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PREPARATION AND REACTIONS OF NEW DIOXYGEN BRIDGED COMPLEXES OF PALLADIUM

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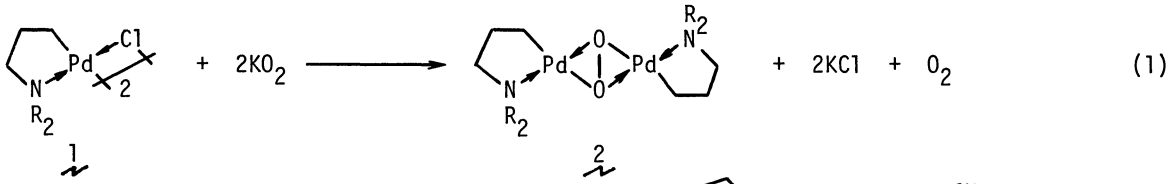
New dioxygen bridged complexes of palladium were prepared by the anion exchange reaction using superoxide ion as dioxygen source. Dioxygen is coordinated as O_2^{2-} in the complexes and reacts with alcohols, acids and various active methylene compounds to give the corresponding palladium complexes and hydrogen peroxide.

Since the dioxygen complex of a cobalt Schiff base was first discovered by Tsumaki in 1938,[1] various types of dioxygen complexes have been prepared involving almost all kinds of transition metal elements. Dioxygen bridged complex, $M\overset{O}{\underset{O}{\diagdown\diagup}}M$ is one of the most popular one, whereas metal element for the complex is mainly restricted to cobalt and dioxygen complexes of this type including other transition metal elements are rather exceptional.[2] Recently, we reported a novel preparation method of dioxygen complexes where superoxide ion was utilized as dioxygen source instead of molecular oxygen.[3] We report here application of the method to formation of palladium amine complexes where dioxygen serves as a bridging ligand and reactions of new dioxygen complexes with various reagents.



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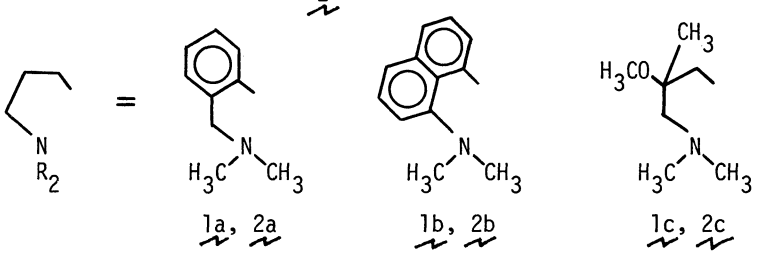

Preparation of dioxygen complexes 2 was carried out by an anion exchange reaction (eq. 1). Binuclear amine complexes of palladium 1[4] were treated by excess amount of potassium superoxide in dry CH_2Cl_2 under nitrogen pressure. The reaction proceeded at room temperature accompanying oxygen evolution[5] and gave the corresponding dioxygen complexes 2 quantitatively.[6] Recrystallization from benzene-ether/pentane afforded yellowish micro prisms which are quite stable for months under dry conditions at room temperature.[7]

Reactions of the complexes 2 with various reagents were examined in order to clarify the nature of the coordinated dioxygen. Treatment of a solution of 2 (a, b and c) in benzene by water (2N, KOH), MeOH and acetic acid at room temperature gave hydrogen peroxide and the corresponding OR^- bridged complexes 3, 4, and 5, respectively. 2 reacts also with salicylaldehyde and 8-hydroxy quinoline to afford mononuclear complexes 6 and 7. Acetylacetone and dimethylmalonate gave mononuclear complexes 8 and 9 in the similar manner. On the contrary, no reactions were observed between the complexes 2 and C-C unsaturations. All these results suggest that dioxygen is coordinated as O_2^{2-}

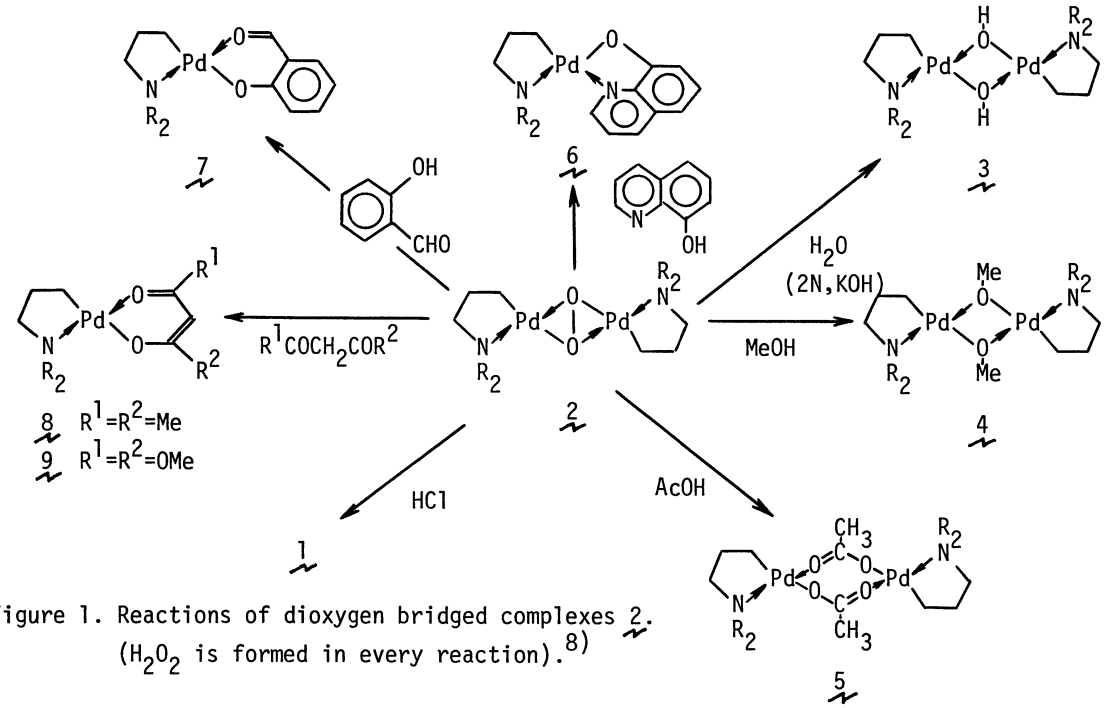

Figure 1. Reactions of dioxygen bridged complexes 2. (H_2O_2 is formed in every reaction).[8]

in the complexes and behaves as a strong base. Fortunately, the complexes 2a and 2c form single crystals suitable for the X-ray analysis which is now in progress.

References and notes

1) T. Tsumaki, Bull. Chem. Soc. Japan, 13, 252 (1938).

2) V. J. Choy and C. J. O'Conner, Coord. Chem. Rev., 9, 145 (1972); J. Valentine, Chem. Rev., 73, 235 (1973); G. Henrici-Olive and S. Olive, Angew. Chem. Int. Ed. Engl., 13, 29 (1974); L. Vaska, Acc. Chem. Res., 9, 175 (1976).

3) H. Suzuki, K. Mizutani, Y. Moro-oka, and T. Ikawa, J. Am. Chem. Soc., 101, 748 (1979).

4) The starting complexes 1 were prepared by the method reported by A. C. Cope, J. M. Kliegman, and C. Friedrich, J. Am. Chem. Soc., 89, 287 (1967); ibid., 90, 909 (1968).

5) Evolution of O_2 was measured by volumetry and confirmed by gas chromatography.

6) The typical procedure for the preparation of dioxygen complexes 2 is as follows. To a suspension of excess amount of finely powdered KO_2 (10.7 mmol, 5.3 equiv.) in CH_2Cl_2 (10ml) was added a solution of 1a (1.0 mmol in 30ml CH_2Cl_2) at -78°C and the resulting mixture was allowed to warm to room temperature. Evolution of oxygen was observed and the mixture was stirred for more 24 hr under dry nitrogen pressure. KCl and excess KO_2 were removed by filtration and evaporation of solvent remained a crude product as yellow powder. Recrystallization from benzene-n-hexane (1 : 1) gave 2a as yellowish needles (yield 76%).

7) 2a; yellow needles. mp 188-190° (dec). NMR($CDCl_3$) δ 2.59(12H,s), 3.60(4H,s), 6.7-7.2(8H,m). Anal: Calcd for $C_{18}H_{24}N_2O_2Pd_2$; C, 42.12; H, 4.68; N, 5.46. Found; C, 42.43; H, 5.07; N, 5.19. Mw (cryoscopy in benzene): Calcd 512.8, Found 530. 2b; yellow powder. mp >195° (dec). NMR ($CDCl_3$) δ 3.25(12H,s), 6.8-7.7(12H,m). Anal: Calcd for $C_{24}H_{24}N_2O_2Pd_2$; C, 49.25; H, 4.10; N, 4.79. Found; C, 49.83; H, 4.49; N, 4.45. Mw: Calcd 584.8, Found 536. 2c; yellow needles. mp 125-126° (dec). NMR($CDCl_3$) δ 1.15(6H,s), 1.95(4H,s), 2.52(4H,s), 2.60(6H,s), 2.85(6H,s), 3.25(3H,s). Anal: Calcd for $C_{14}H_{32}N_2O_2Pd_2$; C, 33.28; H, 6.34; N, 5.55. Found; C, 32.32; H, 6.68; N, 5.23%. Mw: Calcd 504.8, Found 480.

8) Analytical and spectral data for the complexes 1 and 3~9 are satisfactory. Formation of hydrogen peroxide was confirmed by iodometry.

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