Inorganica Chimica Acta, 20 (1976) L15 - L16
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Reaction of Organopalladium Complexes with Thallium Cyclopentadiene

KEINOSUKE SUZUKI and KAZUHIRO HANAKI

Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan 464

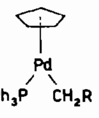
(Received August 10, 1976)

Cyclopentadienyl complexes of palladium containing a Pd–C σ-bond and a tertiary phosphine or a phosphite have been prepared in two ways: (1) reaction of a binuclear halogen-bridged complex with TlC_5H_5 followed by treatment with organic lithium reagents or Grignard reagents [1], (2) reaction of Pd(η^5-C_5H_5)L (L = η^3-2-chloroallyl) [2] with a tertiary phosphine or phosphites. In this paper we report that organopalladium complexes prepared by an oxidative addition of organic halides react with TlC_5H_5 to give cyclopentadienyl derivatives of palladium.

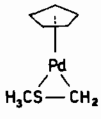
To a suspension of $PdCl(CH_2SCH_3)(PPh_3)$ [3] in benzene TlC_5H_5 was added at room temperature. The mixture turned to deep red in a few minutes. After stirring overnight, the solution was filtered and the solvent was removed *in vacuo* to leave red–brown solids which were recrystallized from diethyl ether–petroleum ether to give a red crystalline (I) (*Anal.* Found: C, 60.37; H, 4.96. Required for $C_{25}H_{25}PSPd$: C, 60.67; H, 5.09%).

Similarly, reaction of $PdCl(CH_2CN)(PPh_3)_2$ [4] with TlC_5H_5 in benzene gave a red–violet crystalline compound (II) (*Anal.* Found: C, 63.10; H, 4.92; N, 3.01. Required for $C_{25}H_{22}NPPd$: C, 63.37; H, 4.68; N, 2.96%).

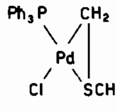
For the complex (I), two kinds of η^5-cyclopentadienyl complexes (a, R = SCH_3 and b) are possible since $PdCl(CH_2SCH_3)(PPh_3)$ has a structure (c) [2].



(a)



(b)



(c)

The ^1H nmr spectrum of (I) is shown in the Figure. The cyclopentadienyl and methylene protons appeared as a doublet due to coupling to the phosphorus atom ($\tau(CH_2)$ = 7.73d, J(PH) = 5.5 Hz; $\tau(C_5H_5)$ = 4.32d, J(PH) = 3.0 Hz), but the methyl protons as a singlet at τ 8.15. The chemical shift and coupling constant of the cyclopentadienyl protons are similar to those reported for Pd(η^5-C_5H_5)(PEt_3)X (X = Cl, Br, I) [1]. Thus we assigned structure (a) to (I). At present we do not have any evidence to indicate the formation of (b).

The complex (II) showed a similar spectrum to that of (I). ($\tau(CH_2)$ = 9.00d, J(PH) = 5.5 Hz. $\tau(C_5H_5)$ = 4.36d, J(PH) = 2.0 Hz). This is consistent with structure (a) (R = CN).

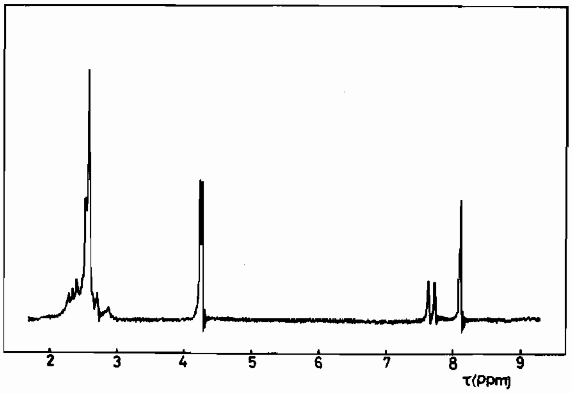
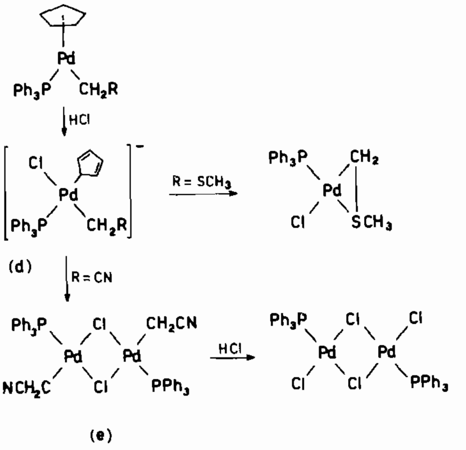


Figure. ^1H nmr spectrum of Pd(η^5-C_5H_5)(CH_2SCH_3)(PPh_3).

Reaction of these complexes with dry hydrogen chloride in $CDCl_3$ was examined. When (II) dissolved in $CDCl_3$ was treated with hydrogen chloride, the solution turned to yellow–orange in a few minutes and then a yellow–brown crystalline solid was precipitated. The far infrared spectrum of this precipitate showed that it was a binuclear chloro-bridged complex, $[PdCl_2(PPh_3)]_2$ [5]. The same result has been obtained in the reaction of PdCl(η^5-C_5H_5)(P(O-*o*-Tol)$_3$ [2]. Similar treatment of (I) in $CDCl_3$ caused a color change from red to yellow, but no precipitate was obtained. Therefore the solution was concentrated and diethyl ether was added to obtain a yellow crystalline compound. Its ^1H nmr spectrum showed that $PdCl(CH_2SCH_3)(PPh_3)$ was reformed.

These results may be interpreted by assuming the formation of an unstable intermediate (d) as shown in the scheme.



When R = CN (d) is probably transformed into (e) because the nitrile group cannot coordinate to the same palladium atom sterically. Then hydrogen chloride further reacts with (e) to form the chloro-bridged dimeric complex. However, when R = SCH_3 the sulfur atom can interact with the palladium to form a three-membered chelate ring. Thus the difference found in the reaction of (I) or (II) with hydrogen chloride seems to depend on the coordinating ability of the organic substituents.

Preparation and reactions of other cyclopentadienyl complexes of palladium are under investigation.

References

1 R. J. Cross and R. Wardle, *J. Chem. Soc. A,* 2000 (1971).
2 D. J. Tune and H. Werner, *Helv. Chim. Acta, 58,* 2240 (1975).
3 G. Yoshida, H. Kurosawa, and R. Okawara, *J. Organometal. Chem., 113,* 85 (1976).
4 K. Suzuki and H. Yamamoto, *J. Organometal. Chem., 54,* 385 (1973).
5 R. J. Goodfellow and P. L. Goggin, *J. Chem. Soc. A,* 1897 (1967).