frozen-solution spectra were computed by using the program POWDER.[38]

Synthesis of the Complexes. The solid compounds were collected on sintered-glass frits and washed, unless otherwise stated, with ethanol and *n*-pentane before being dried in a stream of nitrogen.

Synthesis of [(PP$_3$)Fe(H)$_2$] (3). Method A. $FeCl_2$ (0.05 g, 0.39 mmol) was added to PP$_3$ (0.27 g, 0.40 mmol) in 30 mL of THF, and the mixture was stirred for 10 min, producing a violet solution. $NaBH_4$ (0.1 g, 2.64 mmol) in 10 mL of ethanol was added and the mixture refluxed until an orange color appeared. By addition of ethanol (30 mL) and slow evaporation of the solvent in a stream of dinitrogen, yellow orange crystals of **3** precipitated (yield 80%). Anal. Calcd for $C_{42}H_{44}FeP_4$: C, 69.44; H, 6.10; Fe, 7.68. Found: C, 69.40; H, 6.02; Fe, 7.57.

Method B. To a stirred yellow solution of the (hydride)(η^2-dihydrogen) complex **4** (0.42 g, 0.40 mmol) in THF (30 mL) was added portionwise an equimolar amount of KOBu^t, and this mixture was stirred for 30 min. After $KBPh_4$ was filtered off, ethanol (25 mL) was added and the resulting solution evaporated in a stream of nitrogen until **3** precipitated in 70% yield.

Synthesis of [(PP$_3$)FeH]BF$_4$ (5). Method A. To a stirred suspension of **3** (0.36 g, 0.50 mmol) in ethyl ether (30 mL) was added dropwise an excess of $HBF_4 \cdot Et_2O$ until **3** completely dissolved while converting to violet, very hygroscopic microcrystals of **5**. These were filtered off and abundantly washed with dry ethyl ether (yield 90%). The compound can be carefully recrystallized from THF/ethyl ether. Anal. Calcd for $C_{42}H_{43}BF_4FeP_4$: C, 61.87; H, 5.31; Fe, 6.85. Found: C, 59.38; H, 5.49; Fe, 6.68.

Method B. Compound **4** (0.42 g, 0.40 mmol) was dissolved in a THF/EtOH mixture (4:1 v/v, 35 mL) under an argon atmosphere. On 2 h of bubbling with argon, the solution became deep violet and separated violet needles of **5** after addition of ethanol (30 mL); yield 80%.

Synthesis of [(PP$_3$)CoH]Y. Y = BF$_4$ (7). Method A. $CoBF_4 \cdot 6H_2O$ (0.17 g, 0.50 mmol) in 5 mL ethanol was added to PP$_3$ (0.33 g, 0.50 mmol) in 30 mL of acetone, producing a brown solution. $NaBH_4$ (0.015 g, 0.40 mmol) in 10 mL of ethanol was slowly added and the mixture stirred until red-brown crystals of **7** precipitated (yield 85%). Anal. Calcd for $C_{42}H_{43}CoBF_4P_4$: C, 61.70; H, 5.30; Co, 7.21; P, 15.16. Found: C, 61.00; H, 5.17; Co, 7.28; P, 14.79.

Method B. To a yellow solution of **6** (0.36 g, 0.50 mmol) in 30 mL of THF was added solid $[(C_5H_5)_2Fe]PF_6$ (0.16 g, 0.50 mmol) with stirring. The solution immediately turned red-brown. A 10-fold excess of $[NBu_4]BF_4$ in ethanol (30 mL) was added and the solvent evaporated under a stream of nitrogen until crystals of **7** precipitated (yield 90%).

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Y = ClO$_4$ (8). After exhaustive one-electron macroelectrolysis of **6** in THF at E_w = 0.0 V ($[NBu_4]ClO_4$ as supporting electrolyte), the solvent was fully evaporated. The crude product was washed three times with ethanol. The residue was collected and recrystallized from THF/*n*-heptane to give microcrystals of **8** (yield 75%). Anal. Calcd for $C_{42}H_{43}CoClO_4P_4$: C, 60.77; H, 5.22; Co, 7.10. Found: C, 60.52; H, 5.36; Co, 6.99.

Synthesis of [(NP$_3$)CoH]ClO$_4$ (11). After exhaustive one-electron macroelectrolysis of **9** in THF at E_w = −0.2 V ($[NBu_4]ClO_4$ as supporting electrolyte), the solvent was fully evaporated. The crude produce was washed three times with ethanol. The residue was collected and recrystallized from THF/*n*-heptane to give microcrystals of **11** (yield 40%). Anal. Calcd for $C_{42}H_{42}NCoClO_4P_3$: C, 62.04; H, 5.33; N, 1.72; Co, 7.44. Found: C, 61.12; H, 5.47; N, 1.63; Co, 7.21.

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[38] Courtesy of Prof. A. Bencini, Department of Chemistry, University of Firenze.

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 Firenze, Italy, Dipartimento di Chimica, Università di Siena, Via Pian dei Mantellini 441, 53100 Siena, Italy, and Dipartimento di Chimica Organica, Università di Firenze, 50121 Firenze, Italy

A Novel Oxygen-Carrying and Activating System of Rhodium(III). Oxidation and Oxygenation Reactions of 3,5-Di-*tert*-butylcatechol Catalyzed by a Rhodium(III) Cathecolate through Its (η^1-Superoxo)(η^2-semiquinonato)rhodium(III) Complex

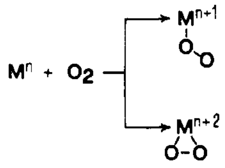
Claudio Bianchini,*[,†] Piero Frediani,[§] Franco Laschi,[‡] Andrea Meli,[†] Francesco Vizza,[†]
and Piero Zanello[‡]

Received March 20, 1990

The coordinatively unsaturated Rh(III) catecholate complex [(triphos)Rh(3,5-DBCat)]$^+$ (**2$^+$**) has been synthesized by oxidative addition of 3,5-DBQ to the 16-electron fragment [(triphos)RhCl] [triphos = $MeC(CH_2PPh_2)_3$; 3,5-DBCat = 3,5-di-*tert*-butylcatecholate; 3,5-DBQ = 3,5-di-*tert*-butyl-*o*-benzoquinone]. Complex **2$^+$** undergoes electron-transfer reactions that encompass the Rh(III), Rh(II), and Rh(I) oxidation states of the metal and the catecholate, semiquinone, and quinone oxidation levels of the quinoid ligand. The Rh(II) derivative [(triphos)Rh(3,5-DBCat)] (**3**) and the Rh(III) semiquinone complex [(triphos)Rh(3,5-DBSQ)]$^{2+}$ (**4^{2+}**) have been characterized by X-band ESR spectroscopy [3,5-DBSQ = 3,5-di-*tert*-butylsemiquinonate]. Below 10 °C, complex **2$^+$** in CH_2Cl_2 or MeCN picks up dioxygen in a reversible manner, forming a diamagnetic dioxygen adduct, which has been identified by NMR and electrochemical techniques as [(triphos)Rh(η^1-O$_2$)(η^2-3,5-DBSQ)]$^+$ (**5$^+$**). The η^1-superoxo complex **5$^+$** is able to oxygenate inorganic substrates such as SO_2 and PPh_3 to sulfate and phosphine oxide, respectively. While the reaction with SO_2 is stoichiometric, leading to the stable η^2-sulfate-*O,O* complex [(triphos)Rh(SO$_4$)]$^+$, that with PPh_3 is catalytic under an oxygen atmosphere. The starting catecholate compound **2$^+$** is recovered intact after the catalysis cycle. 3,5-Di-*tert*-butylcatechol is both oxidized and oxygenated by **5$^+$** in a catalytic way producing *o*-quinone, muconic acid anhydride, and 2*H*-pyran-2-one. The oxidation to quinone, which is the prevailing reaction, is accompanied by production of H_2O_2. The characteristic features of the present nonenzymatic oxygenation of 3,5-di-*tert*-butylcatechol with molecular oxygen are as follows: (i) the process takes place in an intermolecular fashion, (ii) the catechol is oxygenated into the Hamilton intermediates of either the intra-diol or extra-diol type, and (iii) the oxygenation does not proceed through a quinone intermediate.

Due to its ability to accept as many as four electrons, dioxygen can react with transition metals, producing a great variety of oxo compounds.[1] However, in a preliminary stage, the interaction between O_2 and a metal system is a simple one, being practically limited to the formation of 1:1 adducts of either the superoxo or peroxo type (Scheme I). In both cases, the activation process requires an electron transfer from the metal to dioxygen. This

Scheme I



[†] ISSECC, CNR.
[‡] University of Siena.
[§] University of Florence.

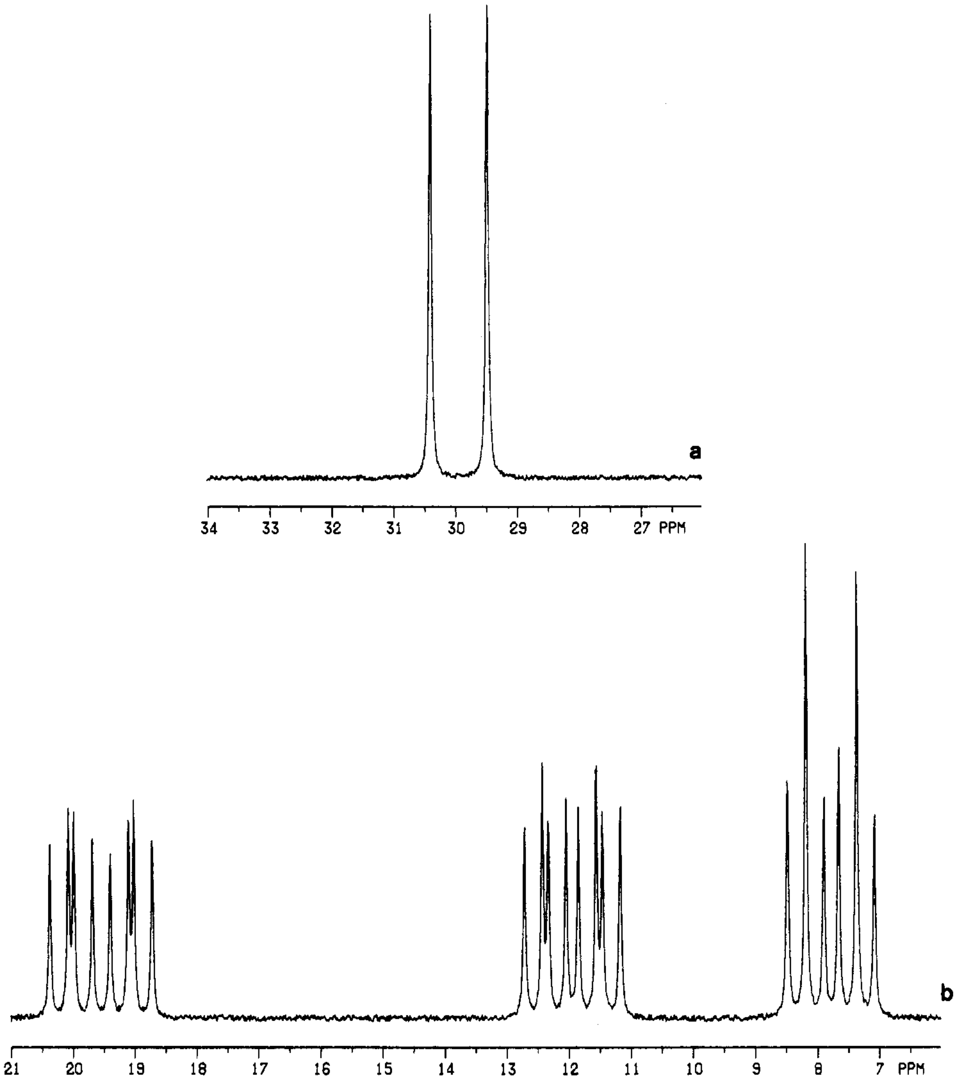


Figure 1. $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2, 121.42 MHz, 258 K) of **2b** under nitrogen (a) and under oxygen (b).

accounts for the widespread use of low-valent metals for the stabilization of η^1- or η^2-O_2 ligands.[1,2]

An alternative route to the activation of O_2 might be provided by metal complexes containing one or more ancillary ligands capable of behaving as electron sinks.[3] In this respect, excellent candidates could be the catecholate groups due to their involvement in the oxidation-reduction sequence shown in Scheme II.[4]

We were intrigued by this second approach and, in particular, by the possibility of exploiting both the reducing power of the catecholate ligands and the ability of metals to function as a medium through which electrons can flow. Therefore we started a research program directed to the synthesis of metal catecholate complexes having a free coordination site or, alternatively, containing a weakly bound coligand.

A few years ago, we reported on the electrochemistry of the five-coordinate Co(III) complex [(triphos)Co(3,5-DBCat)]$^+$ (**1**$^+$) [triphos = $MeC(CH_2PPh_2)_3$; 3,5-DBCat = 3,5-di-*tert*-butylcatecholate].[5] Complex cation **1**$^+$ undergoes electron-transfer reactions that encompass the Co(III), Co(II), and Co(I) oxidation states of the metal and the catecholate, semiquinone, and quinone oxidation levels of the quinoid ligand. Despite its coordinatively unsaturated nature, **1**$^+$ neither forms a dioxygen complex nor activates any dioxygen transfer to appropriate acceptors.

In this paper, we report the synthesis and the characterization of the rhodium analogue of **1**$^+$, namely [(triphos)Rh(3,5-DBCat)]$^+$ (**2**$^+$). The latter complex exhibits redox properties quite similar

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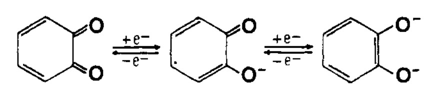
Scheme II



to those of 1^+, but, unlike 1^+, 2^+ is able to pick up dioxygen in a reversible manner, yielding [(triphos)Rh(η^1-O_2)(η^2-3,5-DBSQ)]$^+$ (3,5-DBSQ = 3,5-di-*tert*-butylsemiquinonate). Interestingly, the (η^1-superoxo)(η^2-semiquinonato) complex is able to transfer oxygen atoms to inorganic substrates such as PPh_3 or SO_2, forming phosphine oxide and sulfate, as well as to catalyze both the oxidation and the oxygenation of 3,5-DBCat, producing 3,5-DBQ, muconic acid anhydride, and 2*H*-pyran-2-one. The latter reactions are particularly interesting because of the apparent analogies with the activity of certain important enzymes such as dioxygenases and tyrosinase, which catalyze in the living organism the oxidative carbon–carbon bond cleavage and the oxidation of aromatic systems, notably catechols, respectively.[6]

Results and Discussion

The preparations and the principal reactions described in this paper are summarized in Schemes III and IV.

Synthesis and Characterization of [(triphos)Rh(3,5-DBCat)]Y (Y = BPh_4, PF_6). Dark green crystals of [(triphos)Rh(3,5-DBCat)]Y (Y = BPh_4, **2a**; PF_6, **2b**) are obtained by treatment of [(triphos)RhCl(C_2H_4)][7] in CH_2Cl_2 with an equimolecular amount of 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBQ), followed by addition of either $NaBPh_4$ or NH_4PF_6 in ethanol.

Compounds **2a** and **2b** are air-stable in the solid state and in ambient-temperature solutions, in which they behave as 1:1 electrolytes. The IR spectra of both compounds contain no absorptions in the 1600–1700-cm^{-1} region, where the coordinated quinone ν(C=O) absorptions are expected to fall, indicating that 3,5-DBQ has been reduced. Magnetic moment measurements in the solid state and on CH_2Cl_2 solutions show **2a,b** to be diamagnetic. This is confirmed by ESR measurements as well as the sharpness of the resonances in the ^{31}P and ^1H NMR spectra. Except for containing the typical high-field resonance of the PF_6^- counteranion, the $^{31}P\{^1H\}$ NMR spectrum of **2b** (CD_2Cl_2, 258 K) is identical with that of **2a** and consists of a doublet at 29.93 ppm [*J*(PRh) = 112.0 Hz] (Figure 1a). The A_3X spin system that does not vary in deareated CH_2Cl_2 solutions over the temperature range 308–173 K is consistent with the rapid intramolecular exchange of the three phosphorus atoms of triphos around rhodium. Such a fluxionality is frequently observed for five-coordinate triphos complexes and is attributed to a fast interconversion between square-pyramidal and trigonal-bipyramidal geometries.[7,8] The ^1H NMR spectra of **2a,b** (CD_2Cl_2, 298 K) in the 3–1 ppm region are identical with each other and in line with the fluxionality of the molecule. In fact, the three CH_2 groups of the alkyl chains of triphos appear magnetically equivalent, as shown by the unique resonance at 2.65 ppm (6 H). The resonance of the methyl substituent of triphos falls at 1.55 ppm, while the two nonequivalent *tert*-butyl groups give rise to singlets at 1.46 and 1.43 ppm.

A comparison of the main physical properties of **2a** with those of [(triphos)Co(3,5-DBCat)]BPh_4[5] (**1a**) makes it evident that the two compounds share the same primary structure in solution and in the solid state as well. As authenticated by an X-ray analysis, the cobalt atom in **1a** is coordinated by the three phosphorus atoms of triphos and by the two oxygens of a DBCat ligand in a distorted-square-pyramidal geometry.[5] Like **2a,b**, compound **1a** is highly fluxional in solution and undergoes electron-transfer reactions that encompass the Co(III), Co(II), and Co(I) oxidation states of the metal and the catecholate, semiquinone, and quinone oxidation levels of the quinoid ligand. Since identical redox properties are exhibited by **2a** (see below), one may reasonably conclude that 1^+ and 2^+ exhibit a quite similar electronic configuration too.[5]

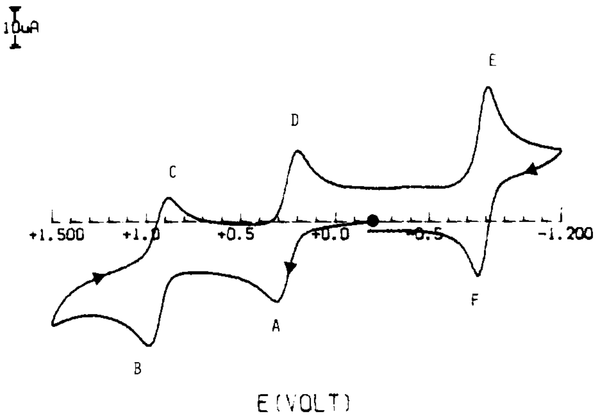


Figure 2. Cyclic voltammogram recorded at a platinum electrode on a deaerated MeCN solution at −15 °C containing **2b** (1.8×10^{-3} mol dm^{-3}) and [NEt_4]ClO_4 (0.1 mol dm^{-3}) (scan rate 0.2 v s^{-1}).

Figure 2 illustrates the main redox changes exhibited by **2b** in acetonitrile solution at −15 °C (this temperature has been chosen just to permit a reliable comparison with the reactions under O_2; see below). Two subsequent oxidation and one reduction processes are displayed, each of which involves a one-electron transfer. Considering that 2^+ contains as potential redox centers the metal ion, susceptible to undergo the reduction sequence Rh(III)/Rh(II)/Rh(I), and the catecholate ligand, inclined to be oxidized to semiquinone and quinone, one can readily assign the two oxidation steps to the catecholate/semiquinone and semiquinone/quinone electron transfers. In turn, the reduction process is assigned to the rhodium(III)/rhodium(II) electron transfer. A further rhodium(II)/rhodium(I) reduction is also present at a more negative potential value, but it is irreversible in character.

Controlled-potential coulometric tests performed in correspondence to the redox steps shown in Figure 2 confirm that each of them involves the consumption of 1 faraday/mol. In addition, the cyclic voltammetric responses recorded after exhaustive electrolysis either at the first cathodic step or at the first anodic step appear complementary to those reported in Figure 2, thus demonstrating the chemical reversibility of the relevant redox changes.

The cyclic voltammetric responses have been analyzed with scan rates varying from 0.02 to 10.24 V s^{-1}. A simple, nearly reversible one-electron reduction can be readily associated with the peak system E/F on the basis of the following parameters.[9] The $i_{p(F)}/i_{p(E)}$ ratio is constantly equal to unity; the current function $i_{p(E)}v^{-1/2}$ is substantially constant; the difference in peak potential values $E_{p(F)} - E_{p(E)} = \Delta E_p$ progressively increases from 67 to 162 mV [notice that under the same experimental conditions, the reversible oxidation of ferrocene, which should display a constant ΔE_p value of 60 mV, really shows a rather similar increase of ΔE_p with v (from 63 to 148 mV)].

The same trend is observed for the electrochemical features of the peak system A/D, the only difference being a slightly greater ΔE_p separation, which ranges from 68 to 214 mV. Taking into account the effect of some uncompensated solution resistance, this more pronounced departure from the pure electrochemical reversibility could be due[10] to the fact that the stereochemical

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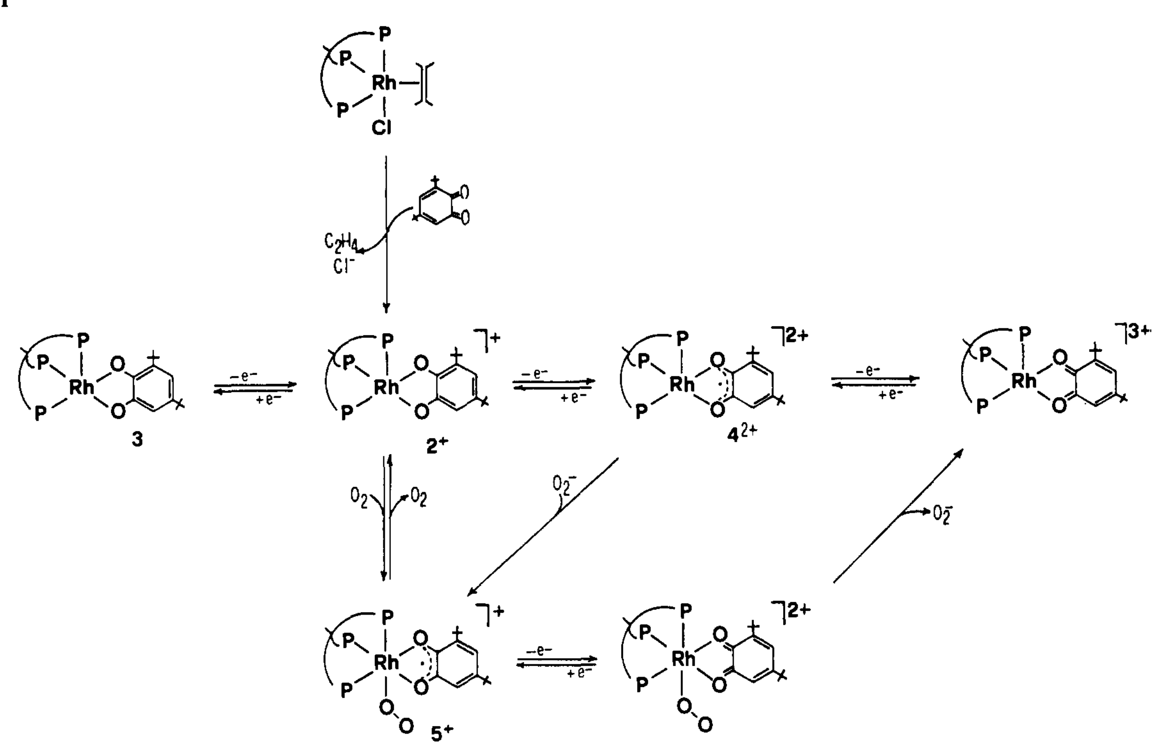
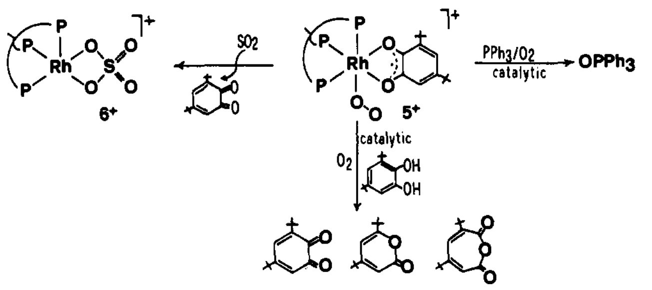
Scheme III



Scheme IV



reorganization accompanying the $[(\text{triphos})\text{Rh}(3,5\text{-DBCat})]^+$/$[(\text{triphos})\text{Rh}(3,5\text{-DBCat})]$ redox change might be slightly lower than that accompanying the $[(\text{triphos})\text{Rh}(3,5\text{-DBCat})]^+$/$[(\text{triphos})\text{Rh}(3,5\text{-DBSQ})]^{2+}$ redox change.

Finally, the peak system B/C displays the features of a quasi-reversible one-electron transfer complicated by subsequent, relatively slow, homogeneous chemical complications. In fact, the $i_{p(C)}/i_{p(B)}$ ratio increases from 0.7 at 0.02 V s^{-1} to 1 at 1.00 V s^{-1}; then it remains constant; the ΔE_p values increases from 86 to 416 mV; the $i_{p(B)}v^{-1/2}$ term decreases by ca. 20%. Assuming a first-order chemical complication, a lifetime ($t_{1/2}$) of ca. 5 s can be computed for $[(\text{triphos})\text{Rh}(3,5\text{-DBQ})]^{3+}$ at −15 °C. Exhaustive two-electron oxidation at 1.1 V of **2b** leads to a yellow solution, which gives rise to cyclic voltammetric responses fully consistent with the following decomposition pathway:[5]

$$[(\text{triphos})\text{Rh}(3,5\text{-DBQ})]^{3+} \xrightarrow[\text{MeCN}]{t_{1/2} = 5\text{ s}} [(\text{triphos})\text{Rh}(\text{NCMe})_3]^{3+} + 3,5\text{-DBQ}$$

Subsequent exhaustive reduction of the released 3,5-DBQ (E_w = −0.5 V) completely restores the starting deep green species **2**$^+$.

As is deducible from Figure 3, raising the temperature to 20 °C only has the effect of more rapidly decomposing the electrogenerable $[(\text{triphos})\text{Rh}(3,5\text{-DBQ}]^{3+}$ complex, which now exhibits at $t_{1/2}$ value of 0.05 s.

Table I summarizes the redox potentials of the redox changes. A comparison is made with the corresponding steps exhibited by the cobalt analogue **1**$^+$.[5]

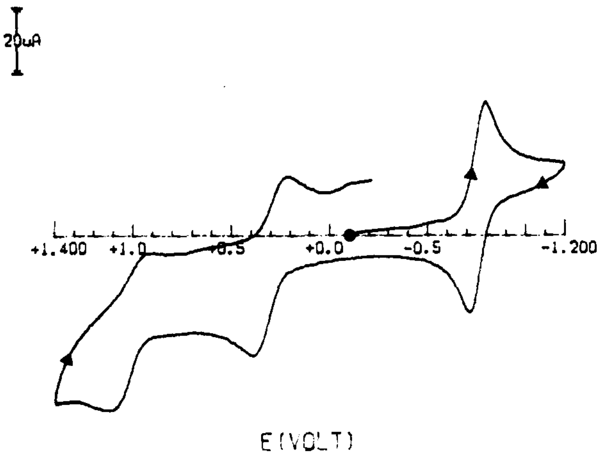


Figure 3. Cyclic voltammogram recorded at a platinum electrode on a deaerated MeCN solution at 20 °C containing **2b** (1.8×10^{-3} mol dm^{-3}) and $[NEt_4]ClO_4$ (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}).

Table I. Formal Electrode Potentials for the Redox Changes Exhibited by $[(\text{triphos})\text{M}(3,5\text{-DBCat})]^+$ (M = Co, Rh) in MeCN Solution[a]

M	$M^{III}(Q)/M^{III}(SQ)$	$M^{III}(SQ)/M^{III}(Cat)$	$M^{III}(Cat)/M^{II}(Cat)$	$M^{II}(Cat)/M^{I}(Cat)$
Rh[b]	+0.94	+0.28	−0.78	−1.56[d]
Rh[c]	+0.97	+0.30	−0.75	−1.57[d]
Co[c]	+1.04	+0.73	−0.49	−1.63[d]

[a] Key: Q = 3,5-DBQ; SQ = 3,5-DBSQ; Cat = 3,5-DBCat. [b] At −15 °C. [c] At 20 °C. [d] Peak potential value for irreversible processes measured at scan rate of 0.2 V s^{-1}.

In view of these electrochemical results, both the Rh(II) species $[(\text{triphos})\text{Rh}(3,5\text{-DBCat})]$ (**3**) and the Rh(III) semiquinone complex $[(\text{triphos})\text{Rh}(3,5\text{-BDSQ})]^{2+}$ (**4**$^{2+}$) are expected to be easily generated. Indeed, the exhaustive electrolysis of **2b** in MeCN at −15 °C at E_w = −1.0 V (0.2 mol dm^{-3} $[NBu_4]ClO_4$ as supporting electrolyte) affords a one-electron-reduced brown solution exhibiting a cyclic voltammetric response qualitatively similar to that shown in Figure 2, but the peak system E/F now appears as due to an oxidation process at peak F, accompanied by rereduction at peak E in the reverse scan. The X-band ESR

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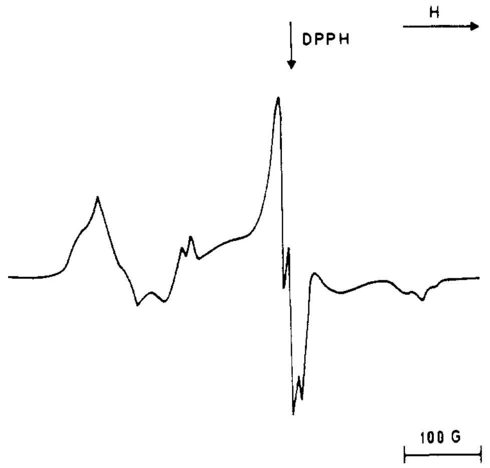

Figure 4. X-Band ESR spectrum at 100 K of a MeCN solution of **2b** exhaustively electrolyzed at E_w = −1.0 V at 258 K (0.2 mol dm^{-3} [NBu$_4$]ClO$_4$ as supporting electrolyte).

spectrum of the brown solution at 100 K (Figure 4) is quite comparable to those of a number of low-spin square-pyramidal Rh(II) complexes stabilized by tripodal polyphosphine ligands, including triphos.[8a,11] The spectrum can be interpreted by using a $S = {}^1/_2$ spin Hamiltonian with $g_\parallel = 1.986$ ($A_\parallel = 262.0$ G) and $g_\perp = 2.078$ ($A_\perp = 210.0$ G). A three-line resolution is present in each perpendicular ($A_P = 14.0$ G) and parallel ($A_P = 22.5$ G) absorption. The present set of ESR parameters is diagnostic for a distorted square-pyramidal symmetry with the unpaired electron in the d_{z^2} orbital.[11,12] In particular, the large $A_\parallel$ and $A_\perp$ values are due to a strong interaction with the apical phosphorus, which faces the d_{z^2} SOMO. The splitting observed in the perpendicular and parallel absorptions is attributed to appreciable interaction of the electron with the basal phosphorus.

The product obtained in MeCN at −15 °C after the exhaustive one-electron oxidation of **2b** at E_w = +0.5 V was also examined by X-band ESR spectroscopy. The ESR data are consistent with the formation of the semiquinone complex $\mathbf{4}^{2+}$. Figure 5 shows the first- (A) and second-derivative (B) spectra at 258 K. The following coupling constants have been introduced to reproduce the spectrum, which exhibits a 1:3:5:7:7:5:3:1 multiplicity: $\langle A_{Rh}\rangle = 3.6$ G, $\langle A_H\rangle = 3.5$ G (H being the meta hydrogen of 3,5-DBSQ), and $\langle A_P\rangle$ = 1.6–1.8 G (P being the three phosphorus atoms of triphos) ($\langle\Delta H\rangle = 7.5$ G). The average $\langle g\rangle$ value is 2.002. Both coupling constants and $\langle g\rangle$ values are clearly indicative of a radical species in which the unpaired electron is largely localized on the semiquinone ligand.[3e,4d,5,13] In particular, the low value of $\langle A_{Rh}\rangle$ and the high value of $\langle A_{H_{meta}}\rangle$ confirm the presence of Rh(III) in a semiquinoid structure. As expected, the frozen-solution spectrum at 100 K consists of a poorly resolved signal with axial symmetry ($g_\parallel = 1.988$, $g_\perp = 2.001$).

Reaction of [(triphos)Rh(3,5-DBCat)]$^+$ with O$_2$. As reported in the preceding section, compounds **2a,b** are stable in oxygenated solutions at ambient temperature. In contrast, a fast reaction occurs on decreasing the temperature, as evidenced by a color change from dark green to yellow. At −15 °C, the dark green CH$_2$Cl$_2$ solutions of **2a,b** turn yellow within a few minutes. The process is reversible; i.e. bubbling N$_2$ or Ar throughout the yellow solutions quantitatively restores **2a,b**. In the absence of O$_2$, no color change even at the lowest temperature is observed. The new product evidenced by the color change is certainly diamagnetic, as shown by the X-band ESR spectrum and magnetic moment measurements by the Evans method. Accordingly, the reaction can be conveniently monitored by ^{31}P and ^{1}H NMR techniques.

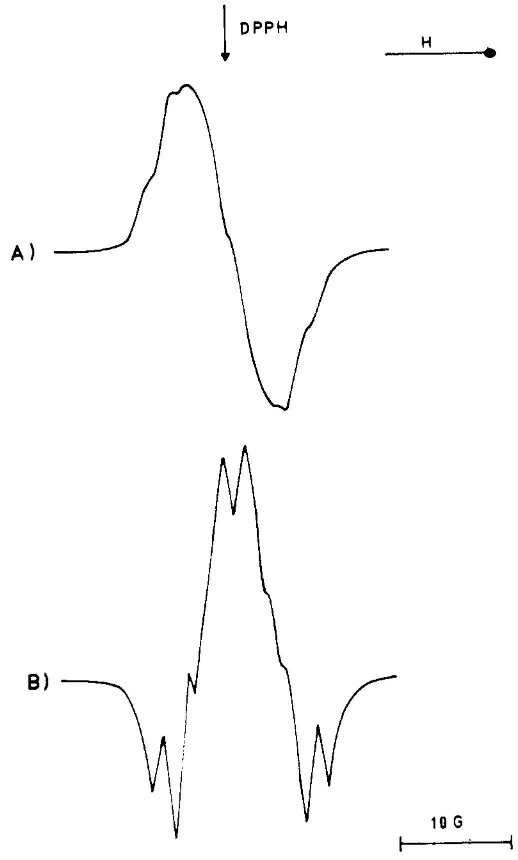

Figure 5. X-Band ESR spectra of a MeCN solution of **2b** exhaustively electrolyzed at E_w = +0.5 V at 258 K (0.2 mol dm^{-3} [NBu$_4$]ClO$_4$ as supporting electrolyte): (A) first-derivative spectrum; (B) second-derivative spectrum.

The ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 258 K, 121.42 MHz) is shown in Figure 1b. A first-order AMQX spin system is clearly evident with the following parameters: δ(P$_A$) 19.53 ppm, δ(P$_M$) 11.93 ppm, δ(P$_Q$) 7.77 ppm, J(P$_A$P$_M$) = 46.33 Hz, J(P$_A$P$_Q$) = 35.86 Hz, J(P$_M$P$_Q$) = 35.31 Hz, J(P$_A$Rh) = 117.72 Hz, J(P$_M$Rh) = 105.47 Hz, J(P$_Q$Rh) = 98.87 Hz. Such a pattern is typical of octahedral rhodium complexes of triphos containing three different ligands trans to each phosphorus.[7b,11c] The product responsible for the AMQX splitting system begins to form at 10 °C, and its concentration progressively increases as the temperature is lowered. At −15 °C, no trace of the doublet indicating **2a,b** remains in the solution. Since no variation of the AMQX pattern is observed over the temperature range 283–173 K, we conclude that the new complex, unlike the parent compounds **2a,b**, is rigid on the NMR time scale. Such a rigidity in solution is shown also by the ^{1}H NMR spectrum (CD$_2$Cl$_2$, 258 K, 300 MHz) in which the CH$_2$ protons of the alkyl chains of triphos give rise to a set of resonances between 2.35 and 2.10 ppm. The *tert*-butyl group resonances appear as two almost overlapped singlets at 1.22 and 1.20 ppm. Unfortunately all our attempts to isolate a stable product from the yellow solutions were unsuccessful. In actuality, the addition of *n*-heptane precipitates a yellow powder, which, however, cannot be stored at all or characterized in the solid state, as it rapidly becomes green, converting to either **2a** or **2b**. As an anticipation of the electrochemical and chemical studies reported below, the yellow complex is assigned the formula [(triphos)Rh(η^1-O$_2$)(η^2-3,5-DBSQ)]$^+$ ($\mathbf{5}^+$).

Valuable information on the electronic structure of $\mathbf{5}^+$ is provided by its redox properties in the anodic region (the cathodic region is obscured by the reduction of excess oxygen). Figure 6 compares the cyclic voltammetric response exhibited by $\mathbf{5}^+$ at −15 °C in MeCN deareated with N$_2$ or Ar (Figure 6a) with that exhibited by the same solution through which dioxygen is bubbled for 10 min (Figure 6b). A perusal of the cyclic voltammogram responses (Figure 6b) shows that the catecholate/semiquinone oxidation step is now absent whereas the semiquinone/quinone

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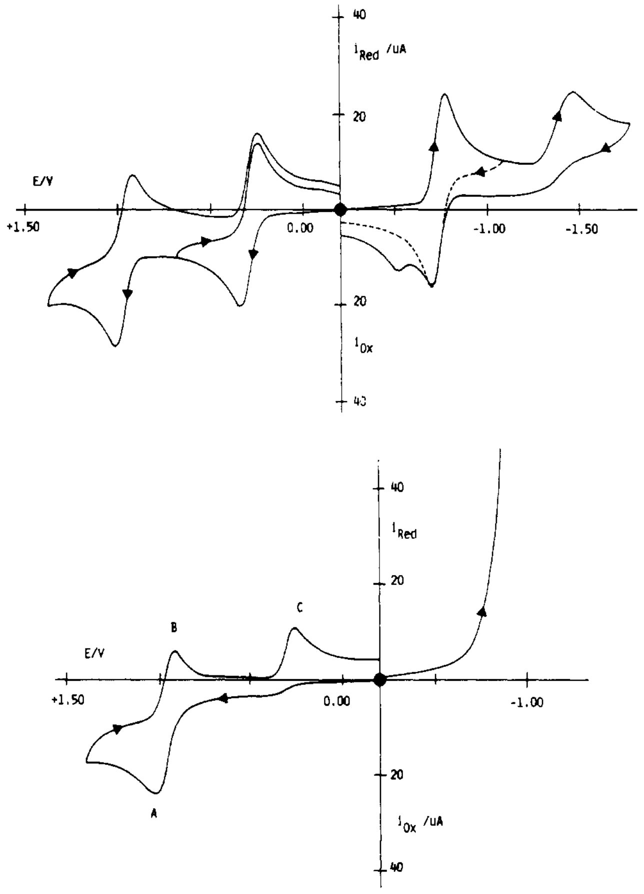

Figure 6. Cyclic voltammograms recorded on a MeCN solution at -15 °C containing **2b** (1.9×10^{-3} mol dm^{-3}) and [NEt_4]ClO_4 (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}). (a, top) deaerated solution; (b, bottom) solution after bubbling with O_2 for 10 min. Potential values are vs an Ag pseudoreference electrode.

step still takes place. The species primarily electrogenerated at the anodic peak A is a transient one: it releases O_2^-, converting to [(triphos)Rh(3,5-DBQ)]$^{3+}$ (notice that peak C in the reverse scan is just coincident with peak D in Figures 2 and 6a). Also, the exhaustive electrolysis of the ESR-silent yellow solution at $E_w = +1.2$ V produces the superoxide ion, as shown by the X-band ESR spectrum, which displays the typical signal at $\langle g \rangle = 2.007$.[3e,14] The most naive interpretation of these results is to think that the quinoid ligand in the starting dioxygen complex already possesses the semiquinone character. This means that, as a result of the binding of dioxygen to the free coordination site at rhodium, one electron is removed from the catecholate ligand, which thus assumes the semiquinoid electronic configuration.

Futher evidence supporting the (η^1-O_2)(η^2-3,5-DBSQ) structure of **5**$^+$ is provided by the reaction of tetramethylammonium superoxide [(TMA)O_2] in MeCN at -15 °C with [(triphos)Rh(3,5-DBSQ)]$^{2+}$ generated in situ by controlled-potential coulometry, which gives **5**$^+$.

$$[\text{(triphos)Rh(3,5-DBSQ)}]^{2+} + O_2^- \rightarrow [\text{(triphos)Rh}(O_2)\text{(3,5-DBSQ)}]^+$$

This reaction can be conveniently monitored by ESR and electrochemical methods as follows. A sample of **2b** is exhaustively electrolyzed in MeCN at -15 °C ($E_w = +0.4$ V) to give a solution of **4**$^{2+}$, which is authenticated by ESR spectroscopy. To this solution is added an equimolecular amount of (TMA)O_2. As a result, the signal of **4**$^{2+}$ at $\langle g \rangle = 2.002$ disappears while the cyclic voltammogram in the anodic region is identical with that shown in Figure 6b. Interestingly, no reaction occurs between (TMA)O_2 and **2b**, suggesting that a precise electronic configuration of the [(triphos)Rh(3,5-DBquinoid)] system is required for the formation of a dioxygen complex.

Oxygen-Transfer Reactions Assisted by 2a,b. Having found that **2a,b** can pick up dioxygen in a reversible manner, we decided to study the eventual oxidation and oxygenation properties of the resulting (η^1-O_2)(η^2-3,5-DBSQ) derivative **5**$^+$. In a typical procedure, dioxygen is bubbled throughout a solution of **2a,b** in CH_2Cl_2 at -15 °C until a complete color change from dark green to yellow occurs. At this point, a 30-fold excess of the appropriate substrate is added with stirring. Under these conditions, sulfur dioxide is rapidly and stoichiometrically oxygenated to the sulfate ion (Scheme IV). This displaces the quinoid ligand from the coordination sphere of rhodium, and the η^2-sulfate-*O,O* complexes [(triphos)Rh(SO_4)]Y (Y = BPh_4, **6a**; PF_6, **6b**) are obtained by addition of ethanol. Compounds **6a,b** were identified by comparison with specimens prepared by treatment of the known complex [(triphos)RhCl(SO_4)] with $NaBPh_4$ and $TlPF_6$ as chloride scavengers.[15] Compounds **6a,b** are stable both in the solid state and in deareated solutions in which they behave as 1:1 electrolytes. The $^{31}P\{^1H\}$ NMR spectra of the two compounds are identical with each other and consist of an AM_2X spin system with $\delta(P_A)$ -6.31 ppm and $\delta(P_M)$ 20.53 ppm [$J(P_AP_M) = 32.02$ Hz, $J(P_ARh) = 79.60$ Hz, $J(P_MRh) = 116.25$ Hz]. A set of IR absorptions at 1264, 1228, 1140, 924, and 622 cm^{-1} are diagnostic for a bidentate sulfate ligand.[15] After solvent evaporation, the crude product of the reaction between **5**$^+$ and SO_2 is extracted twice with diethyl ether to give a yellow solution, which is shown to contain 3,5-DBQ.

Unlike the reaction with SO_2, that with PPh_3 is catalytic, producing phosphine oxide (Scheme IV). The conversion of PPh_3 to $OPPh_3$ completes within 5 h, thus exhibiting a turnover number of 6 ((mol of product/mol of catalyst)/h). The starting catecholate complexes **2a,b** are quantitatively recovered after the catalysis cycle by quenching the reaction with dinitrogen.

A quite interesting result is observed for the reaction with a 30-fold excess of 3,5-di-*tert*-butylcatechol (this catechol has been chosen for the stability of its oxidation products). After 24 h, 66 (2)% catechol is converted to 3,5-DBQ [92 (1)%], 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione [5 (1)%], and 2,4-di-*tert*-butyl-2*H*-pyran-2-one [3 (0.5)]% (Scheme IV) (numbers in parentheses are estimated standard deviations).

In order to shed some light on the mechanism of this reaction, the following pieces of experimental information are noteworthy. Monitoring the reaction at regular intervals by $^{31}P\{^1H\}$ NMR spectroscopy shows that the only metal species to be detected is the (η^1-O_2)(η^2-3,5-DBSQ) complex. After the reaction is quenched with N_2, the starting 3,5-DBCat complex can be recovered intact. During the reaction, hydrogen peroxide accumulates in the solution in an amount which nearly corresponds to that of 3,5-DBQ. In the absence of added catechol, no formation of 3,5-DBQ, muconic acid anhydride, or 2*H*-pyran-2-one occurs when **2a,b** are reacted with O_2 in MeCN at -15 °C for 24 h. Finally, neither muconic acid anhydride nor 2-pyrone forms when a 30-fold excess of 3,5-DBQ is reacted with **2a,b** under the usual reaction conditions.

Surveying these experimental data, one may readily draw the following conclusions. Both the oxidation to 3,5-DBQ and the oxygenation to muconic acid anhydride or to 2*H*-pyran-2-one appear as intermolecular reactions between an η^1-O_2 ligand and the catechol. The *o*-quinone is not an intermediate for either the intra-diol or extra-diol ring cleavage, as it occurs in the oxygenation of 3,5-di-*tert*-butylcatechol catalyzed by $RuCl_2(PPh_3)_3$.[16] The formation of 3,5-DBQ is accompanied by production of H_2O_2. The oxidation of the catechol to 3,5-DBQ much prevails over the intra- or extra-diol ring cleavage.

Both the oxidation of catechols to *o*-quinones and the oxidative cleavage of catechols by dioxygen are widespread occurrences in nature.[6] As an example, the enzyme tyrosinase catalyzes the oxidation of catechols to *o*-quinones, pyrocatechase causes in-

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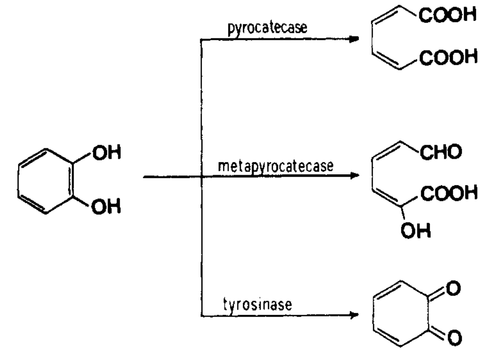
Scheme V



tra-diol ring cleavage of catechols, and metapyrocatechase initiates the extra-diol opening (Scheme V).[6] Such enzymes require either iron or copper as the cofactor that participates in the reaction center. A proposed role for the metal in the enzymes is the binding and activation of molecular oxygen after substrate reduction of the metal ion to its lower oxidation state.

A great number of biomimetic approaches have been so far developed to try to understand the mechanism and structure of catechol dioxygenases, including studies on catecholate complexes to elucidate their coordination modes,[4,17] mechanistic studies to gain insight into the metal activation of dioxygen or of dioxygen/catechol mixtures, and catalytic studies to mimic the enzymatic oxygenations.[3a,c,18] From the viewpoint of the model for dioxygenases, a fundamental work appears by Funabiki et al. on the catalytic extra- and intra-diol oxygenations of 3,5-di-*tert*-butylcatechol by a (bipyridine)(pyridine)iron(III) complex.[18o] According to this work, a 1:1 complex between 3,5-DBCat and iron forms, which successively undergoes dioxygen attack on the catecholate ligand to give a catecholate with a peroxide. The subsequent aromatic ring cleavage occurs in an intramolecular way. Our results, using a rhodium catecholate for the activation of O_2, exhibit both analogies and differences as compared to those of Funabiki. In fact, a 1:1 catecholate–metal adduct is still the active system but the following oxidation or oxygenation of 3,5-di-*tert*-butylcatechol seems to proceed in an intermolecular fashion. Also, the ring opening of the catechol is not the favored reaction pathway, as we find that the prevailing process is the oxidation to *o*-quinone.

In conclusion, our results appear similar to those reported by Postel et al.[3c] and by Vigato, Vidali, and Fenton[18m] on the oxygenation of catechols catalyzed by vanadium(IV) complexes. In particular, Postel describes a catalytic oxygenation of 3,5-di-*tert*-butylcatechol assisted by a vanadium(IV) tetrachlorocatecholate, which yields a product composition qualitatively similar to ours. The starting vanadium catecholate complex does not itself react with O_2; only in the presence of an excess of 3,5-di-*tert*-butylcatechol does a reaction occur. On this basis and, likely, taking for granted the intramolecular process proposed by Funabiki, the authors suggest that the tetrachlorocatecholate moiety is displaced by 3,5-di-*tert*-butylcatechol. In light of our data, it may be the case that also Postel's reaction is an intermolecular one; i.e. in the absence of externally added catechol no oxygenation occurs. Regardful of this, it is worth noticing that Postel also reports the formation of 2,4-di-*tert*-butyl-2*H*-pyran-2-one.

Experimental Section

General Data. All the reactions and manipulations were routinely performed with standard Schlenk tube techniques under a nitrogen atmosphere unless otherwise stated. $[(\text{triphos})\text{RhCl}(C_2H_4)]$,[7] 2,4-di-*tert*-butyl-2*H*-pyran-2-one,[16] 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione,[19] and tetramethylammonium superoxide[3c] $[(\text{TMA})O_2]$ were prepared according to literature methods. Triphenylphosphine and 3,5-di-*tert*-butylcatechol were recrystallized from ethanol and *n*-pentane solutions, respectively. Dichloromethane and acetonitrile were purified over P_2O_5 and CaH_2, respectively, and distilled under nitrogen just prior to use. All the other chemicals were reagent grade and were used as received from commercial suppliers. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 spectrometer. Chemical shifts are relative to tetramethylsilane as external reference or calibrated against the solvent as the reference signal. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 121.42 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Conductivities were measured with a Model 990101 ORION conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions at room temperature. Magnetic susceptibilities of solid samples were measured on a Faraday balance. The materials and the apparatus used for the electrochemical experiments have been described elsewhere. Unless otherwise stated, the potential values are relative to an aqueous calomel electrode (SCE) and refer to a controlled temperature of 20 ± 0.1 °C. Low-temperature macroelectrolysis tests were performed by using an Ag/AgCl reference electrode, the potential of which was −0.02 V vs SCE. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at +0.38 V. X-Band ESR spectra were recorded with an ER 200-DSRC Bruker spectrometer operating at $\omega^\circ = 9.78$ GHz. The control of the external magnetic field was obtained with a microwave bridge ER 041 MR Bruker wavemeter. The temperature was varied and controlled with an ER 4111 VT Bruker device with an accuracy of ± 1 °C. In order to estimate accurate g_{iso} and g_{aniso} values over the temperature range of interest, the diphenylpicrylhydrazyl free radical (DPPH) was used as field marker (g_{iso} DPPH = 2.0036). In order to ensure quantitative reproducibility, the samples were placed into calibrated quartz capillary tubes permanently positioned in the resonance cavity.

Synthesis of the Complexes. The solid compounds were collected on sintered-glass frits and washed, unless otherwise stated, with ethanol and *n*-pentane before being dried in a stream of nitrogen.

Synthesis of [(triphos)Rh(3,5-DBCat)]BPh$_4$ (2a). 3,5-DBQ (0.22 g, 1 mmol) in CH_2Cl_2 (10 mL) was added to a CH_2Cl_2 (30 mL) solution of $[(\text{triphos})\text{RhCl}(C_2H_4)]$ (0.79 g, 1 mmol). There was an immediate color change from orange to deep green. After 10 min, $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (30 mL) was added, and the resulting solution, slowly concentrated in a stream of nitrogen, gave green crystals, which were recrystallized twice from CH_2Cl_2 and ethanol; yield 85%. Anal. Calcd for $C_{79}H_{79}BO_2P_3Rh$: C, 76.88; H, 6.28; Rh, 8.12. Found: C, 76.12; H, 6.17; Rh, 8.01. $\Lambda_M = 48\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. The PF_6 derivative **2b** was obtained in 80% yield by using NH_4PF_6 instead of $NaBPh_4$ and *n*-heptane to complete the precipitation. Anal. Calcd for $C_{55}H_{59}F_6O_2P_4Rh$: C, 60.44; H, 5.44; Rh, 9.42. Found: C, 60.31; H, 5.47; Rh, 9.31. $\Lambda_M = 79\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

Reaction of 2a,b with O$_2$. A solution of **2a,b** in CH_2Cl_2 (or MeCN) was cooled at −15 °C under an oxygen atmosphere. There was a gradual color change from green to yellow (ca. 5 min). On addition of cold *n*-heptane to the solution, a yellow powder was obtained. This product could be neither stored nor characterized in the solid state, as it rapidly converts to **2a,b**. On the basis of spectroscopic and electrochemical measurements (see text), the yellow product was assigned the formula $[(\text{triphos})\text{Rh}(\eta^1\text{-}O_2)(\eta^2\text{-}3,5\text{-DBSQ})]Y$ (Y = BPh_4, **5a**; PF_6 = **5b**). In-

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creasing the temperature or replacing oxygen with nitrogen or argon gave **2a,b**, as determined by ^{31}P NMR spectroscopy. The formation of the η^1-O_2 adduct was found to be reversible, and the oxygenation–deoxygenation cycle could be repeated several times.

Reaction of 5a,b with SO_2. SO_2 was bubbled for 15 min through a yellow CH_2Cl_2 (20 mL) solution of **5a,b** (0.2 mmol) prepared as above and maintained under oxygen at −15 °C. The reaction mixture was allowed to reach room temperature, and then ethanol was added. On concentration, yellow crystals of $[(triphos)Rh(SO_4)]Y$ ($Y = BPh_4$, **6a**; PF_6 = **6b**) precipitated in 80–85% yield. They were collected by filtration, and the filtrate was evaporated to dryness. The residue was extracted twice with diethyl ether. The ethereal solution was evaporated at reduced pressure to give 3,5-DBQ. Anal. Calcd for $C_{65}H_{59}BO_4P_3RhS$ (**6a**): C, 83.31; H, 5.20; Rh, 9.00. Found: C, 68.12; H, 5.09; Rh, 8.91. $\Lambda_M = 52\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{41}H_{39}F_6O_4P_4RhS$ (**6b**): C, 50.84; H, 4.06; Rh, 10.62. Found: C, 50.67; H, 4.07; Rh, 10.48. $\Lambda_M = 81\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Catalytic Reaction of 5a,b with PPh_3. A 30-fold excess of PPh_3 (0.31 g, 1.2 mmol) was added to a yellow CH_2Cl_2 (10 mL) solution of **5a,b** (0.04 mmol) prepared as above and maintained under oxygen at −15 °C for 5 h. After that time, nitrogen was bubbled throughout the yellow solution at room temperature until it became green. The solution was then concentrated to 2 mL and analyzed by ^{31}P NMR spectroscopy. Only the resonances due to $OPPh_3$ (δ 29.86 ppm) and **2a,b** were observed.

Catalytic Reaction of 5a,b with 3,5-BDCat. A 30-fold excess of 3,5-BDCat (0.27 g, 1.2 mmol) was added to a yellow CH_2Cl_2 (10 mL) solution of **5a,b** (0.04 mmol) prepared as above and maintained under oxygen at −15 °C for 24 h. The reaction mixture, after being quenched with nitrogen to stop further oxidation, was extracted with water, and the aqueous layer was analyzed by the usual method of iodometry.[21] The amount of H_2O_2 accumulated during the reaction was found to be nearly correspondent to that of 3,5-DBQ. The CH_2Cl_2 layer was evaporated at reduced pressure and the residue extracted twice with *n*-pentane. The undissolved solid was authenticated as **2a,b** by ^{31}P NMR spectroscopy (CD_2Cl_2, 298 K). The liquid phase was concentrated to dryness to give a solid that was chromatographed on a silica gel column by using chloroform as eluant. Over six different reactions, a 66 (2)% conversion was found for 3,5-di-*tert*-butylcatechol with the following product distributions: 3,5-DBQ [92 (1)%], 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione [5 (1)%], and 2,4-di-*tert*-butyl-2*H*-pyran-2-one [3 (0.5)%] (numbers in parentheses are estimated standard deviations). The products were characterized by comparison of their ^1H NMR and mass spectra with those of authentic specimens.

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Contribution from the Department of Chemistry,
University of Florence, Florence, Italy

Electronic Structure and Reactivity of Dioxolene Adducts of Nickel(II) and Copper(II) Triazamacrocyclic Complexes

Cristiano Benelli, Andrea Dei,* Dante Gatteschi,* and Luca Pardi

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Five-coordinate $[M(Me_3[12]N_3)(DTBSQ)]ClO_4$ and $M(Me_3[12]N_3)(TCCat)$ complexes (M = Ni, Cu; $Me_3[12]N_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene; DTBSQ = 3,5-di-*tert*-butyl-*o*-semiquinonate; TCCat = 3,4,5,6-tetrachlorocatecholate) were obtained from reaction of $[M(Me_3[12]N_3)OH]_2(ClO_4)_2$ with the appropriate catechol. The magnetic interaction in the nickel(II)–semiquinonate complex is antiferromagnetic ($\mu = 1.89\ \mu_B$), and it is ferromagnetic in the corresponding copper(II) derivative ($\mu = 2.80\ \mu_B$). All the isolated complexes have been found to undergo to one-electron redox processes, and the reaction products have been characterized by electronic and EPR spectroscopy. Evidence is presented that oxidation of the dioxolene ligand originates the redox chain M(II)–Cat, M(II)–SQ, M(II)–Q (Cat = 3,5-di-*tert*-butylcatecholate, M = Ni, Cu; Cat = tetrachlorocatecholate, M = Ni; SQ = semiquinoate; Q = quinone), but it is apparent that the species Cu(I)–TCQ (TCQ = tetrachloro-*o*-benzoquinone) results from one-electron oxidation of the Cu(II)–TCCat complex. The electronic spectra of all the stable species are reported and assigned. The role of the electronic structure of the adducts in determining the physical properties and the reactivity is discussed.

Introduction

Adducts between paramagnetic metal ions and organic radicals provide stimulating examples for understanding the interactions between separate paramagnetic centers.[1-29] Among the most intensively studied systems are those formed by nitroxides[2,4-15] and semiquinones.[1,3,17-29] Since the latter are much stronger ligands than the former, any interaction may be predicted to be more intense for semiquinones than for nitroxides.

Most semiquinone complexes so far investigated have been found to exhibit a strong antiferromagnetic coupling,[1,3,17-23] a feature that often has caused ambiguities about the proper formulation of the correct formal oxidation state of the metal ions

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