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PREPARATION OF A NOVEL DINUCLEAR COMPLEX OF PALLADIUM BRIDGED BY DIANION OF DIACETONE ALCOHOL

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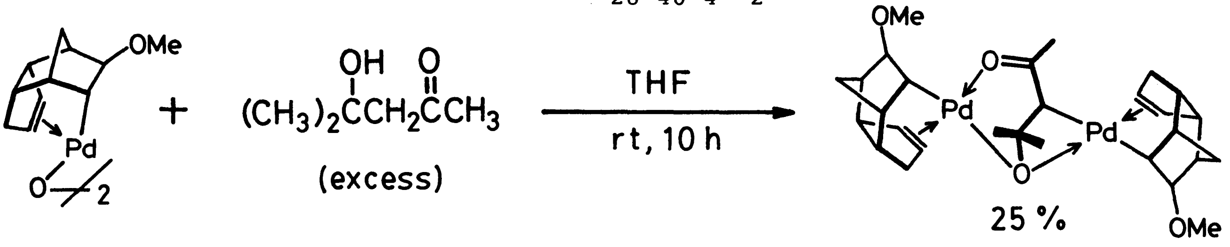
Novel dinuclear complex of palladium coordinating dianion of diacetone alcohol is prepared by the reaction of a μ-peroxo complex of palladium with acetone or diacetone alcohol. Coordination of the dianion of diacetone alcohol is confirmed by means of X-ray structural analysis.

In the preceding paper, we demonstrated that the dioxygen ligand in the μ-peroxo complexes of palladium, platinum, and rhodium served as a base in the reaction with alcohols, amines, thiols, and active methylene compounds.[1] We describe herein the preparation and the structure of dinuclear palladium complex bridged by the dianion of diacetone alcohol.

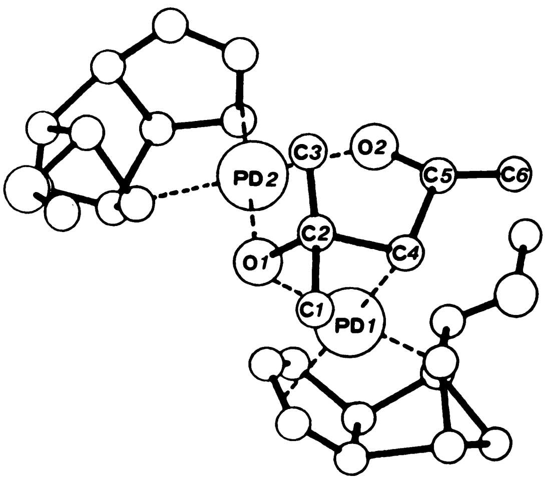
Treatment of previously reported μ-peroxobis(8-*exo*-methoxytricyclo[5.2.1.0^{2,6}]-dec-3-en-9-yl)dipalladium (1)[1] (0.27 g, 0.5 mmol) with diacetone alcohol (0.65 g, 6 mmol) in 10 ml of dry tetrahydrofuran at room temperature for 10 h gave a yellowish orange solution. The solvent and excess diacetone alcohol were removed by bulb-to-bulb distillation. To the bright yellow solid left in the distilling flask was added 5 ml of dry *n*-pentane. Resulting solution was filtered, and concentration of the filtrate followed by standing at 0°C for a week yielded 2 (81 mg, 25% yield based on 1) as orange prisms. 2: dec. >80°C. ^{1}H-NMR (CCl_4-TMS; ppm) δ1.50 (1H, s), 1.53 (3H, s), 1.59 (3H, s), 1.92 (3H, s). IR (KBr; cm^{-1}) 1510~1485 (broad peak centered at 1492 cm^{-1}, νC=O), 1084 (νC-O). Elemental analysis was also well consistent with the composition of $C_{28}H_{40}O_4Pd_2$.



1 2

The same complex was prepared in 4.4% yield together with the formation of diacetone alcohol by the reaction of μ-peroxo complex 1 with a large excess (133 equiv) of acetone in dry diisopropyl ether at ambient temperature.

Preliminary result of X-ray structural analysis illustrated in Fig. 1 indicates that coordination planes around two palladium atoms are essentially square planar, and are nearly perpendicular. Pd(1)-C(4) and Pd(2)-O(1) bond lengths (2.07 and 2.00 Å each) suggest that they are both σ-bonds. Upfield shift of ^{1}H-NMR signal of the proton bonded to C(4) (δ1.50 ppm) is well consistent with the structure established by X-ray analysis. The C(5)=O(2) bond length of 1.28 Å together with its stretching vibration of 1510-1485 cm^{-1} also suggests strong coordination of the carbonyl oxygen to one of the palladium center. From these results, it is considered that the bridging ligand, the dianion of diacetone alcohol, is stabilized by two cationic center of palladium.

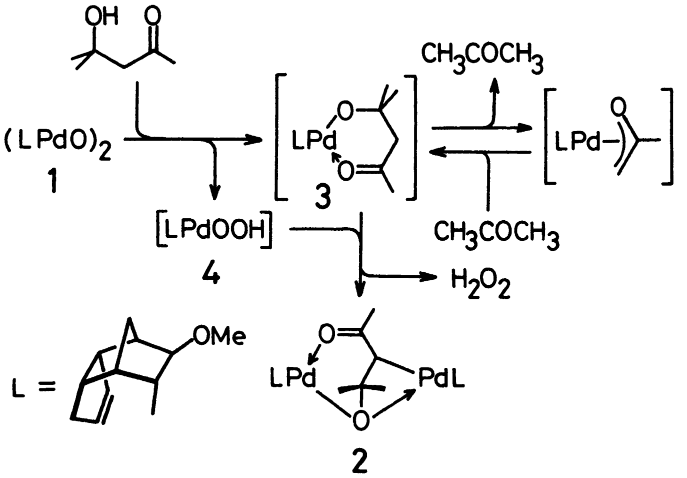


Bond Length (Å)		Bond Angle (deg.)	
Pd1-O1	2.18	O1-Pd1-C4	71
Pd1-C4	2.07	O1-Pd2-O2	91
Pd2-O1	2.00	O2-C5-C4	123
Pd2-O2	2.15	O2-C5-C6	116
O2-C5	1.28	C4-C5-C6	121
C4-C5	1.43		

Figure 1. A perspective drawing of the complex 2. Selected bond lengths and angles are listed.

Formation of the complex 2 is reasonably explained by the mechanism outlined in Scheme 1. Abstraction of a proton from diacetone alcohol by the coordinated dioxygen would give intermediary 2-oxo-4,4-dimethylbutoxopalladium (3) accompanied by the formation of palladium hydroperoxo species 4,[2] which would successively abstract proton from 2-oxo-4,4-dimethylbutoxo ligand of 3 to give the dinuclear complex 2.

Scheme 1



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