

DI- $\mu$ -CHLORO-DICHLOROBIS(DI-t-BUTYLACETYLENE)DIPALLADIUM AND RELATED  
COMPLEX

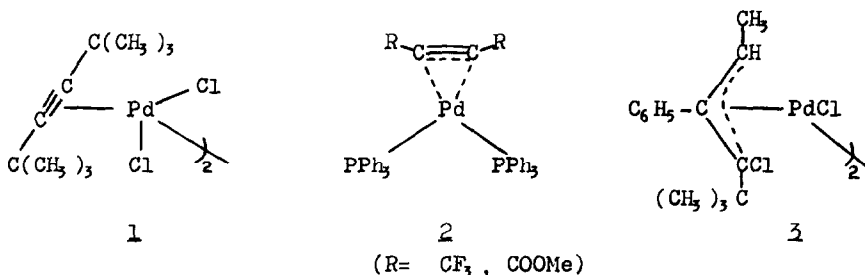
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In a previous communication,<sup>1)</sup> we have reported the synthesis of 1,2-di-t-butyl substituted cyclobutadiene palladium chloride complex from the reaction of t-butylphenylacetylene with dichlorobis(benzonitrile)palladium. We wish to report here the synthesis of a new stable acetylene palladium complex (1), i.e., di- $\mu$ -chloro-dichlorobis(di-t-butylacetylene)dipalladium(II).

Although  $\pi$ -complexes of platinum with acetylenes can be readily obtained from the direct displacement of ethylene in ethyleneplatinous chloride by acetylenes bearing bulky substituents,<sup>2,3)</sup> such a palladium complex of type 1 has not yet been known.\* Only a few example of palladium complexes with acetylenes known, are those of a monomeric type 2.<sup>4)</sup> Then we have attempted to prepare such complexes of type 1 by the displacement reaction of the ethylene in  $((C_2H_4)_2PdCl_2)_2$  by similar acetylenes. In the case of di-t-butylacetylene, the complex 1 was



\*<sub>1</sub> Although A. V. Babaeva et al.<sup>5)</sup> have briefly reported the complexes formed from 2,5-dimethylhexa-2,5-diol and palladium(II) salts, these structures have not been clarified.

successfully prepared by this reaction. In contrast, with *t*-butylphenylacetylene, the complex **2** but not **1** has been obtained via the insertion of that acetylene into a Pd-Cl bond.

Thus, to a solution of  $((C_2H_5)_2PdCl_2)_2$  (0.41 g, 1 mmole) in benzene (25 ml) was added di-*t*-butylacetylene (0.32 g, 2 mmoles). After stirring for 1 hr at room temperature, ethylene gas evolution was completed. After evaporation of the solvent, there were obtained red needles (**1**, 0.16 g, 0.26 mmole, mp 164-165° (decomp), 26 % yield) which was recrystallized from benzene-petroleum ether. When  $(PhCN)PdCl_2$  was employed instead of  $((C_2H_5)_2PdCl_2)_2$ , the same complex was also obtained in a rather lower yield. Elemental analysis and molecular weight determination showed that **1** has a formula of  $(C_{10}H_{18}PdCl_2)_2$ . The nmr spectrum of **1** (in  $CDCl_3$ ) exhibited only a sharp singlet at 8.41  $\tau$  due to *t*-butyl groups.

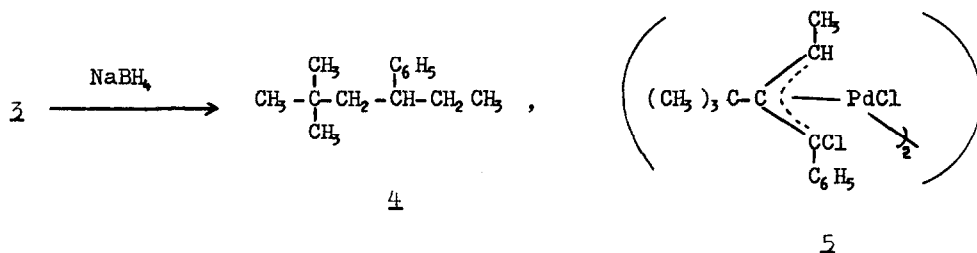
Now, the ir spectra of  $\pi$ -complexes of platinum (type **1**) are reported to show a band usually at around  $2000\text{ cm}^{-1}$ , assigned to the acetylenic  $C\equiv C$  stretching frequency, which has been reduced by  $\sim 250\text{ cm}^{-1}$  compared with that in free acetylenes,<sup>2)</sup> whereas this band is greatly lowered by  $\sim 500\text{ cm}^{-1}$  in platinum<sup>6)</sup> or palladium<sup>4)</sup> of the type **2**. In the present complex **1**, the absorption of the coordinated  $C\equiv C$  triple bond was exhibited at  $2050\text{ cm}^{-1}$ ,\*<sub>2</sub> indicating clearly that **1** is the  $\pi$ -complex of palladium.

Then, preparation of the type **1** complex of *t*-butylphenylacetylene was attempted. Unexpectedly, the acetylene did not afford the type **1** complex, but resulted in the insertion into a Pd-Cl bond. To the solution of  $((C_2H_5)_2PdCl_2)_2$  (0.41 g, 1 mmole) in benzene (25 ml) was added *t*-butylphenylacetylene (0.32 g, 2 mmoles). The mixture was stirred for 1 hr at room temperature and after work-up as usual manner, there was obtained the yellow stable complex (**2**, 0.19 g, 0.27 mmole, mp 195-196.5° (decomp)). No ethylene gas evolution was observed in this reaction and hence ethylene can be considered to be incorporated in complex **2**. In fact, elemental analysis and molecular weight determination of **2** showed a formula of  $(C_{14}H_{18}PdCl_2)_2$ , indicating that **2** is a 1 : 1 adduct of *t*-butylphenylacetylene and  $((C_2H_5)_2PdCl_2)_2$ . The nmr spectrum of **2** (in  $CDCl_3$ ) also exhibited the presence of

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\*<sub>2</sub> Increased frequency of  $C\equiv C$  bond of complex **1** compared with platinum complex<sup>2)</sup> would show that the M-C bond is weaker than platinum analogous. This is in accord with the stability of **1**; namely, **1** is stable in the solid state but decomposes slowly in solution, whereas platinum complex is stable in both states.

$-\overset{1}{\text{C}}\text{HCH}_3$  group which was derived from the hydrogen shift from  $\text{C}_1$  to  $\text{C}_2$  at ethylene; a quartet at  $4.62\tau$  ( $J=6$  Hz) and a doublet at  $9.03\tau$  in a ratio of 1 : 3, besides the signals due to phenyl group ( $2.55\tau$ - $2.78\tau$ ) and *t*-butyl ( $8.75\tau$ ). The complex showed the ir absorption at  $650\text{ cm}^{-1}$  (C-Cl) and bands at  $278\text{ cm}^{-1}$  and  $222\text{ cm}^{-1}$ , arised from an asymmetrical  $\text{PdCl}_2\text{Pd}$  bridge,<sup>7)</sup> were observed. From these results, we assigned the complex  $\underline{3}$  as 1-methyl-2-phenyl-3-chloro-3-*t*-butyl- $\pi$ -allyl palladium chloride ( $\underline{3}$ ).<sup>\*3</sup> Another isomeric structure  $\underline{5}$  of  $\underline{3}$  can be eliminated by the production of 2,2-dimethyl-4-phenylhexane ( $\underline{4}$ , bp  $110$ - $112^\circ/2$  mmHg) on  $\text{NaBH}_4$  reduction of  $\underline{3}$ . The structure of  $\underline{4}$  was deduced from elemental analysis and spectroscopic properties.



An interesting feature in this case is that ethylene ligand reacts with acetylene forming a C-C bond in  $\underline{3}$  without releasing ethylene as in the former reaction. The scope of these reactions is required further investigations.

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\*3 Although a  $\sigma$ - $\pi$  structure is also considered for  $\underline{3}$ , it can be eliminated because of its unstability.

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