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Reaction of Dioxygen Complexes with Catechols

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Synopsis. The square planar dioxygen complexes $MO_2(PPh_3)_2$($M=Pt$, Pd) reacted with catechols at low temperature to give H_2O_2 and the corresponding catecholato complexes, characterized by their physical properties, in high yields. A similar treatment of $PtO_2(PPh_3)_2$ with *o*-substituted anilines afforded the corresponding adducts and H_2O_2 in moderate yields.

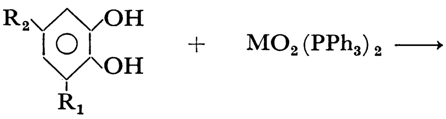
A number of reports have appeared on the formation of catecholato complexes by oxidative addition of *o*-quinones to metal complexes having mainly d^6, d^8, and d^{10} electron configurations.[1-7] We have found that these complexes can also be obtained in high yields by an other route. In this paper we deal with the reaction of dioxygen complexes with catechols which results in the selective formation of catecholato complexes and H_2O_2. The reactivity of dioxygen complexes toward *o*-substituted anilines was also studied, the reactions of square planar dioxygen complexes $MO_2(PPh_3)_2$-($M=Pt$, Pd)[8-10] with catechlos being carried out in CH_2Cl_2 or CH_2Cl_2–EtOH(1 : 1 by volume) solvent at low temperature. Hydrogen peroxide formed during the course of reaction was transferred under vacuum (*ca.* 10^{-2} Torr) and then titrated by the conventional iodometric method. The transfer efficiency for H_2O_2 was about 98 percent.

TABLE 1. YIELD OF H_2O_2 AND CATECHOLATO COMPLEXES IN THE REACTION OF DIOXYGEN COMPLEXES WITH PHENOLS OR AROMATIC DIAMINES AT 2 °C[a)]

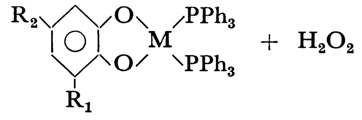
Dioxygen complex (1.97×10^{-2} M)	Phenol or diamine (8.25×10^{-2} M)	Yield(%)	
		H_2O_2	Catecholato complex
$PtO_2(PPh_3)_2$	**1a**[b)]	85.1	87.8
	1a[b)]	1.22[c)]	87.8
	1b	68.3	77.6
	1c	66.5	75.7
	o-Aminophenol	83.2	64.0
	o-Phenylenediamine	57.6	51.5
	Hydroquinone	5.34	
	p-Aminophenol	7.40	
	p-Phenylenediamine	—[d)]	
$PdO_2(PPh_3)_2$[e)]	**1a**	72.1	68.9
	1b	65.7	63.7
	1c	59.1	65.7
	o-Aminophenol	36.5	
	o-Phenylenediamine	3.58	
	p-Aminophenol	4.44	
	p-Phenylenediamine	—[d)]	

a) All the reactions were carried out in 4 ml of CH_2Cl_2-EtOH(1 : 1 by volume) under N_2 for 1 h. b) Reacted in 4 ml of CH_2Cl_2. c) Treated with catalase prior to titration. d) No peroxide was detected by iodometry. e) $[PdO_2(PPh_3)_2]$ was 1.68×10^{-2} M.

$PtO_2(PPh_3)_2$ reacted with catechol(**1a**), 4-*t*-butylcatechol(**1b**), and 3,5-di-*t*-butylcatechol(**1c**) under nitrogen atmosphere to give peroxide in 66—85% yields based on the dioxygen complexes (Table 1). The fact that the amount of peroxide formed considerably decreases by treatment with catalase prior to titration indicates that the peroxide transferred is principally H_2O_2. H_2O_2 was also obtained in moderate yields in the reaction of $PtO_2(PPh_3)_2$ with *o*-aminophenol and *o*-phenylenediamine. Similarly reaction of $PdO_2(PPh_3)_2$ with **1a**, **1b**, and **1c** gave H_2O_2 in 59—72% yields. No H_2O_2 is formed under N_2 in the absence of $MO_2(PPh_3)_2$. This suggests that the peroxide titrated was driven from the coordinated molecular oxygen of $MO_2(PPh_3)_2$. The yields of H_2O_2 obtained in the reactions of the dioxygen complexes with *p*-substituted phenols were much less than those obtained by use of the corresponding *o*-isomers. A possible explanation may beth at catechol dianions are suitable ligands for the formation of these complexes.



1a; $R_1=R_2=H$ $M=Pt$, Pd
1b; $R_1=H$, $R_2=t$-Bu
1c; $R_1=R_2=t$-Bu



2a; $M=Pt$, $R_1=R_2=H$
2b; $M=Pt$, $R_1=H$, $R_2=t$-Bu
2c; $M=Pt$, $R_1=R_2=t$-Bu
2d; $M=Pd$, $R_1=R_2=H$
2e; $M=Pd$, $R_1=R_2=t$-Bu

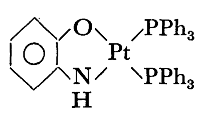
1a reacted with $MO_2(PPh_3)_2$ to yield, along with H_2O_2, new four-coordinate complexes, **2a** and **2d**, as yellow and blue crystals, respectively. Similarly **1b** and **1c** reacted with $PtO_2(PPh_3)_2$ to yield orange complexes, **2b** and **2c**, respectively. The results of elemental analyses are in line with the proposed structures(**2a** Found: C, 60.03; H, 4.01; P, 6.99%. Calcd for $C_{42}H_{34}O_2P_2Pt$: C, 60.94; H, 4.15; P, 7.48%. **2b** Found: C, 62.35; H, 4.62; P, 6.98%. Calcd for $C_{46}H_{42}O_2P_2Pt$: C, 62.50; H, 4.82; P, 7.01%. **2c** Found: C, 63.98; H, 5.35; P. 6.69%. Calcd for $C_{50}H_{50}O_2P_2Pt$: C, 63.88; H, 5.37; P, 6.59%. **2d** Found: C, 68.81; H, 4.60; P, 8.36%. Calcd for $C_{42}H_{34}O_2P_2Pd$: C, 68.25; H, 4.65; P, 8.38%. NMR($CDCl_3$)[11)] **2a**: δ 7.21(m, 30H, PPh_3) *ca.* δ 6.42(m, 4H, C_6H_4). **2b**: δ 7.23(m, 30H, PPh_3), δ 6.50—6.41(m, 3H, C_6H_3), δ 1.23(s, 9H, Bu^t). **2c**:

Table 2. IR data (cm^{-1}) of the complexes in Nujol a)

Complex	Bands characteristic of the *o*-diolato ligands						$\nu(PPh_3)$	ν(O-O)
2a	1570 w		1267 s	1256 s	1093 sh	998 w	1098 s	
2b	1564 w	1282 m		1259 s	1096 sh	998 w	1098 s	
2c	1557 m	1290 s		1244 s	*ca.* 1097 b)	996 w	1099 s	
2d	1565 w		1264 s	1253 s	1094 sh	998 w	1098 s	
2e	1551 m	1283 s		1244 s	*ca.* 1097 b)	996 w	1098 s	
$PtO_2(PPh_3)_2$ c)							1098 s	821 s
$PdO_2(PPh_3)$ c)							1098 s	869 s

a) The IR spectra were calibrated with polystyrene film. w weak, m medium, s strong, sh shoulder.
b) Overlapping with the strong PPh_3 band. c) In CH_2Cl_2 solution.

δ 7.26(m, 30H, PPh_3), δ 6.43(br d, 2H, C_6H_2), δ 1.23 (s, 9H, 5-Bu^t), δ 0.99(s, 9H, 3-Bu^t). **2e**: δ 7.24(m, 30H, PPh_3), δ 6.33(br s, 2H, C_6H_2), δ 1.23(s, 9H, 5-Bu^t), δ 0.92(s, 9H, 3-Bu^t).). The infrared spectra (Table 2) of the complexes are similar to each other. The parent catechols show intense hydroxyl absorption at *ca.* 3500 cm^{-1}, but none in the 4000—3100 cm^{-1} region. In the 1800—1500 cm^{-1} region no bands were observed except for a weak band at 1570—1551 cm^{-1} which seems to be the characteristic of the reduced form of the ligand as reported for $Pt(C_6Cl_4O_2)(PPh_3)_2$.5) All the complexes exhibited intense IR absorption at 1098 cm^{-1} characteristic of the coordinated PPh_3. Other new bands in the complexes were observed at *ca.* 1260, 1093, and 998 cm^{-1} where the parent catechols show no characteristic absorption. The results support the structures illustrated above.



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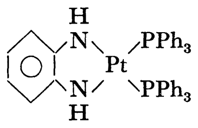

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3 and **4** were obtained in moderate yields as brown and reddish brown crystals, respectively, by similar reactions of $PtO_2(PPh_3)_2$ with *o*-aminophenol and *o*-phenylenediamine. Analytical data of complexes **3** and **4** are as follows: **3** Found: C, 61.47; H, 4.48; N, 1.44%. Calcd for $C_{42}H_{35}ONP_2Pt$: C, 61.01; H, 4.28; N, 1.66%. **4** Found: C, 60.51; H, 4.54; N, 3.17%. Calcd for $C_{42}H_{36}N_2P_2Pt$: C, 61.08; H, 4.40; N, 3.39%. IR(Nujol) **3**: 3410, 1572, 1291, 1270, 1098, and 997 cm^{-1}, **4**: 3400, 1567, 1298, 1098, and 997 cm^{-1}. Complex **4** is unstable in solution at ambient temperature, decomposing in a few hours to give black precipitates. However, the NMR spectrum of **4** in $CDCl_3$ solution exhibits a singlet absorption at 5.25 and a multiplet at 7.21 ppm. This also indicates the formula $Pt(C_6H_4NHO)(PPh_3)_2$ and $Pt(C_6H_4N_2H_2)(PPh_3)_2$ for **3** and **4**, respectively.

Experimental

Melting points were determined on a Yazawa hot-stage apparatus and are uncorrected. IR spectra were recorded as Nujol mulls on a Nippon Bunko IR-G spectrophotometer (4000—400 cm^{-1}), calibrated with polystyrene film. ^1H NMR spectra were measured in $CDCl_3$ solution on a JEOL JMN PMX 60 spectrometer.

Preparation of Catecholato Complexes. The general procedure for the preparation of catecholato complexes is as follows. Excess catechol(0.22 g, 2.0 mmol) dissolved in EtOH (10 ml) was added dropwise to a stirred solution of $PtO_2(PPh_3)_2\cdot 1.5C_6H_6$(0.44 g, 0.5 mmol) in CH_2Cl_2(2 ml) at 0 °C. The solution was then stirred for 1 h at 0 °C. At the end of the reaction, the mixture containing an appreciable amount of precipitates was filtered and washed twice with EtOH. Recrystallization from $CHCl_3$ gave yellow crystals in 88% yield. A similar procedure for the preparation of other complexes was employed(yields were 50—80%). Infrared data for individual complexes are given in Table 2.

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11) No NMR spectrum of **2d** was available owing to its low solubility in usual solvents.