## REACTION OF $\pi$ -ALLYL COMPOUNDS OF PALLIDIUM WITH Ge(II) AND Sn(II) HALIDES

S. P. Gubin, A.Z. Rubezhov, L.I. Voronchikhina, and A.N. Nesmeyanov

UDC 542.957:547.359.8

Previously we have shown [1] that  $(\pi - C_3H_5PdCl)_2$  (I) under mild conditions reacts with metallic mercury with the formation of allyl compounds of mercury (reaction of  $\pi - \sigma$  transfer). A mechanism for the transfer reactions of a  $\pi$ -allyl ligand was proposed for the reactions of  $\pi$ -allyl complexes of Pd with the iron and cobalt carbonyls ( $\pi - \pi$  transfer) [2, 3], and then was extended to the reaction with metallic mercury [4]. According to this mechanism, insertion of the Hg at the Pd—Cl bond occurs in the first step, which leads to a cleavage of the  $\mu$ -halo bridge in the (I) molecule. It is known that Sn(II) and Ge(II) halides, possessing carbenoid properties, are easily inserted at a transition metal—halogen covalent bond with the formation of compounds containing an N—M bond [5]. In addition, GeCl<sub>2</sub> can be inserted at the transition metal—carbon bond [6]. In view of this it was interesting to study the reaction of (I) with GeCl<sub>2</sub> or SnCl<sub>2</sub> in order to find new examples of reactions for the transfer of the  $\pi$ -ligand from Pd to the atom of a nontransition metal.\*

Quite rapid reaction occurs when an excess of  $MX_2$  (X = halogen) is added to (I) in either benzene or THF, the color of the reaction mixture changes from yellow through cherry red to colorless, the quantitative deposition of Pd is observed, and an oily liquid remains when the solvent is removed, the reaction of which with  $C_6H_5MgBr$  gives the tetraphenyl derivatives of the corresponding metal and a small amount of biphenyl. GLC analysis of the volatile portion of the reaction mixture discloses the presence of biallyl. The reaction of (I) with  $MX_2$  proceeds according to the general scheme:

$$(C_3H_5PdCl)_2 + MX_2 \rightarrow 2Pd + MX_4 + C_3H_5C_3H_5$$
(1)

Consequently, the reaction of the allyl compounds of Pd with Ge and Sn halides differs from the reactions with Hg: the allyl ligand does not attach itself to the nontrasition metal, and instead a twinning of the allyl radicals occurs.

It was necessary to ascertain at which specific step the difference between the reaction with mercury and the  $MX_2$ , studied in the present paper, begins to appear.

We will examine the first step of the reaction for transfer of the allyl ligand, namely insertion at the Pd-Cl bond. In the reaction with Hg the deposition of Pd began immediately after contact with the mercury surface. In the present case the Pd deposition proceeds with a certain induction period, the duration of which depends on the solvent. In THF, for example, Pd does not deposit for several hours, and instead forms homogeneous and stable solutions. When triphenylphosphine was added to a reaction mixture composed of (I) and SnCl<sub>2</sub> a complex of composition  $\pi$  -C<sub>3</sub>H<sub>5</sub>PdSnCl<sub>3</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (II) was isolated, which corresponds to the product of SnCl<sub>2</sub> insertion at the Pd-Cl bond. A similar compound was obtained when  $\pi$  -C<sub>3</sub>H<sub>5</sub> ·PdCl·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (III) and SnCl<sub>2</sub> are reacted in acetone [9]. The formation of (II) confirms the first step of the transfer of the  $\pi$ -allyl ligand, namely cleavage of the  $\mu$ -halo bridge in dimer (I) with insertion of the attacking agent at the Pd-Hal bond.

\* It could be expected that when the reaction for the transfer of the allyl ligand proceeds successfully the reaction products will be compounds of composition  $C_3H_5MCl_3$  (M = Ge or Sn). According to [7], these compounds are unstable liquid compounds, but their triphenyl derivatives are stable and convenient to work with [8].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.6, pp.1368-1372, June, 1972. Original article submitted October 23, 1970.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

It is possible to assume that the initial insertion of the metal halide at the Pd--Cl bond also occurs in the case of  $\text{GeX}_2$ , since the end reaction product is also  $\text{GeX}_4$ . However, when triphenylphosphine is added to a reaction mixture composed of (I) and  $\text{GeX}_2$  we mainly isolated the triphenylphosphine complexes of the Pd(II) halides, contaminated with a small amount of (III) or the corresponding iodide.

All of the reactions with  $\text{GeX}_2$  proceed much more rapidly than do the analogous reactions with  $\text{SnCl}_2$ . This is in good agreement with the known differences in the reduction and carbenoid properties of the Ge(II) and Sn(II) halides, in both cases they are expressed more strongly for Ge than for Sn.

As a result, in the first step of the reaction we failed to notice any substantial differences in the reaction of (I) with metallic mercury and with  $MX_2$ . Cleavage of the  $\mu$ -halo bridge with insertion of the attacking agent at the Pd-Cl bond occurs in both cases. We will examine the subsequent steps of the reaction.

In the proposed reaction mechanism for transfer of the  $\pi$ -allyl ligand from one metal to another, following the insertion step, were postulated the steps of the successive transition of the  $\pi$ -allyl ligand to the  $\pi$ ,  $\sigma$ - and  $\sigma$ -bonded states under the influence of the powerful electron-donor trans-effect of the inserted groupings. In all of the described cases, when such reactions proceed in harmony with the proposed mechanism, the group, attached to Pd, facilitates the  $\pi \longrightarrow \sigma$  transition of the allyl ligand mainly due to its  $\sigma$ -electron-donor effect (-HgCl,  $-\text{Fe}(\text{CO})_4$ ,  $-\text{CO}(\text{CO})_4$  [10]). In contrast to the enumerated groups, SnCl<sub>3</sub> possesses a strong  $\pi$ -acceptor effect, and apparently also a strong  $\sigma$ -acceptor effect [11]. The value of  $\sigma^*$  (which characterizes the  $\sigma$ -acceptor effect) changes when going from -HgCl to  $-\text{SnCl}_3$  from 0.83 to 2.26 [12]. It is possible to assume that the GeCl<sub>3</sub> group will possess analogous properties.

Consequently, the main reason for the absence of reactions for transfer of the allyl ligand from Pd to Ge and Sn must be considered to be the impossibility of transition of the  $\pi$ -allyl ligand to the  $\pi$ ,  $\sigma$ - and  $\sigma$ -bonded states in the intermediately formed insertion product. The results, obtained in the present study, again corroborate the general tenet that transfer of the  $\pi$ -allyl ligand from one metal to another should include the necessary step of a  $\sigma$ -bonded allyl ligand.

One of the products of the studied reactions is biallyl. Its formation can be explained by the symmetrization of (I) under the influence of excess reducing agent.

$$HC \begin{pmatrix} CH_2 & CH_2 & CH_2 \\ Pd & Pd & Pd \end{pmatrix} CH + MX_2 \longrightarrow HC \begin{pmatrix} CH_2 & CH_2 \\ Pd & Pd \end{pmatrix} CH + MX_4 + Pd$$

$$(2)$$

Similar reactions were observed previously on the example of the  $\pi$ -allyl compounds of nickel [12]. The formed bis-( $\pi$ -allylpalladium) decomposes further with the formation of biallyl.

$$\begin{array}{ccc} & & CH_2 & CH_2 \\ HC & Pd & CH \rightarrow Pd + C_3H_5 - C_3H_5 \\ CH_2 & CH_2 \end{array}$$
(3)

It is obvious that combining Eqs. (2) and (3) gives the overall process depicted in scheme (1).

## EXPERIMENTAL SECTION

The bis- $(\pi$ -allylpalladium halides) [13], anhydrous SnCl<sub>2</sub> [14], GeCl<sub>2</sub> as the complex with dioxane [15], GeI<sub>2</sub> [16], triphenylphosphine [17], and solution of C<sub>6</sub>H<sub>5</sub>MgBr in ether [18], were obtained by methods described in the literature. All of the operations were run in an argon atmosphere. The obtained compounds were identified by the elemental analysis, and by a comparison of the IR and NMR spectra with the spectra of authentic specimens. The IR spectra were taken on UR-10 and FiS-1 instruments. The NMR spectra were recorded on a R-12 spectrometer (60 MHz), using hexamethyldisiloxane as the internal standard. All of the employed solvents were distilled in an argon atmosphere immediately prior to use. The THF was distilled twice over LiAlH<sub>4</sub>.

Reaction of bis- $(\pi$ -Allylpalladium Halides) with MX<sub>2</sub> and Subsequent Treatment with Phenylmagnesium Bromide. To 1.0 g of (I) in 100 ml of absolute benzene was added excess MX<sub>2</sub> in one portion, and the mixture was stirred at room temperature until completely colorless (~6-8 h). Then the Pd precipitate and unreacted  $MX_2$  were filtered, and the clear colorless filtrate was evaporated to dryness in a rotor evaporator at 30-35°C, \* and the pale yellow oily residue was dissolved in 100 ml of absolute ether. The obtained solution was added in drops to a solution of  $C_6H_5MgBr$  in ether [the amount of Grignard reagent was calculated on the basis of the amount of taken (I)]. The reaction mixture was refluxed for 4 h and then decomposed with conc. aqueous  $NH_4Cl$  solution. The ether layer was separated, washed with water, and dried over  $CaCl_2$ . The solvent was distilled off in a rotor evaporator (temperature < 30°), and the dry residue was dissolved in light petroleum ether (bp 40-60°) and chromatographed on  $Al_2O_3$ . Hexane was used to elute 0.05 g of biphenyl, mp 67-68° (hexane); from [19]: mp 69°. Benzene was used to elute ( $C_6H_5/_4$  M (M = Ge or Sn), yield ~60-80% [when based on taken (I)]. Recrystallization from absolute alcohol gave either: ( $C_6H_5/_4Sn$ , mp 225°; from [20]: mp 225°, or ( $C_6H_5/_4Ge$ , mp 226-228°; from [21]: mp 225-228°.

Reaction of bis- $(\pi$ -Allylpalladium Halides) with GeX<sub>2</sub> (X = Cl, I) and the Subsequent Addition of Triphenylphosphine. The addition of the reactants was done in the same manner as in the preceding experiment, after which the reaction mixture was stirred until the Pd began to deposit (~3-4 h), and then was added an equimolar amount of triphenylphosphine, when based on the amount of (I) taken for reaction. The mixture was stirred for 1 h, filtered, and the filtrate was evaporated to dryness in a rotor evaporator (see the footnote to the preceding experiment). The residue was extracted with benzene, and the benzene was evaporated. After several recrystallizations from acetone we obtained (X = CI) pure (III), mp 180-182°; from [13]: mp 181°. Then the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the solvent was evaporated. We obtained the monomeric complex  $Cl_2Pd[P(C_6H_5)_3]_2$ , mp 296-300°; from [22]: mp 297-298°. Found: C 61.03; H 4.45%. C<sub>36</sub>H<sub>30</sub>PdCl<sub>2</sub>P<sub>2</sub>. Calculated: C 61.10; H 4.27%. The residue from the extraction was recrystallized from a large amount of  $CH_2Cl_2$ . We obtained the dimeric complex  $Cl_4Pd_2 \cdot [P(C_6H_5)_3]_2$ , mp 260-265° (decompn.) from [23]: mp 250-270° (decompn.). Found: C 49.80; H 3.75; Cl 16.50; P 7.17%. C<sub>36</sub>H<sub>30</sub>Pd<sub>2</sub>Cl<sub>4</sub>P<sub>2</sub>. Calculated: C 49.10; H 3.40; Cl 16.20; P 7.05%. In a similar manner, for X = I was obtained  $\pi$  -C<sub>3</sub>H<sub>5</sub>PdIP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, mp 200-230° (decompn.). Found: C 46.81; H 3.59%. C21H20PdPI. Calculated: C 46.99; H 3.76%. From the CH2Cl2 extract was isolated I<sub>2</sub>Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>, mp 300° (decompn.). Found: 49.09; H 3.64; I 28.40; P 7.29%. C<sub>36</sub>H<sub>30</sub>Pd- $P_2I_2$  Calculated: C 48.87; H 3.42; I 28.26; P 7.03%. The residue from the extraction was recrystallized from CHCl<sub>3</sub> to give I<sub>4</sub>Pd<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>, mp 300° (decompn.). Found: C 35.26; H 2.50; I 39.60; P 5.46%. C<sub>36</sub>H<sub>30</sub>-Pd<sub>2</sub>I<sub>4</sub>P<sub>2</sub>. Calculated: C. 34.75; H 2.71; I 40.08; P 4.98%.

Reaction of (I) with  $SnCl_2$  and the Subsequent Addition of Triphenylphosphine. The reaction was run in the same manner as with  $GeCl_2$ . The reaction mixture was evaporated to dryness, the frothy residue was dissolved in  $CH_2Cl_2$ , heptane was added, and the mixture was evaporated in a rotor evaporator at ~25°. Recrystallization from acetone gave pale yellow crystals of (II) in quantitative yield, which crystallize with one molecule of acetone, mp 112-113°. Found: C 42.42; H 3.81%.  $C_{21}H_{20}PdCl_3PSn \cdot CH_3COCH_3$ . Calculated: C 41.60; H 3.71%.

## CONCLUSIONS

1. A study was made of the reaction of the  $\pi$ -allyl compounds of palladium with the halides of divalent germanium and tin; SnCl<sub>2</sub> inserts itself at the Pd-Cl bond with the formation of the complex  $\pi$ -C<sub>3</sub>-H<sub>5</sub>PdSnCl<sub>3</sub>·P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

2. Decomposition of the  $\pi$ -allylpalladium halides occurs when reaction is with germanium halides, with the formation of biallyl; the triphenylphosphine complexes of palladium were isolated when triphenylphosphine was added to the reaction mixture.

## LITERATURE CITED

- 1. S. P. Gubin, A. Z. Rubezhov, L. I. Denisovich, and A. N. Nesmeyanov, Izv. Akad. Nauk, Ser. Khim., 1680 (1966).
- 2. A. N. Nesmeyanov, S. P. Gubin, and A. Z. Rubezhov, J. Organomet. Chem., 16, 163 (1969).
- 3. R. F. Heck, J. Am. Chem. Soc., 90, 319 (1968).
- 4. A. N. Nesmeyanov, A. Z. Rubezhov, L. A. Leites, and S. P. Gubin, J. Organomet. Chem., <u>12</u>, 187 (1968).
- 5. T. Blackmore, J. D. Cotton, M. J. Bruce, and F. G. A. Stone, J. Chem. Soc., A, 2931 (1968).

\* When the experiments were repeated, the distillate obtained in this step was analyzed by GLC and shown to contain biallyl in a yield equal to 30-35% of theory when based on taken (I).

- 6. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1950 (1969).
- A. D. Petrov, V. F. Mironov, and I. E. Dolgii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1146 (1956);
   D. Seyferth and F. G. A. Stone, J. Am. Chem. Soc., <u>79</u>, 515 (1957).
- 8. M. M. Koton and T. M. Kiseleva, Zh. Obshch. Khim., 27, 2553 (1957).
- 9. R. Mason, G. B. Robertson, P. O. Whimp, and D. A. White, Chem. Commun., 1655 (1968); M. Sakakibara, Y. Takaheshi, S. Sakai, and Y. Ishii, Inorg. Nucl. Chem. Lett., 427 (1969).
- 10. A. A. Ioganson, A. B. Antonova, B. V. Lokshin, N. E. Kolobova, K. N. Anisimov, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1957 (1969).
- 11. R. V. Lindsey, G. W. Parshal, and U. G. Stolberg, J. Am. Chem. Soc., 87, 658 (1965).
- 12. T. G. Golenko, K. L. Makovetskii, V. A. Libina, A. N. Karaseva, E. I. Tinyakova, and B. A. Dolgoplosk, Izv. Akad. Nauk SSSR, Ser. Khim., 2269 (1968).
- 13. A. Z. Rubezhov, Dissertation [in Russian], Moscow (1967).
- 14. W. Fisher and R. Gewehr, Z. Anorg. Allgem. Chem., 242, 188 (1939).
- 15. S. P. Kolesnikov, V. I. Shiryaev, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 584 (1966).
- 16. E. Flood, L. Foster, and E. Pietrusza, Inorganic Syntheses, 3, 63 (1950).
- 17. J. Dodonov and H. Medox, Chem. Ber., 61, 907 (1928).
- 18. Organic Syntheses [Russian translation], IL (1949), Vol.1, p.207.
- 19. C. Courtot and C. C. Lin, Bull. Soc. Chim. France, 49, 1053 (1931).
- 20. K. A. Kocheshkov, Synthetic Methods in the Domain of Organometallic Compounds [in Russian], Izd. AN SSSR (1947), p. 38.
- 21. D. M. Harris, W. H. Nebergall, and O. H. Johnson, Inorganic Syntheses, 5, 70 (1957).
- 22. P. M. Maitlis and F. G. A. Stone, Proc. Chem. Soc., 331 (1962).
- 23. J. Chatt and L. M. Venanzi, J. Chem. Soc., 2351 (1957).