Tetrahedron Letters No.35, pp. 3021-3024, 1969. Pergamon Press. Printed in Great Britain.

1,2-DI-t-BUTYL-3,4-DIPHENYLCYCLOBUTADIENE PALLADIUM CHLORIDE COMPLEX*

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(Received in Japan 13 June 1969; received in UK for publication 23 June 1969)

We wish to report the synthesis of a new cyclobutadiene complex, i.e. 1,2-di-t-butyl-3,4-diphenylcyclobutadiene palladium chloride complex, by the reaction of t-butylphenylacetylene with dichlorobis(benzonitrile)palladium. This is a first example of the cyclobutadiene complex substituted by two t-butyl group in 1,2-position.

Although the syntheses of some tetra-aryl substituted cyclobutadiene palladium chloride complexes have been accomplished by the reaction of diarylacetylene with $(PhCN)_2PdCl_2$,(1-3) the application of this reaction to monoarylacetylenes or alkynes usually results in the formations of trimer and oligomers.(4,5) However, an introduction of a bulky t-butyl group into monoarylacetylene hindered the oligomerization, and the dimer complex was successfully prepared by this reaction.

A solution of t-butylphenylacetylene (0.51 g, 3.2 mmoles) and $(PhCN)_2PdCl_2$ (1.19 g, 3.2 mmoles) in benzene (50 ml) was stirred for four hours at a room temperature. There was obtained reddish brown precipitates (complex A, 0.62 g, mp 250°(decomp)) but it was hardly purified by the recrystallization because of its low solubilities in various organic solvents. After several reprecipitations, the complex A showed approximate composition of $C_6H_5C{\equiv}C(CH_3)_3 \cdot PdCl_2$. The fact that the complex A contains the cyclobutenyl residue is indicated by

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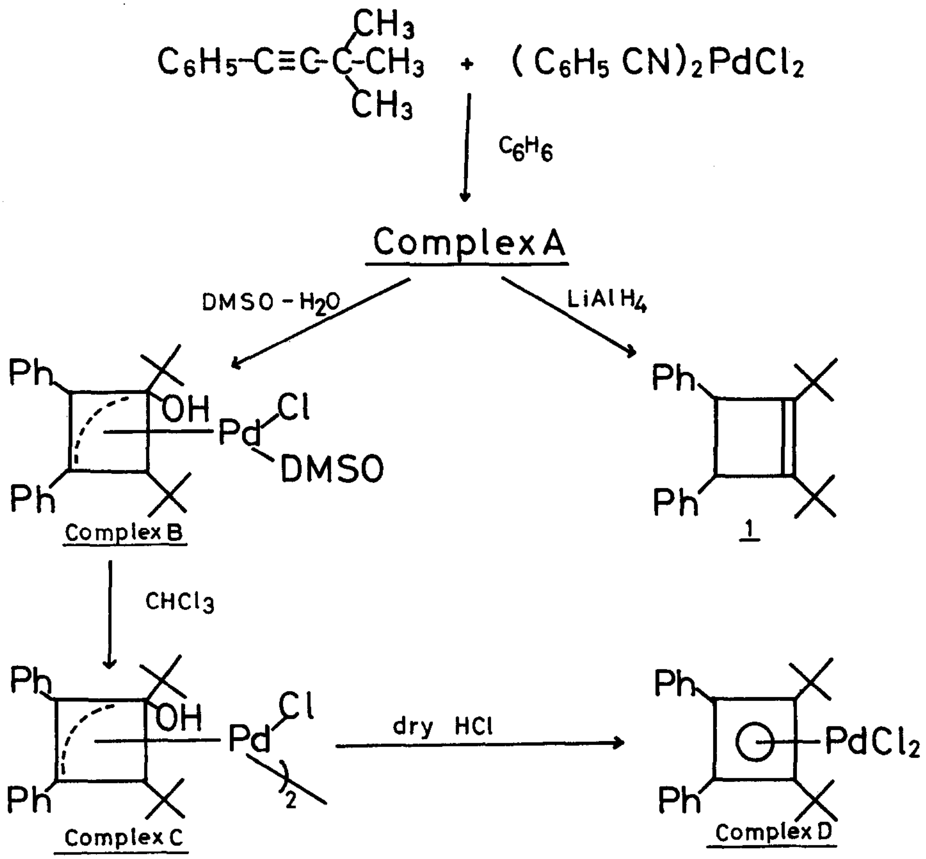
* All new compounds described in the present letter showed satisfactory results on the elemental analyses and molecular weight determinations. Melting points are uncorrected.

the production of 1,2-di-t-butyl-3,4-diphenylcyclobut-1-ene (1), mp 76-78°, on $LiAlH_4$ reduction of A.

The symmetrical and non-conjugated structure for 1 was deduced from nmr, uv, and ir spectra. In the nmr spectrum, it exhibited only one kind of tertiary protons (5.52τ, 2H) and one kind of t-butyl protons (8.48τ, 18H) besides aromatic protons (3.26τ, 10H). This fact indicates that two tertiary protons locate at the closely similar position and the same is also true for two t-butyl groups. This is only in accord with the structure 1. Moreover, the position of the tertiary proton (5.52τ) is very similar to that of 1,2,3,4-tetraphenylcyclobut-1-ene (5.38τ)(6) supporting that the tertiary protons in 1 are in the benzylic position. The compound 1 decolorized the testing solutions of bromine in carbon tetrachloride and potassium permanganate in water, but its stretching vibration was practically absent in the ir spectrum. This inactive C=C stretching is also an indication of the symmetrical structure for 1. The uv spectrum (in ethanol) showed maxima at 212 mμ (logε. 4.46), 243 mμ (3.38), 248 mμ (3.41), 255 mμ (3.45), and 261 mμ (3.39). This is apparently not the spectrum expected from the cis-stilbene structure and hence it can be concluded that the double bond in 1 should be between two carbon atoms substituted by the t-butyl group.

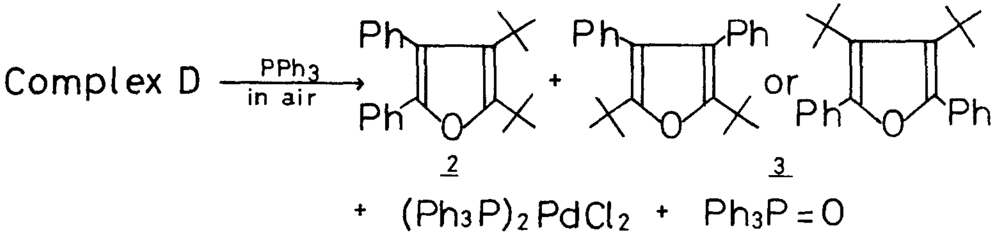
Now, when the complex A (0.50 g) was dissolved in 98 % aqueous dimethyl sulfoxide (15 ml) at a room temperature, the yellow crystalline material precipitated instantaneously (complex B, 0.15 g, mp 153-155° (decomp)). In this new complex, a notable facts are the inequivalency of two t-butyl groups (nmr in $CDCl_3$ at 8.70τ and 9.01τ) and the existences of a DMSO residue and a hydroxyl group. A dissolution of B (0.43 g, 0.78 mmole) into chloroform resulted in the quantitative conversion to a new yellow complex C (0.37 g, 0.39 mmole, mp 185-186° (decomp)) in that DMSO was no more present and the complex was stabilized by a dimerization (molecular weight). Two t-butyl groups in the complex C are found to be inequivalent again. All of available data indicate that the organic ligand in the complex B and C is 1,2-diphenyl-3,4-t-butyl-4-hydroxy-π-cyclobutenyl. This is also consistent with the very similar uv pattern of C (uv maxima in CH_2Cl_2 , 242 mμ (logε. 4.56) and 278 mμ (4.42)) to that of endo-



4-ethoxy-π-1,2,3,4-tetraphenylcyclobutenyl palladium chloride dimer (uv maxima in CH_2Cl_2 , 242 mμ (logε. 4.62) and 280 mμ (4.55)).(1,8)

The treatment of the yellow complex C (0.33 g, 0.35 mmole) with dry hydrogen chloride(1) gave orange-yellow crystalline complex D (0.31 g, 0.31 mmole, mp 245-246° (decomp)). This complex D exhibited all of the features as the cyclobutadiene complex. The elemental analysis and molecular weight determination indicated that the complex D was 1,2-di-t-butyl-3,4-diphenylcyclobutadiene palladium chloride complex. Two t-butyl groups in D are taking the equivalent position as indicated by a single t-butyl signal in the nmr (8.38τ). The remaining signal (2.13-2.76τ) is due to the phenyl groups and the ratio of two signals is 18 : 10. The absence of the hydroxy group in D is evident from its ir and nmr spectra. The cyclobutadiene structure for D is most strongly supported by its uv spectrum; the uv maxima were found at considerably longer wave length than those of the complex B and C. They were at 246 mμ (logε. 4.16), 287 mμ (4.07), 310 mμ^{sh}(3.99), and 356 mμ (3.77), and these were quite similar to those of 1,2,3,4-tetraphenylcyclobutadiene palladium chloride.(9)

The structure of D was confirmed further by its reaction with triphenylphosphine. The reaction of the complex D (0.34 g, 0.68 mmole) with PPh_3 (0.71 g, 2.72 mmoles) in CH_2Cl_2 gave 1,2-diphenyl-3,4-di-t-butylfuran (2, mp 121°), its isomer 3 (3, mp 162-164°), dichlorobis(triphenylphosphine)palladium, and triphenylphosphine oxide. The structure of 2 and 3 were deduced from the analytical and spectroscopic data.*



In conclusion, the reaction of t-butylphenylacetylene with $(PhCN)_2PdCl_2$ produced the dimer complex from which a new cyclobutadiene palladium complex was synthesized. The present preparation also opens a rout to prepare the furan derivatives substituted by two bulky groups in 1,2-position.

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* The nmr spectra tell that two phenyl groups and two t-butyls are both inequivalent in 2 (four singlets at 2.69τ, 3.02τ, 8.84τ, and 8.81τ in a ratio of 5:5:9:9), but they are equivalent in 3 (two singlets at 3.07τ and 8.84τ in a ratio of 10:18). However the spectral data could not allow to decide the positions of the substituents in 3. The combined yield of 2 and 3 was 26.4 %.

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