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Reaction of μ-Peroxo Complexes of Palladium with Alcohols, Amines, and Thiols

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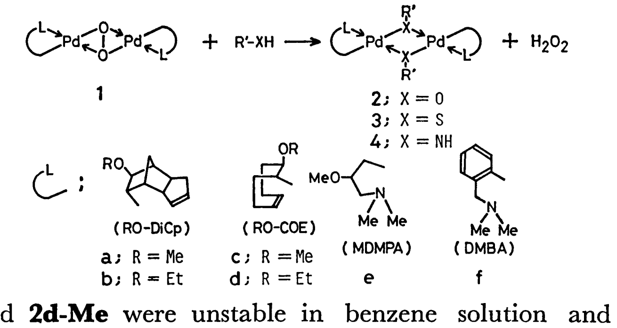
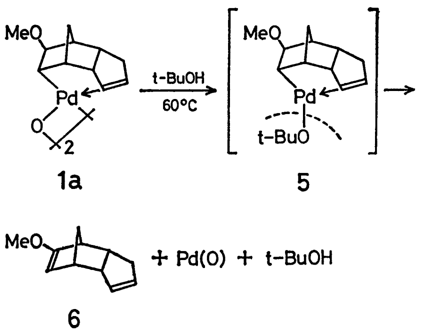
Synopsis. Reactions of μ-peroxo complexes of palladium with alcohols, amines, and thiols proceed at room temperature to afford hydrogen peroxide and alkoxo-, amido-, and alkylthio-bridged complexes of palladium, respectively.

In the previous papers we reported a novel preparation method of μ-peroxo complexes of palladium, platinum and rhodium having olefinic ligands *via* an anion exchange reaction of μ,μ'-dihalo complexes with potassium superoxide in dichloromethane and suggested that μ-peroxo ligand in the complexes behaved as a base and did not participate in the oxygenation of the olefinic ligands.[1-3] Such basic nature of dioxygen ligands was also reported for the mononuclear peroxo complexes of transition metal elements.[4-6] Important role of the basic nature of the coordinated dioxygen of the cobalt Schiff base complex was demonstrated by Nishinaga *et al.* in the catalytic oxidation of substituted phenols.[7] In the present investigation, reactions of μ-peroxo ligand with a series of alcohols, amines, and thiols have been examined in order to clarify the nature of μ-peroxo complexes of palladium.

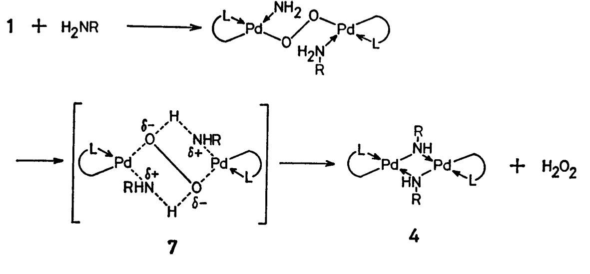
Results and Discussion

Reactions of dioxygen complexes **1** with alcohols, thiols and amines were carried out in dry benzene at room temperature under dry nitrogen atmosphere. Treatment of **1a** with methanol gave μ,μ'-bis(methoxo) complex **2a-Me** in a 50% yield accompained with liberation of hydrogen peroxide. Formation of hydrogen peroxide was confirmed by the iodometry. Methoxy-bridged complex **2d-Me** was prepared in a similar manner. Methoxy-bridged complexes **2a-Me** and **2d-Me** were unstable in benzene solution and decomposed immediately with heating at 30—40 °C to deposit metallic palladium. Even in the solid state, they decomposed after standing for one day at ambient temperature under dry nitrogen atmosphere. Ethoxy-bridged complexes **2a-Et** and **2c-Et** were also prepared by the reaction of **1** with ethanol. It was found that they were less stable than the corresponding methoxy-bridged ones. Further attempts to prepare the alkoxy-bridged complexes of bulky alcohols were resulted in vain. The starting μ-peroxo complex was recovered in the reaction of **1a** with 2-propanol (pK_a 18) or *t*-butyl alcohol (pK_a 19) at room temperature. Decomposition of complex **1a** in *t*-butyl alcohol proceeded giving a cyclic diene **6** at higher reaction temperatures (40—60 °C). Abstraction of proton from such alcohols is well supported by the fact that **1a** is basic enough to abstract active hydrogen from acetone (pK_a 20). Steric repulsion between Me-DiCp ligand and bulky alkoxo groups may force the β-elimination of Pd–H from a coordinatively unsaturated intermediate **5**. Yoshida *et al.* reported that treatment of $[\mathrm{Ni(CCl{=}CCl_2)(\mu\text{-}OMe)(PPh_3)}]_2$ in alkaline solution gave $[\mathrm{Ni(CCl{=}CCl_2)(\mu\text{-}OH)(PPh_3)}]_2$ *via* an anion exchange reaction.[8] In the present work, the bridging methoxy group was readily exchanged with ethoxy group by treatment of **2a-Me** with a large excess of ethanol in benzene at room temperature, and *vice versa.*





μ-Peroxo complexes also reacted with thiols to yield the corresponding alkylthio-bridged complexes. Alkylthio-bridged complex **3a-Et** was obtained by the dropwise addition of a diluted solution of ethanethiol to a rigorously stirred solution of **1a** in benzene. Analogous alkylthio complex **3e-Et** and phenylthio-bridged complexes **3a-Ph** and **3f-Ph** were prepared similarly. All these alkylthio-bridged complexes were stable sufficiently so that decomposition was not observed after standing for several months without special care. The reaction of the μ-peroxo complexes with benzylamine or acrylamide also gave the corresponding amido-bridged complex **4** and hydrogen peroxide at room temperature. A similar reaction of mononuclear peroxo complex of platinum with phenylenediamine was previously studied by Pizzotti *et al.* and they reported that the reaction afforded an amido complex with hydrogen peroxide.[9] Since an ordinary μ-peroxo complex does not react with compounds hav-



Scheme 1.

TABLE 1. REACTIONS OF DIOXYGEN COMPLEXES **1** WITH ALCOHOLS, THIOLS, AND AMINES

Dioxygen complex	RXH (X=O, S, NH)	Product[a)]	Yield %	Mp °C	Found (Calcd) (%) C	H	N	S
[(MeO-DiCp)PdO]$_2$	MeOH	[(MeO-DiCp)PdOMe]$_2$	50	155	47.81 (47.94)	6.02 (6.03)		
[(MeO-DiCp)PdO]$_2$	EtOH	[(MeO-DiCp)PdOEt]$_2$	28	180	49.76 (49.76)	6.21 (6.37)		
[(MeO-COE)PdO]$_2$	EtOH	[(MeO-COE)PdOEt]$_2$	81	130	45.83 (45.45)	7.19 (6.94)		
[(EtO-COE)PdO]$_2$	MeOH	[(EtO-COE)PdOMe]$_2$	47	140	45.07 (45.45)	7.15 (6.94)		
[(MeO-DiCp)PdO$_2$	EtSH	[(MeO-DiCp)PdSEt]$_2$	58	114	47.45 (47.21)	6.22 (6.09)		8.35 (9.69)
[(MeO-DiCP)PdO]$_2$	PhSH	[(MeO-DiCp)PdSPh]$_2$	41	105	50.71 (50.78)	5.70 (5.68)		8.80 (9.04)
[(DMBA)PdO]$_2$	EtSH	[(DMBA)PdSEt]$_2$	22	161—163	42.90 (43.79)	5.50 (5.68)	4.42 (4.46)	11.42 (10.63)
[(MDMPA)PdO]$_2$	PhSH	[(MDMPA)PdSPh]$_2$	66	197—203	51.33 (51.51)	4.40 (4.90)	3.67 (4.00)	8.80 (9.17)
[(MeO-COE)PdO]$_2$	$PhCH_2NH_2$	[(MeO-COE)PdNHCH$_2$Ph]$_2$	67	135	53.81 (54.63)	6.06 (6.59)	4.61 (3.98)	
[(MeO-COE)PdO]$_2$	CH_2=CHCONH$_2$	[(MeO-COE)Pd(CH$_2$=CHCONH)]$_2$	64	62	45.26 (45.66)	6.24 (6.07)	4.10 (4.40)	

a) For all products, satisfactory ^{1}H-NMR and IR spectra were obtained.

ing pK_a values higher than 20, the reaction observed in this strudy is not explicable by the direct interaction of the coordinated dioxygen with amines. A zwitter ionic transition state **7** resulted from the coordination of amine to the μ-peroxo complex may assist the abstraction of proton to form amido-bridged complex **4** and hydrogen peroxide.

Experimental

General. All reactions were run under a pressure of dry nitrogen. ^{1}H-NMR spectra were determined in $CDCl_3$ on a Hitachi R-24B instrument. Chemical shifts are reported in the δ unit, parts per million (ppm) downfield from tetramethylsilane and coupling constants are reported in hertz. Melting points were obtained on a Yanagimoto MP-apparatus and are uncorrected.

Diethyl ether and benzene for the solvent were distilled from sodium benzophenone ketyl. Pentane was distilled from sodium. Dichloromethane was purified by washing with water and dried over calcium hydride and then distilled from phosphorous pentoxide under a pressure of dry nitrogen. Methanol and ethanol were distilled from magnesium turnings. Isopropanol and *t*-butyl alcohol were dried over molecular sieve 3A and distilled prior to use. Benzylamine was dried over potassium hydroxide pellets. Acrylamide, ethanethiol, and thiophenol were used without further purification. Dioxygen complexes (**1a**—**f**) were prepared according to the procedure reported previously.[1—3)]

*Reaction of **1a** with Methanol.* To a solution of 0.176 g (0.38 mmol) of **1a** in 5 cm^3 of dry benzene was added 0.2 cm^3 of dry methanol followed by 3 cm^3 of dry diethyl ether at room temperature. The solution was stirred for a few minutes and was allowed to stand for 20 h in a refrigerator. Pale yellow prisms precipitated in the solution were collected by suction and washed with dry pentane, then dried *in vacuo* to give 0.115 g (50%) of di-μ-methoxybis(8-*exo*-methoxytricyclo[5.2.1.0^{2,6}]dec-3-en-9-yl)dipalladium. Mp (dec.) 155 °C; IR (KBr) ν(C–O) 1082, 1053 (bridging) cm^{-1}; NMR ($CDCl_3$) δ 3.18 (6H, s, OCH_3), 3.40 (6H, s, OCH_3), 5.16 (2H, m, olefinic), 5.63 (2H, m, olefinic); Mol wt (cryoscopy in benzene) calcd 600.8, found 645.

In a similar procedure, alkoxo-bridged complexes were prepared and characterized. Yields, mps, and results of elemental analyses are summarized in Table 1.

*Reaction of **1a** with Ethanethiol.* To a suspension of 0.329 g (0.58 mmol) of **1a** in 25 cm^3 of dry diethyl ether was added dropwise 1.63 cm^3 of a solution of ethanethiol in benzene (0.7 mmol/cm^3). The solution was stirred for 6 h at room temperature. The resulting orange solution was filtered and filtrate was dried in vacuo to give red powder. Recrystallization from a mixed solvent of benzene, diethyl ether and pentane (1:1:1 vol ratio) gave di-μ-ethylthiobis(8-*exo*-methoxytricyclo[5.2.1.0^{2,6}]dec-3-en-9-yl)dipalladium (**3a-Et**) as yellowish orange prisms (0.259 g, 58%). Mp (dec.) 114 °C; IR (KBr) ν(C–S) 1250, ν(C–O) 1080 cm^{-1}; NMR ($CDCl_3$) δ 1.41 (6H, t, J=7, S-CH$_2$-$\underline{H_3}$), 2.53 (4H, q, J=7, S-C$\underline{H_2}$-), 3.26 (6H, s, OCH_3), 5.87 (2H, m, olefinic), 6.35 (2H, m, olefinic).

*Reaction of **1c** with Benzylamine.* To a suspension of 0.174 g (0.33 mmol) of **1c** in 25 cm^3 of dry diethyl ether was added slowly 1.4 cm^3 of a solution of benzylamine in benzene (0.47 mmol/cm^3). The solution was stirred for 10 h at ambient temperature. The resulting yellow solution was filtered and the filtrate was concentrated under a reduced pressure. Addition of dry pentane and storage in a refrigerator for 40 h yielded di-μ-benzylaminobis(8-*exo*-methoxy-4-cyclooctenyl)dipalladium (**4c-Bz**) as pale yellow precipitates (0.152 g, 67%). Mp (dec.) 135 °C; IR (KBr) ν(N–H) 3450, ν(C–O) 1090 cm^{-1}. NMR ($CDCl_3$) δ 3.10 (3H, s, OCH_3), 4.13 (2H, d, Ph-C$\underline{H_2}$-), 5.25 (2H, br, olefinic), 7.0—7.5 (5H, aromatic). Mol wt (cryoscopy in benzene) Calcd 702.8; Found 714.

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