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Preparation and Suggested Structure of a Binuclear Palladium Complex containing Two Cyclopentadienyl Groups

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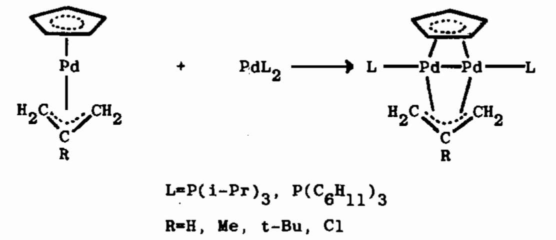
A cyclopentadienyl group is one of the most important ligands in organometallic chemistry. Recently Werner *et al.* [1] and Turner *et al.* [2] have synthesized new dimeric palladium(I) complexes which contain a cyclopentadienyl group coordinated to the Pd(I)–Pd(I) bond. Further, Werner *et al.* [3] presented an interesting synthetic method which led to formation of complexes of type (I).

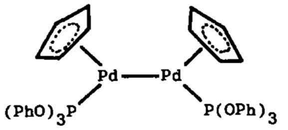


(I)

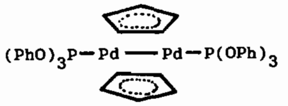
However this method is not suitable for the synthesis of a complex containing two bridging cyclopentadienyl groups, because starting material palladocene has not been obtained yet. Turner *et al.* [4] also tried the reaction of μ-(η^3-C_5H_5)-μ-BrPd$_2$L$_2$ (L = PPh$_3$, P(i-Pr)$_3$) with TlC$_5$H$_5$ in an attempt to replace the bridging bromine atom with a cyclopentadienyl group without success. In this paper we describe the preparation of [μ-(C_5H_5)PdP(OPh)$_3$]$_2$ (II).

To a solution of 1.7 g of NaC$_5$H$_5$ in 200 ml of tetrahydrofuran cooled to 0 °C under nitrogen was added with stirring 4.3 g of Pd$_2$Cl$_4${P(OPh)$_3$}$_2$ in 200 ml of tetrahydrofuran. After a short time the solvent was distilled off under vacuum and the residue was washed with ether and water and recrystallised from CHCl$_3$–n-pentane to give a yellow crystalline compound (II). *Anal.* Found: C, 57.4; H, 4.7; P, 6.5. Required for $C_{46}H_{40}O_6Pd_2P_2$: C, 57.3; H, 4.2; P, 6.4. Mol. wt. Found: 1060. Required for $C_{46}H_{40}O_6Pd_2P_2$: 963.

The analytical data and molecular weight of the complex (II) strongly indicate that (II) is a dimeric palladium complex [μ-(C_5H_5)PdP(OPh)$_3$]$_2$ for which two structures (A) and (B) are possible.



(A)



(B)

We can distinguish between (A) and (B) by the ^{1}H nmr spectrum of the cyclopentadienyl protons which couple with the two phosphorus atoms. Thus we can expect a doublet of doublets for (A) and a triplet for (B). As Fig. 1 shows, the cyclopentadienyl and the phenyl protons appear as a triplet (τ 4.93) and a singlet (τ 2.7) respectively. Their intensity ratio 1:3:2 (C_5H_5:P(OPh)$_3$ is in agreement with the formulation of (II). These results allowed us to assign the structure (B) – the structure containing two bridging C_5H_5 groups – to the complex (II). The coordination mode of the C_5H_5 groups is not clear at present: recently, Turner *et al.* [2] showed that the C_5H_5

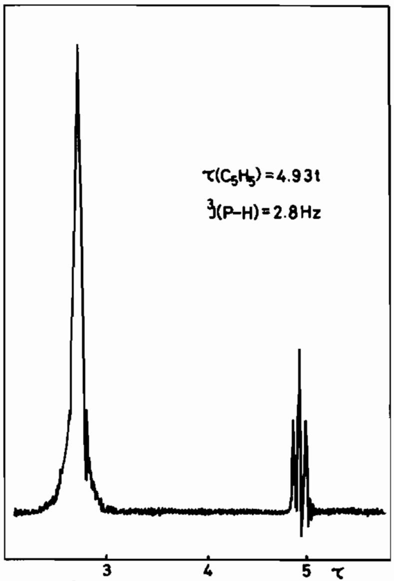


Fig. 1. ^{1}H nmr spectrum of [μ-(C_5H_5)PdP(OPh)$_3$]$_2$.

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bridge in μ-(η^3-C_5H_5)-μ-$BrPd_2\{P(i\text{-}Pr)_3\}_2$ can be regarded as an allyl plus alkene group. Further, a complex incorporating two bridging allyl groups, [μ-(η^3-C_3H_4)$PdP(i\text{-}Pr)_3]_2$, has been synthesised [4]. Therefore, it might be reasonable to assume that the C_5H_5 groups in (II) behave as bridging allyl groups. The reactions of (II) with other compounds are under investigation.

References

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4 H. Felkin and G. K. Turner, *J. Organometal. Chem., 129,* 429 (1977).