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Preliminary communication

SYNTHESIS OF BENZYLPALLADIUM CHLORIDE EMPLOYING PALLADIUM ATOMS

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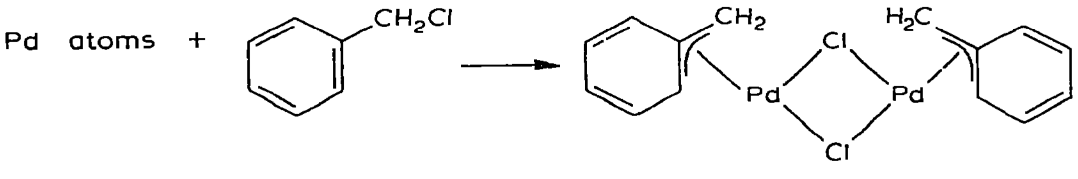
Summary

Benzylpalladium chloride is formed in good yield when palladium atoms are condensed in a low temperature matrix with benzyl chloride. The surprising stability and spectral properties of the $C_6H_5CH_2PdCl$ indicate *trihapto*-allyl type bonding of the benzyl system with the palladium atom.

When palladium atoms [1] and benzyl chloride are cocondensed in a −196°C matrix and then warmed to room temperature, the novel benzylpalladium chloride dimer (I) is isolated (from organic solvents). (Anal. found C, 36.2; H, 3.16; Cl, 15.3. $C_{14}H_{14}Cl_2Pd_2$ calcd.: C, 36.1; H, 3.02; Cl, 15.2%.) It is dark red in color, and is formed in about 50% yield, based on metal vaporized. Solubility problems have precluded obtaining good molecular weight data. Osmotic values obtained from "turbid" solutions were 560 (acetone) and 580 (benzene). The dimer has a molecular weight of 464, and values higher than that would be expected in cases of poor solubility.

We have tentatively assigned the structure as being a h^3-benzyl system on the basis of five pieces of information.



(I)

(1) The PMR spectrum of I is compatible with allylic type bonding. Thus, the spectrum of I is very similar to that reported by Stevens and Shier [2] for the bis(triethylphosphine)-h^3-benzylpalladium cation. The *ortho* protons are moved

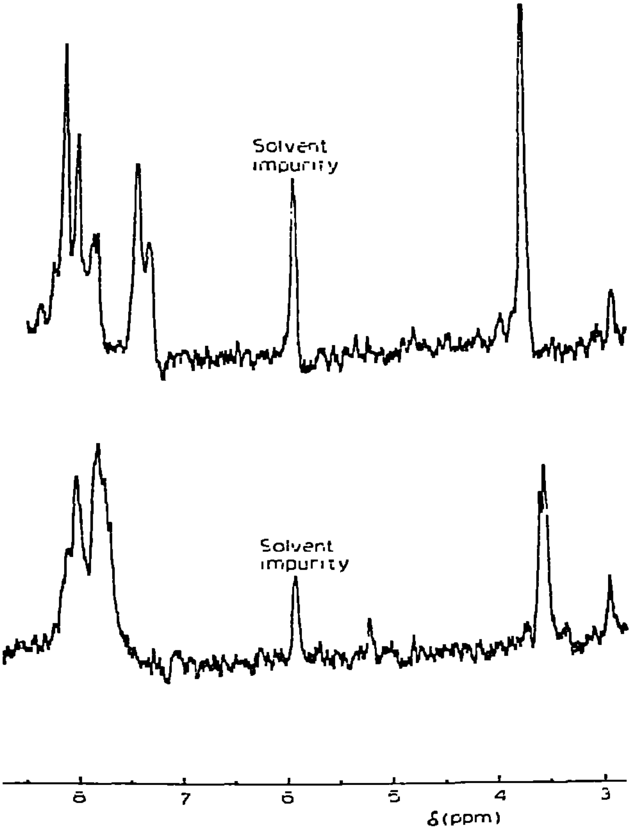


Fig. 1. (Upper) PMR spectrum of I,(lower) PMR spectrum of I after addition of one equivalent Et$_3$P/Pd atom. Note the doublet splitting of the benzyl protons by phosphorus, and the shift of the *ortho* protons to lower field (Et$_3$P absorptions not shown).

upfield substantially, and no preferential conformations could be detected at a probe temperature variance of 40 to −85°C. PMR (I in CD_2Cl_2, σ (ppm)), 7.92, 7.78, 7.65 (*meta* and *para* protons), 7.11, 7.00 (*ortho* protons), and 3.58 (benzylic protons) (cf. Fig. 1).

(2) Incremental addition of Et_3P to I in solution indicated that two equivalents of Et_3P (one per Pd atom) resulted in a $\pi \rightarrow \sigma$ rearrangement, thus causing the CH_2 protons to be split into a doublet (by P, cf. Fig. 1) and the *ortho* protons to be shifted downfield into the normal region for aryl protons in such σ-bonded compounds, i.e. bis(triethylphosphine)benzylpalladium chloride (II). Addition of two equivalents of Et_3P resulted in the formation of II, and analogous results were obtained with pyridine-d_5. These results are similar to those found for Et_3P additions to allyl-bonded compounds [3].

(3) σ-Benzyl systems are known to rearrange to h^3-benzyl systems when the metal to which the benzyl group is attached becomes coordinatively unsaturated [4, 5].

(4) The thermal stability of I is striking in comparison with that of other aryl and alkyl RPdX compounds which we have prepared [1]. Thus, I decomposes

at 100-110° in the solid state, and about 40° in solution. Normal RPdX ($R = CH_3$, C_6H_5) compounds are stable only below −100°C [1b, d].

(5) UV and IR spectra of I show a gross distortion of the aryl π-system. Thus, the normal bands for aryl-in-plane C=C stretching are not observed in the IR, and the strongest band in the UV is moved down to 2380 Å (from 2600 Å in benzyl chloride and 2640 Å and 3100 Å in bis(triethylphosphine)benzylpalladium chloride (II)). IR (I, cm^{-1}, KBr pellet); 3030 m, 2930 w, 1530 w, 1482m, 1470m, 1448m, 1431m, 1268(sh), 1255m, 1210m, 1070s, 1025m, 1005(sh), 955m, 912m, 855m, 825m, 805w, 760(sh), 750(sh), 742vs, 725(sh), 692s, 682(sh), 615w, 571s, 540m, 455m, UV (I, Å, $CHCl_3$); 2380s, 2900(sh), 3850w.

Heck [6] has proposed benzylpalladium chloride as an intermediate in the palladium acetate-catalyzed reaction of benzyl chloride with methyl acrylate. The main product formed was *trans*-methyl-4-phenyl-3-butenoate. We have found that substitution of I for palladium acetate gave the same products observed by Heck and Nolley.

In CH_2Cl_2 solution, I reacts readily with carbon monoxide at room temperature and atmospheric pressure. Palladium metal precipitates from solution and upon addition of methanol, methyl phenylacetate is obtained. Compound I also reacts with acetate ion in acetic acid to yield benzyl acetate.

Currently, we are studying substituted benzylpalladium chloride compounds in order to further elucidate the mode of bonding in these materials. Interactions of other metal atoms with benzyl chloride also appear promising based on preliminary data.

Acknowledgement

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References

1 (a) K.J. Klabunde and J.Y.F. Low, J. Organometal. Chem., 51 (1973) C33; (b) J. Amer. Chem. Soc., in press; (c) K.J. Klabunde, J.Y.F. Low and H.F. Efner, ibid., 96 (1974) 1984; (d) K.J. Klabunde, Angew. Chem., in press.

2 R.R. Stevens and G.D. Shier, J. Organometal. Chem., 21 (1970) 495.

3 J. Powell, S.D. Robinson and B.L. Shaw, Chem. Commun., (1965) 78; R. Mason and D.R. Russell, ibid., (1966) 26.

4 R.B. King and A. Fronzaglia, J. Amer. Chem. Soc., 88 (1966) 709.

5 F.A. Cotton and M.D. LaPrade, J. Amer. Chem. Soc., 90 (1968) 5418; F.A. Cotton and T.J. Marks, ibid., 91 (1969) 1339; F.A. Cotton, Accounts Chem. Res., 1 (1968) 257.

6 R.F. Heck and J.P. Nolley, Jr., J. Org. Chem., 37 (1972) 2320.