more slowly than the bridged π-allyl compounds, giving metallic palladium and a white amorphous product soluble in hot acetylacetone but practically insoluble in common organic solvents. The IR-spectrum of this compound was completely analogous to that of mercury bis(acetylacetonate), prepared by an independent synthesis from mercuric chloride and sodium acetylacetonate in alcohol. The second product in the reaction of XVII was diallylmercury. Thus, the reaction of mercury with π-allylpalladium acetylacetonate follows the equation:

$$\pi\text{-}C_3H_5PdC_5H_7O_2 + Hg \rightarrow Pd + (C_3H_5)_2Hg + (C_5H_7O_2)_2Hg$$

Compound XV, produced in the reaction of triphenylphosphine with π-allylpalladium chloride, was found not to react with metallic mercury. No precipitation of palladium takes place and the initial π-allylpalladiumtriphenylphosphine chloride may be isolated unchanged. The replacement of benzene by more polar solvents (methanol, THF), and the application of some surface active compounds (camphor) do not produce the desired result.

π-Allyl-π-cyclopentadienylpalladium (XVII) does not react with mercury under the conditions described. However, at room temperature after several days standing over metallic mercury, the benzene solution decolourised, and a solid precipitated, but no organomercury salts could be isolated from the mixture.

Cationic π-allylpalladium complexes (XIII, XIV) react irregularly with metallic mercury: there is no precipitation of palladium and among the reaction products the ethylenediaminepalladium chloride complex, of composition $(Pden_2)Cl_2$, was identified polarographically.

3. *Di-π-allyl compounds*

We have also studied the reaction of metallic mercury with di-π-allyl-Ni-Pd and -Pt compounds, which have been prepared quite recently. They are unstable both in air and thermally, have low fusibility and sublime readily. They (especially the di-π-allylnickel compound) can only be isolated in the pure form with difficulty. Ether or pentane solutions of these compounds were usually used in the reaction with metallic mercury.

Pentane solutions of $(C_3H_5)_2Pd$ and $(C_3H_5)_2Pt$ react readily with metallic mercury at room temperature in an inert gas atmosphere to give the free metals. The colorless reaction mixture was rapidly filtered and hydrogen chloride was passed through the flask with cooling, after which the mixture was immediately poured into water. Then allylmercury chloride was produced. The reaction proceeds according to the scheme:

$$(C_3H_5)_2M+Hg \rightarrow M+(C_3H_5)_2Hg$$

$$(C_3H_5)_2Hg+HCl \rightarrow C_3H_5HgCl+C_3H_6 \qquad (M = Pd, Pt)$$

Under analogous conditions, the ether solution of di-π-allylnickel does not react with metallic mercury; no loss in colour or precipitation of solid were observed. At higher temperatures di-π-allylnickel decomposes but no allylmercury compound is produced.

4. *π-Allylnickel halides*

We have attempted to carry out the reaction with metallic mercury using the red benzene solution of π-allylnickel halide. As in the case of the di-π-allylnickel compounds, π-allylnickel halides do not react with mercury under the usual conditions. Increasing the temperature and replacement of benzene with more polar solvents, did not facilitate the reaction.

5. *The reaction of π-allylpalladium chloride with other metals*

The reactions of π-allylpalladium chloride with stronger metal reducing agents than mercury have been studied.

Granulated magnesium (MGF-4), which, without activation, reacts with the only slightly reactive alkyl and aryl halides, does not react with π-allylpalladium chloride under normal conditions.

Activated copper powder also does not react with π-allylpalladium chloride under reflux with THF. At first glance, these negative results could be explained by the fact, that the surface conditions of magnesium and copper are less favourable than in the case of mercury. However, low-melting gallium, which is liquid under the reaction conditions does not react with $(\pi\text{-}C_3H_5PdCl)_2$ under reflux with benzene.

A detailed investigation of the reaction of $(\pi\text{-}C_3H_5PdCl)_2$ with powdered zinc and magnesium was carried out.

When a benzene solution of $(\pi\text{-}C_3H_5PdCl)_2$ at room temperature was passed through a column filled with activated zinc powder palladium was precipitated. A colourless solution was eluted with ether. After the solvent had been removed, an oily light-yellow product was obtained, which contained C, H, halogen and zinc; this was not an allylzinc compound. It formed no complex with dioxane or *o*-phenanthroline and did not react with mercuric chloride or ketones under the conditions for allylzinc compounds. In these cases, π-allylpalladium chloride probably reduces in the presence of the metal-hydrogen ion couple*.

DISCUSSION

Although allylmercury compounds were first obtained in the last century[6], only recently information has appeared on the preparation of some substituted allylmercury halides[7]. Unlike other types of organomercury compounds. the methods of syntheses of allylmercury derivatives are few and inadequate. The basic method for the preparation of allyl compounds of mercury was until recently Zinin's reaction[6] of allyl iodides with metallic mercury. Other methods discovered accidentally, consisting in reactions of mercury salts with organozinc[8] and -magnesium compounds[7] have also been reported. The main reason for the dearth of methods is the scarcity of substituted allyl halides.

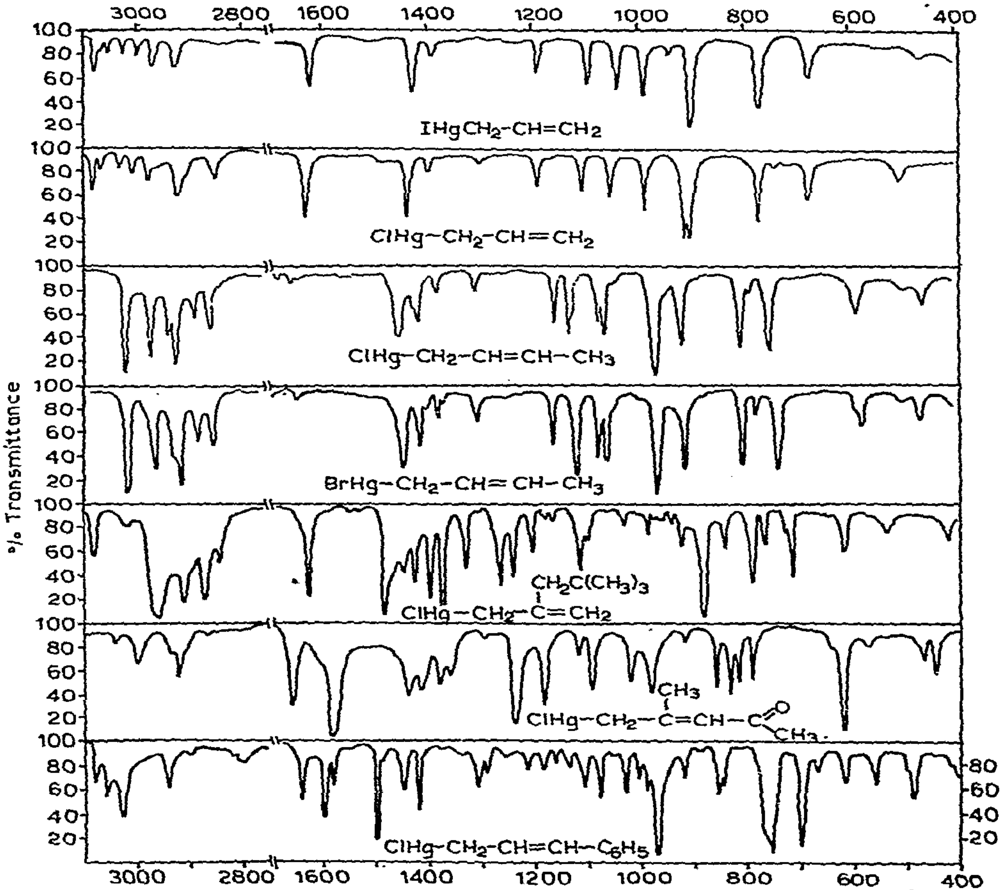


Fig. 1. The IR spectra of the allylmercury compounds obtained.

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* We have activated metals (zinc, cadmium) with dilute hydrochloric acid. Inactivated zinc and cadmium (or thoroughly washed from traces of hydrogen chloride) did not react with $(\pi\text{-}C_3H_5PdCl)_2$. The addition of HCl caused immediate precipitation of metallic palladium.

In the present paper we describe a method, which gives good yields and is comparatively simple, for the preparation of allylmercury compounds from the corresponding olefins and dienes through π-allylpalladium complexes. It is possible to prepare by this method, for example, the allyl compounds of mercury having such substituents as the CH_3CO-group, the classical preparation of which is difficult. The important fact is, that in all the cases investigated, unsymmetrically substituted π-allylpalladium compounds may provide mercury derivatives of definite structures, where the mercury atom could be combined with the unsubstituted methylene group.

This could be confirmed by the IR spectra shown in Fig. 1.

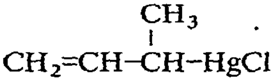
It should be noted, that there have been no studies of the vibrational spectra of substituted allylmercury compounds, except for the brief communication of Winstein *et al.*[7] on the IR spectrum of *trans*-crotylmercury bromide.

Egorov *et al.*[9] have provided a detailed analysis of the vibrational spectra for the allyl derivatives of Group IV elements as well as of some other elements of the Periodic Table. The spectra of compounds of type $CH_2{=}CH{-}CH_2MX$ have been shown to change regularly, depending on the nature of the metal atom. We have established that these regular changes are also true for compounds of mercury of type $CH_2{=}CH{-}CH_2HgX$. The vibrational frequencies of the CH_2 group do not change, and remain practically the same as the frequencies of the allyl compounds of tin and germanium: antisymmetric C–H stretching vibration at 3080 cm^{-1}, non-planar C–H vibration at 980 cm^{-1}, planar deformations of the $C{<}^{H}_{H}$ angle at 1425 cm^{-1} were observed in the spectra. The so-called "frequency of double bond C=C" undergoes a further small shift to 1620 cm^{-1} with respect to $CH_3{-}CH{=}CH_2$ (1642 cm^{-1}), $R_3GeCH_2{-}CH{=}CH_2$ (1630 cm^{-1}) and $R_3SnCH_2{-}CH{=}CH_2$ (1625 cm^{-1}). Increase in atomic mass, M, causes a notable shift in the frequency of the non-planar CH-vibration in C–CH to 900 cm^{-1} with respect to $Cl_3GeCH_2{-}CH{=}CH_2$ (930 cm^{-1}). The deformation vibration frequency of M–C–H angles also shift to 1050–1100 cm^{-1}.

In Fig. 1, the IR spectra of crotylmercury chloride and crotylmercury bromide are shown to be similar. The elucidation of the structures of these compounds has been of principal importance. Upon reaction with mercury crotylpalladium chloride can lead to two isomers, (A) and (B).

$$CH_3{-}CH{=}CH{-}CH_2{-}HgCl$$

(A)



$$CH_2{=}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}HgCl$$

(B)

The IR spectra support only structure (A). In fact, there is no frequency corresponding to the vibration of the $CH_2{=}CH_2$ group (3080 cm^{-1}). Evidence of R–CH=CH is supported by a strong band at 3015 cm^{-1}, characterizing the C–H stretching vibration of the $={C}{<}^{H}_{R}$ group.

The low intensity of the band corresponding to the so-called C=C vibration near 1650 cm^{-1} is surprising. However, it should be noted that the same weak band in the same area is also observed[10] in the IR spectra of crotylgermanium compounds, $X_3GeCH_2{-}CH{=}CH{-}CH_3$, which exhibit a C=C vibration (1650 cm^{-1}) of considerable intensity in the Raman spectrum.

The IR spectra of other unsymmetrically substituted allyl compounds:

2-methyl-1-acetylallyl mercury chloride (IX) and cinnamylmercury chloride (VI), have also been obtained.

In the spectrum of the compound prepared from the complex of palladium chloride with mesityl oxide (IX) the bands corresponding to the C=C and C=O groups are shifted to 1580 and 1660 cm^{-1}, respectively, as expected for the C=C–C=O conjugated system. As in the case of crotyl compounds, no C–H vibrations, characteristic of the terminal CH_2 group (3080 cm^{-1}) were observed.

The structure of 2-neopentylallylmercury chloride was confirmed by IR bands at 3080 cm^{-1} and 1625 cm^{-1}, corresponding to terminal $C{=}CH_2$ group vibrations.

The IR spectrum of VI gives no possibility of choosing between the (A) and (B) structures, owing to the superimposition of the vibrations of the phenyl nucleus and terminal group. The only conclusion to be drawn on the basis of this spectrum is the existence of conjugation between the monosubstituted benzene nucleus and the double bond (C=C). However, assuming the reaction of metallic mercury with all the above π-allyl compounds of palladium to proceed analogously, we assign the structure of cinnamylmercury chloride to compound IV.

Thus, the reaction of substituted π-allylpalladium halides with metallic mercury independently on a substituent proceeds in such a way, that the mercury atom attacks the μ-halide bridge standing in the *trans*-position in respect to the substituted methylene group of the π-allyl ligand, *i.e.*, the reaction always leads to γ-substituted allylmercury derivatives. In the case of 1-substituted π-allylpalladium halides, the IR spectra indicate[7] that *trans*-isomers of substituted allylmercury derivatives are usually produced as would be expected, since the literature data report the syn-form for 1-substituted π-allylpalladium halides. Thus the transfer of the π-allyl ligand from palladium to mercury proceeds with retention of the allyl group configuration, *i.e.*, in this reaction, the allyl radical cannot exist as a kinetically independent particle.

Reaction mechanism

One of the most interesting properties of the reaction discovered is its rate which is comparable to the rates of ionic reactions in solutions. This fact is surprising when it is remembered that this process is heterogeneous and proceeds in a non-polar solvent such as benzene. The reactions of organometallic compounds with free metals are not usually very fast; for example, a complete exchange of biphenylmercury with isotope ^{203}Hg requires about 3–4 h at room temperature[11]. Approximately the same rate was found in the reactions of organometallic compounds with other metals, *e.g.*, the alkaline metals. In the last case, according to Seyferth *et al.*[12], anion-radicals were generated as intermediates. A number of reactions of mercury with a variety of organometallic compounds described by Razuvaev *et al.*[13], following radical mechanism, have lower rates than our reactions. In all the above examples, the metal usually acts as a reducing agent.

The reaction of allylpalladium complexes with metallic mercury is a redox reaction: $(C_3H_5PdCl)_2 + 2\ Hg \rightarrow 2\ C_3H_5HgCl + Pd$.

We have shown previously[14], that π-allylpalladium complexes could be readily reduced electrochemically or by means of various reducing agents. On the other hand, it is well known that mercury reduces palladium and platinum ions in polarography without matching the potentials. However, in our case a simple electron transfer process is not a motive force of the reaction.

This is proved first by the fact, that metals that are stronger reducing agents than mercury (Mg, Zn, Cd and Ga) do not react with π-allylpalladium chloride under the conditions described. The experiments with liquid gallium and finely dispersed zinc, cadmium and magnesium powders have shown that the state of metal surface is not of importance. However, the reaction with metallic mercury undoubtedly proceeds on its surface since the solubility of mercury, as shown by Pollard and Westwood[11], is insufficient to provide a homogeneous reaction.

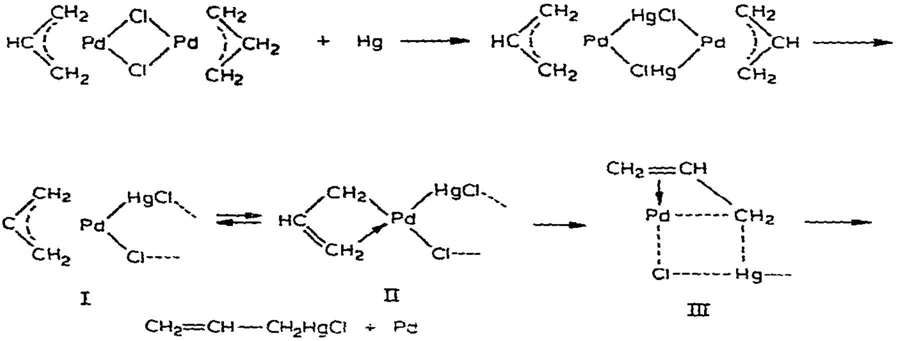
Another argument against the simple oxidation–reduction reaction scheme is that not all the palladium compounds investigated react with metallic mercury. Thus, for example, γ-substituted palladium bis(acetylacetonates) and even the most readily reduceable $(CN-C_5H_6O_2)_2Pd$ do not react with metallic mercury[15]. The cleavage of the halogen bridges by triphenylphosphine or the complete replace of halide atoms by a π-cyclopentadienyl group, lead to compounds inactive to mercury. On the other hand, the product of substitution of the halide atom by the acetylacetonate ligand (π-allylpalladium acetylacetonate) reacts (although slowly) with metallic mercury under the above conditions.

Thus a combination of these two factors, *i.e.*, a tendency to facilitate a reduction, and the existence of bridged groups, are necessary conditions for the reaction of π-allyl complexes with metallic mercury. In accord with this, π-allyl-nickel halides, containing bridged halide atoms, but reduced much more slowly than palladium compounds, do not react with metallic mercury. Probably, the first factor—a tendency to facilitate a reduction— is the most important, since di-π-allyl compounds of palladium and platinum containing no bridged groups but easily reduced with mercury, do react with the latter under the conditions described.

It is more convenient to consider the reaction mechanism choosing π-allylpalladium halides, as example. The first stage could be the adsorption of π-allylpalladium chloride molecules on the surface of metallic mercury. The adsorption could be facilitated by coordination and by the electron unsaturation of the sixteen-electron molecule of $(\pi\text{-}C_3H_5PdCl)_2$. Then mercury atoms are inserted in the weak palladium–chlorine bridged bond. At this stage some unstable intermediates of (I) containing the Pd–Hg bond are produced. Similar stable compounds with mercury have recently been reported for ruthenium and osmium[16]. In general, platinum-group metals readily bond with non-transition elements. For example, complexes of Pt, Pd, Rh, Ir and Ru with such ligands as $SnCl_3$, $SiCl_3$, GeR_3 etc., have been described[17]. As a rule, these complexes are comparatively stable for all these metals except palladium. It has also been noted that in passing from platinum to palladium there is a sharp decrease in stability of the above complexes, especially in solution. For example, unlike the stable $(R_3P)_2Pt(GeR_3)_2$, the isostructural palladium compound decomposed in solution even at $-20°$, giving metallic palladium. It is likely that there is an analogous decrease in stability for compounds containing a M–HgCl bond.

It is of interest to obtain a qualitative estimation of how the bond between the π-allyl group and the Pd atom changes during a transition into the intermediate complex (I) bearing in mind that HgCl as ligand is less electronegative than the halogen atom[19]. Such an unsymmetric cleavage of the μ-halide bridges results in the following: the electronic density on the palladium atom increases and as a result the interaction with the occupied ψ_1 orbitals in the C_3H_5-radical[20] will decrease; on the other hand the interaction with unfilled antibonding orbitals ψ_3 will increase. However, the π-allyl group, unlike the π-bonded olefine, is not able to participate in back-donation[20] and will, therefore, attempt to transform into the state in which the π-bonding will be realized by means of antibonding orbitals of lower energy. This condition could be satisfied by the intermediate structure (II) in which the fragment C=C participates in π-bonding as in the case of the olefine complexes of Zeise's salt type[21].

The next stage consists in *cis*-insertion of the HgCl-ligand along the palladium–carbon bond, *i.e.*, in *cis*-migration of the π, σ-allyl group to the mercury atom. The theoretical aspects of this rearrangement have been recently discussed by Cosee, mainly for some transition-metal complexes[22]. The overlap of metal *d*-orbitals with the π-orbitals of the C=C bond during this rearrangement, favours the migration of the allyl ligand from palladium to mercury. Owing to this overlap, the allyl group remains bonded to the palladium atom when the σ-bonded methylene link migrates to mercury. This migration provides an intermediate transition state III. At the next stage, the internal redox reaction occurs producing metallic palladium and alkylmercury chloride. Thus, the reaction represents a π–σ-transfer of the allyl group from the palladium atom to the mercury atom.



In the reaction of π-allylnickel halides, the process probably stops just at the redox stage, since the reducing power of the mercury atom is not strong enough for "displacing" metallic nickel. On the other hand, the donor properties of the HgCl-ligand are too weak to provide a π–σ-transition in the allyl group, since for the π-allylnickel complexes similar rearrangements are known[4] to proceed with much more difficulty.

Thus, the reaction of π-allylpalladium halides with metallic mercury, by its nature and by the mechanism suggested, is another interesting and (from the preparative point of view) important nucleophilic reaction in the π-allyl transition-metal compounds series.

EXPERIMENTAL

Bis(π-allylpalladium halides) were synthesized by methods already described[25].

Di-π-allyl-Ni, -Pd and -Pt compounds were prepared by the modified method of Wilke *et al.*[4] by the reaction of anhydrous metal halides with allylmagnesium bromide in ether solution.

Bis(π-allylnickel halides) were prepared from di-π-allylnickel and the respective allyl halide[26].

Di-π-allyl compounds as well as bis(π-allyl-nickel halides) were not isolated in their crystalline form but were used in solution in pentane, benzene or ether. In the case of the nickel derivatives the complex was determined by means of a complexometric titration of nickel with EDTA[27].

(1) *Reaction of bis(π-allyl halide)complexes of palladium and nickel with metallic mercury*

General procedure. The solution of the corresponding bridged π-allyl derivative (0.5–1.0 g; 0.003–0.005 mole) in 100 ml of benzene was stirred vigorously with a large excess of metallic mercury (about 20–30 g). After the colour had disappeared (3–5 min), the reaction mixture was filtered and the solvent evaporated *in vacuo*. The residue obtained was recrystallized from a convenient solvent.

Thus, the following compounds have been obtained:

1. Allylmercury chloride (from π-allylpalladium chloride) in quantitative yield. m.p. 110–111° (alc.) (lit. 110–111°[23]).

2. Allylmercury bromide (from π-allylpalladium bromide) in quantitative yield, m.p. 125° (alc.) (lit. 125°[23]).

3. Allylmercury iodide (from π-allylpalladium iodide) in quantitative yield, m.p. 135° (alc.) (lit. 135°[23]).

4. Crotylmercury chloride (from π-crotylpalladium chloride) in quantitative yield, m.p. 76° (alc.). (Found: C, 16.73, 16.60; H, 2.65, 2.64; Cl, 12.63, 12.67; Hg, 68.11, 67.95. C_4H_7ClHg calcd.: C, 16.49; H, 2.42; Cl, 12.21; Hg, 68.87%.)

5. Crotylmercury bromide (from π-crotylpalladium bromide) in 94% yield, m.p. 91° (alc.) (lit. 91–91.5°[7]). (Found: C, 14.36; H, 2.10; Br, 23.92; Hg, 59.78. C_4H_7BrHg calcd.: C, 14.32; H, 2.10; Br, 23.81; Hg, 59.98%.)

6. Cinnamylmercury chloride (from 1-phenyl-π-allylpalladium chloride) in 74% yield, m.p. 123–124° (alc.). (Found: C, 30.41, 30.46; H, 2.57, 2.56; Cl, 10.96, 11.02; Hg, 55.77, 55.77; C_9H_9ClHg calcd.: C, 30.60; H, 2.59; Cl, 10.04; Hg, 56.97%.)

7. 2-Phenylallylmercury chloride (from 2-phenyl-π-allylpalladium chloride). Yield 68%*, m.p. 56–57° (methylene chloride–hexane). (Found: C, 30.27, 30.11; H, 2.43, 2.56; Cl, 10.33, 10.43; Hg, 56.69, 56.72. C_9H_9ClHg calcd.: C, 30.60; H, 2.59; Cl, 10.04; Hg, 56.97%.)

8. 2-Neopentylallylmercury chloride. Yield 77%*, m.p. 64–65° (methanol). (Found: C, 27.72, 27.71; H, 4.33, 4.35; Cl, 11.05, 10.83; Hg, 57.05, 56.99. $C_8H_{15}ClHg$ calcd.: C, 27.59; H, 4.34; Cl, 10.18; Hg, 57.88%.)

9. 2-Methyl-1-acetylallylmercury chloride. Yield 64%*; m.p. 67–68° (methanol). (Found: C, 21.68, 21.53; H, 2.84, 2.84; Cl, 10.84, 10.95; Hg, 59.63, 59.50. C_6H_9ClHgO calcd.: C, 21.63; H, 2.72; Cl, 10.64; Hg, 60.20%.)

(2) *Reaction of mercury with bis(1-chloromethyl-π-allylpalladium chloride)*

From 0.9 g (0.004 mole) of bis(1-chloromethyl-π-allyl-palladium chloride) 1.2 g of grey powdery solid was obtained. The solid was insoluble in water and organic solvents. (Found: C, 27.73; H, 2.69; Cl, 19.67; Hg, 54.49%.)

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* The yield given is for the pure compound. The yield of crude material was quantitative.

(3) *Reaction of mercury with bis(2-chloro-π-allylpalladium chloride)*

From 0.9 g (0.004 mole) of bis(2-chloro-π-allylpalladium chloride), 1.1 g of a white crystalline solid was obtained; this decomposed on purification giving mercuric chloride and allene.

(4) *Reaction of mercury with π-allylpalladiumtriphenylphosphine*

On mixing 10 g (0.002 mole) of π-allylpalladiumtriphenylphosphine with metallic mercury, no metallic palladium precipitated. The starting material was isolated quantitatively.

(5) *Reaction of bis(π-allylnickel chloride) with mercury*

50 ml of benzene containing 0.8 g (0.006 mole) of bis(π-allylnickel chloride) were stirred vigorously with excess metallic mercury. The mixture did not decolourise. The application of heat led to the decomposition of bis(π-allylnickel chloride) and precipitation of metallic nickel. Not even traces of allylmercury compounds could be isolated.

(6) *Reaction of mercury with π-allylpalladium acetylacetonate*

0.5 g (0.002 mole) of π-allylpalladium acetylacetonate was stirred vigorously with excess metallic mercury until the solution became colourless (about 15–20 min). The white substance precipitated on the flask walls, was collected, washed with benzene and ether and dried *in vacuo*. 0.34 g of the bis(acetylacetonate) of mercury was obtained. Yield 95%, m.p. 220° (decomp.) (lit. 220° (dec.)[24]).

The compound obtained was identical with mercury bis(acetylacetonate), prepared from mercuric chloride and sodium acetylacetonate in THF[24].

(7) *Reaction of mercury with π-allylpalladium acetate*

1.0 g (0.005 mole) of π-allylpalladium acetate in 50 ml of benzene was stirred vigorously with excess mercury until the solution was decolourised. The solvent was removed *in vacuo* and the residue recrystallized from benzene–hexane (1 : 1) mixture. 1.4 g of allylmercury acetate was obtained. Yield 97%, m.p. 109–110°. (Found: C, 19.54, 19.59; H, 2.83, 2.87. $C_5H_8O_2Hg$ calcd.: C, 19.60; H, 2.66%.)

(8) *Reaction of mercury with bis(π-allyl)-nickel, -palladium and -platinum compounds*

General procedure. 50 ml of an ethereal solution of the di-π-allyl compound containing about 0.5 g (0.0003–0.0002 mole) of the di-π-allyl complex was stirred vigorously with excess metallic mercury until the mixture was decolourised. A current of hydrogen chloride was passed through the filtered solution for 10 min with cooling. The mixture was quickly poured into water, extracted with benzene, dried over $CaCl_2$ and evaporated *in vacuo*. The residue was recrystallized from alcohol.

Thus, the reaction of mercury with ethereal solutions of di-π-allyl-palladium and -platinum compounds resulted in allylmercury chloride m.p. 110–111° (lit. 110–111°[23]).

When mercury was added to a solution of di-π-allylnickel no decolourisation of the mixture was observed. Heating decomposed di-π-allylnickel and metallic nickel was precipitated. Not even traces of allyl mercury compounds could be isolated.

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