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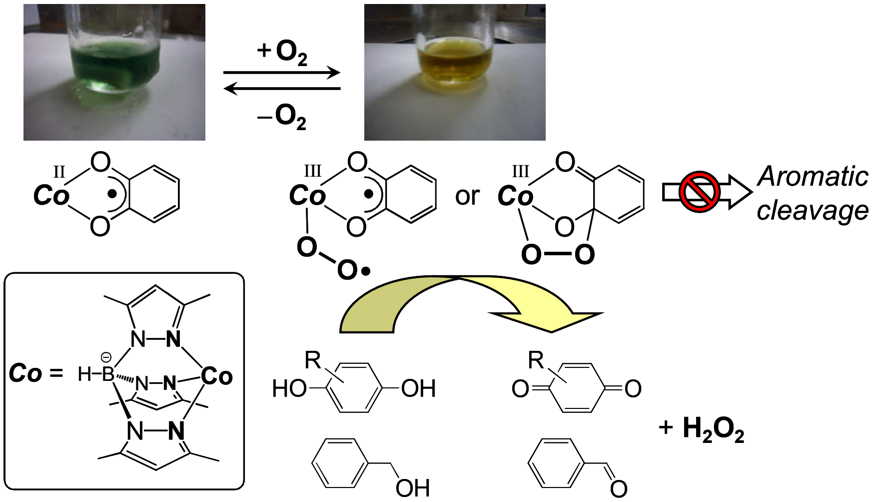
Short text and Figure for TOC

A cobalt(II)-semiquinonato complex can bind O_2 at low temperature and catalyzes aerobic oxidations of hydroquinones and alcohols concomitant with the generation of hydrogen peroxide.



O_2 activation and external substrate oxidation capability of Co(II)-semiquinonato complex

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Abstract

Synthesis, characterization and catalytic oxidizing activity of a cobalt(II)-semiquinonato complex with hydrotris(3,5-dimethyl-1-pyrazolyl)borate (= $\mathrm{Tp^{Me2}}$) have been investigated. The cobalt(II)-semiquinonato complex can be synthesized by two alternative routes that dehydrative condensation of a cobalt(II)-hydroxo complex with 3,5-di-*tert*-butylcatechol and following O_2 oxidation, or one-electron oxidation of catechol by a dinuclear cobalt(III)-bis(μ-oxo) complex. The synthesized cobalt(II)-semiquinonato complex can bind O_2 at low temperature and catalyzes the oxidation of *ortho*- and *para*-hydroquinones to the corresponding benzoquinones concomitant with the generation of hydrogen peroxide. The resulting H_2O_2 is utilized as oxidant for the epoxidation of allyl alcohol catalyzed by peroxotungstate. Aerobic oxidation of benzyl alcohol to the corresponding aldehyde is also promoted by the cobalt(II)-semiquinonato complex.

Introduction

Oxidation of organic compounds with molecular oxygen is still important subject for modern synthetic chemistry in order to develop the environmentally benign chemical transformation processes.[1] Some metalloenzymes catalyze organic compounds oxidation with O_2 under physiological mild condition. Therefore, design and synthesis of O_2 activating complexes of transition metals are attractive approach to green oxidation catalysts based on bio-inspired concept.[2]

In the active sites of some non-heme metalloenzymes such as galactose oxidase[3] and catechol dioxygenases,[4] redox-active ligand complexes are formed during the catalytic cycles. The ligand-based radical might work as an accepter of another radicals such as H atom derived from substrate and metal-bound superoxide anion radical (= $O_2^{-}\bullet$). As well as the radical trapping, intramolecular electronic communication between the metal center and the redox-active ligands are indispensable for the emergence of catalysis. Therefore, combination of redox-active ligands and transition metal ions is interesting approach for designing the bio-inspired oxidation catalyst.[5]

To date, a large number of redox-active transition metal complexes with dioxolene ligands have been investigated. The chemistry of iron-dioxolene complexes have been extensively attracted much attention because of the relevance to catechol dioxygenases, which catalyze oxidative aromatic ring cleavage to carbonyl compounds.[6] Copper-dioxolene complexes have also been investigated from an interest in catecholases, which catalyze oxidation of catechols to quinones.[7] Cobalt complexes with dioxolene ligands, including cobalt(II)-semiquinonato and cobalt(III)-catecholato complexes, have been investigated mainly from the viewpoint of their unique electronic configuration and magnetism.[8] However, O_2 reduction capability as well as organic substrate oxidation potential of cobalt(II)-semiquinonato complexes have not been turned attention so far, although O_2 binding ability and oxidizing catalyses of the same group 9 metal complexes (Rh and Ir) have been investigated.[9] As similar to the active site of the non-heme metalloenzymes mentioned above, the cobalt(II)-semiquinonato complexes are composed of the radical ligand and the redox-active transition metal center. Therefore, such complexes are expected to show multi-electronic oxidaizing activity. In this study, potentials of a cobalt(II)-semiquinonato complex, $[Co^{II}(DTBSQ)(Tp^{Me2})]$ (**1**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate, DTBSQ = 3,5-di-*tert*-butylsemiquinonate) to promote biomimetic oxidation of OH-containing substrates have been explored.

Results and discussion

Synthesis and characterization of cobalt(II)-semiquinonato complex 1

Compound **1** could be synthesized according to the similar procedures for the previously reported cobalt(II)-semiquinonato complexes.[10] Oxidation of the stoichiometric reaction mixture of $DTBCH_2$ and the cobalt(II)-hydroxo complex, $[(Co^{II}Tp^{Me2})_2(\mu\text{-}OH)_2]$ (**2**),[11] yielded a dark green compound **1** (Scheme 1). UV-vis spectral pattern of **1** was similar to that of the bulky Tp^R ligand analogue, $[Co^{II}(DTBSQ)(Tp^{Cum,Me})]$ ($Tp^{Cum,Me}$ = hydrotris(3-cumyl-5-methylpyrazolyl)borate) reported by Pierpont and coworkers[10]; both complexes exhibited the strong LMCT band around 380 nm as well as the semiqunonate ligand-based absorption bands around 300 nm and 720 nm (Fig. 1(a)). In addition, **1** showed paramagnetically-shifted ^1H NMR signals from –62 to +61 ppm region at room temperature (Fig. S1). These spectral characteristics support the assignement of **1** as the cobalt(II)-semiquinonato complex. These spectral features are very similar to those of an an analogous cobalt(II)-DTBSQ complex with Tp^{Me3} (= hydrotris(3,4,5-trimethylpyrazolyl)borate), of which the molecular structure has been confirmed by X-ray crystallography (See Figs. S2 and S3 and Tables S1 and S2 in supporting information). The shortening of the O–C lengths and the lost of aromaticity of the six-membered ring imply the dioxolene ligand is semiquinonate as found in the Pierponts' compound.[10]

[Scheme 1]

[Fig. 1]

Compound **1** could be synthesized alternatively by reaction of a dinuclear cobalt(III)-bis(μ-oxo) complex, $[(Co^{III}Tp^{Me2})_2(\mu\text{-}O)_2]$ (**3**),[11] with two equiv. of $DTBCH_2$ under argon (Scheme 1). When one equiv. of $DTBCH_2$ was added, 50 % of **3** was consumed to yield **1**. This fact suggests that the formation of the cobalt(II)-SQ species **1** proceeds through $1e^-$ oxidation of $DTBCH_2$ by **3**, or reaction of a basic oxo ligand of **3** with $DTBCH_2$ yielding a putative cobalt(III)-catecholato species and following intramolecular electron transfer from the catecholate ligand to cobalt. It should be noted that reaction of dinuclear copper(III)-bis(μ-oxo) species with $DTBCH_2$ lead to $1e^-$ or $2e^-$ oxidation of catechol depending on the metal supporting ligands: a 1,4,7-tribenzyl-1,4,7-triazacyclononane ligand complex plays as a $1e^-$ oxidant to yield a copper(II)-SQ species, whereas an *N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine ligand complex works as a $2e^-$ oxidizing reagent to give *o*-benzoquinone.[12]

Compound **1** exhibited an affinity toward O_2 as shown in Fig. 1.

Introduction of O_2 to the CH_2Cl_2 solution of **1** at low temperature (203 K) resulted in the color change from dark green to pale brown, and the initial dark green color was recovered by evacuation even at 203 K (Fig. S4). Such color change were not observed under argon atmosphere at 195 K and under O_2 atmosphere at ambient temperature. Therefore, an O_2 adduct of **1** (= **1**•O_2) forms in the pale brown solution, but we have not met with success to isolate **1**•O_2 due to low O_2 binding affinity of the cobalt center of **1**. To date, the molecular structure of the alkylperoxo complexes of rhodium(III) and iridium(III), which are derived from the reaction of O_2 with the corresponding catecholato precursors have been charactrized.[9c,d] In line with an analogy of the catecholase activity of **1**•O_2 and the iridium(III)-alkylperoxo complex with tridentate phosphine ligand[9c] (see below), it is plausible that an assignment of **1**•O_2 is a cobalt(III)-alkylperoxo species (Compound **P** in Scheme 2). Disappearance of the absorption band of **1** around visible to near-IR region (~ 720 nm) upon contacts with O_2 at low temperature seems to suggest the lost of radical character of the dioxolene ligand,[10] and that is consistent with the structure of the postulated alkylperoxo complex. At this moment, however, we cannot exclude the possibility that **1**•O_2 is a cobalt(III)-superoxo species with DTBSQ ligand (Compound **S** in Scheme 2).[13] Attempt to detect an O–O vibration by IR spectroscopy of the solution of the *in situ* generated **1**•O_2 at 193 K was failed (Fig. S5).

[Scheme 2]

Previously, we have demonstrated that a related iron(III)-catecholato complex, [Fe^{III}(DTBC)(Tp^{iPr2})] (**4**; Tp^{iPr2} = hydrotris(3,5-di-*iso*-propylpyrazolyl)borate, DTBC = 3,5-di-*tert*-butylcatecholate), exhibits catechol dioxygenase activity: The iron-bound DTBC ligand is converted to the corresponding oxygenated compounds (intra- and extradiol cleavage products) and no DTBQ (= 3,5-di-*tert*-butylquinone) is formed upon stoichiometric reaction (i.e., reaction of **4** with O_2 in the absence of external $DTBCH_2$).[14] In an analogous manganese chemistry, reaction of DTBCH and a dinuclear manganese(III)-bis(μ-oxo) complex with Tp^{iPr2} yields an O_2 sensitive manganese(II)-semiquinonato complex, $[Mn^{II}(DTBSQ)(Tp^{iPr2})]$ (**5**), and reaction of **5** and O_2 yields the both intra- and extradiol cleavage products as well as DTBQ.[15] In contrast to these iron and manganese analogues **4** and **5**, further oxidation of the coordinated semiquinonate ligand giving oxidative ring-cleavage products did not occur from **1**•O_2. Notably, the cobalt(II)-substituted extradiol enzyme retains primary catalytic activity.[16] The postulated intermediates in the enzymatic system are cobalt(II)-SQ-O_2^-• and cobalt(II)-alkylperoxo species and following O–O activation will lead to the oxygenation of the substrate. No dioxygenase activity of **1**•O_2 might arise from the difference of the oxidation state of the cobalt centre. In our synthetic compound system, the oxidation state of the cobalt center of **1**•O_2 is +3 and further O–O activation is difficult due to high oxidation potential of cobalt(III) to cobalt(IV).

Hydroquinone oxidation and concomitant H_2O_2 generation catalyzed by 1

Compound **1** exhibited catecholase activity, although the structure of **1** is different from the dicopper active site of the enzyme. O_2 oxidation of *ortho*- and *para*-hydroquinones to the corresponding benzoquinones were catalyzed by **1** as summarized in Table 1.[17] Not only the non-substituted and alkyl-substituted *para*-hydroquinones but also a halogenated derivative were oxidized although the reaction rate for the halogenated substrate was relatively low (Fig. S6). Oxidation rates of hydroquinone were depended on the reaction conditions as shown in Fig. S7.

[Table 1]

As similar to the previously reported iridium(III)-catecholato complex,[9c] hydrogen peroxide was formed concurrent with the consumption of the hydroquinone substrates.[18,19] When less water-soluble DTBCH$_2$ was used as a substrate, the catalytically generated H_2O_2 could be extracted to an aqueous phase under organic (toluene) – water (acetate buffer; pH 4.4) biphasic condition. In toluene phase, DTBCH$_2$ was oxidaized to DTBQ by action of **1** (1 mol %) under O_2 (1 atm) at 313 K. At the same time, generated H_2O_2 was extracted to 2.0 mL of the aqueous phase, and the concentration of H_2O_2 was 0.13 mol/L (34 % of the generated DTBQ) determined by iodometry (entry 1 of Table 2).

[Table 2]

Also, we examined trapping of H_2O_2 by easy-oxidizable substrate Ph_3P in homogeneous reaction media. Co-existence of *para*-hydroquinone and Ph_3P with **1** in the homegeneous solution resulted in the catalytic oxidation of the both substrates (Fig. 2 and entry 2 of Table2). In the absence of hydroquinone, **1** could not catalyze Ph_3P oxygenation. Therefore, the catalytically generated H_2O_2 during hydroquinone oxidation was trapped by Ph_3P. In contrast to the sole hydroquinone substrate system, the presence of Ph_3P affected the oxidation rate of hydroquinone (Fig. S8): Ph_3P seems to work as a competitive inhibitor for the O_2 activation by the cobalt center of **1**, whereas the consumption of H_2O_2 by Ph_3P leads to accelate catalytic turnover. Notably, the rhodium-catecholato complex catalyzes Ph_3P

oxygenation with O_2.[9a] Lack of the oxygen atom-transfer ability of **1**•O_2 implies hardness of further O–O bond activation, and that may be consistent with no dioxygenase activity toward the DTBSQ ligand. In general, stoichiometry of the substrate to oxidant in the O_2 oxidation of hydroquinones by metal catalysts is represented as hydroquinones:O_2 = 2:1. One plausible explanation for this stoichiometry is that the redox active catalyst mediate the disproportionation of the intermediary generated H_2O_2 to water and O_2.[20] In contrast, compound **1** was inactive for H_2O_2 degradation and that resulted in the catalytic generation of H_2O_2.

[Figure 2]

The biphasic reaction system could be applied to oxidation of another organic compound. Combination with a H_2O_2-activating peroxotungstate catalyst, $[\{W(=O)(\eta^2\text{-}O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ (**6**),[21] resulted in the catalytic epoxidation of allyl alcohol concomitant with the O_2 oxidation of $DTBCH_2$ catalyzed by **1** (entry 3 of Table 2). Catalytic $DTBCH_2$ oxidation by **1** with O_2 proceeded in the organic solvent (toluene) phase, and the resulting H_2O_2 was extracted in water phase and consumed for the epoxidation of allyl alcohol catalyzed by **6** (Scheme 3). In this catalytic epoxidation reaction, O_2 and $DTBCH_2$ (hydroquinone) are formally oxidant and reductant, respectively.[22] From biomimetic viewpoints, the redox of quinone/hydroquinone is often utilized as the electron transfer mediator for the turnover of the catalysts of the oxidation reactions.[23] Taking the place of NADH in biological system, hydroquinones work as proton and electron source in our system, and the combination with the reductive O_2 activation and H_2O_2 activation systems leads to mimic the reaction catalyzed by monooxygenases.

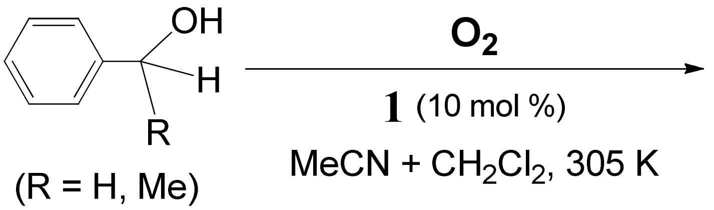
[Scheme 3]

It should be noted that the cobalt(II)-hydroxo complex **2**, which is the precursor of **1**, also catalyzed oxidation of *para*-hydroquinones to the corresponding benzoquinones. When hydroquinone was a sole substrate, TOF of **2** (> 20 min^{-1}) was higher than that of **1** (ca. 1.5 min^{-1}). When both hydroquinone and Ph_3P were used as co-substrate, however, only a trace amount of $Ph_3P{=}O$ was yielded upon the reaction by **2**. These facts suggest that the catalytic reaction mechanism of **1** is different from that of **2**, and the DTBSQ ligand of **1** might remain to coordinate during the oxidation of *para*-hydroquinones. A candidate of the active oxidant for 2e^{-} oxidation of the hydroquinones coupled with H_2O_2 generation is the alkylperoxo species (**P** in Scheme 2) as well as the iridium complex.[9c] Another candidate is the cobalt(III)-DTBSQ-O_2^{-}• species (**S** in Scheme 2), which may be a transient intermediate from **1** to the alkylperoxo species: The superoxide ligand captures H atom and H^+ from substrate to give H_2O_2. Electron transfer from the resulting semiquinonate radical (derived from the substrate) to the cobalt(III) center leads to turnover to **1**.

Alcohol oxidation capability

We also examined aerobic alcohol oxidation ability of **1**, because **1** is composed of the radical ligand with the redox-active transition metal center and this composition is similar to that of the active species of the galactose oxidase.[3,24,25] Galactose oxidase catalyzes oxidation of primary alcoholic moiety of substrate to the corresponding aldehyde product concomitant with reduction of O_2 to H_2O_2. An active site of the enzyme is a mononuclear copper complex with a cysteine-cross linked tyrosine radical ligand. This unique phenoxy-radical ligand is proposed as a hydrogen atom acceptor from the C–H moiety adjacent to OH of the alcoholic substrate. Two electron oxidation of alcohol to aldehyde is achieved due to combination of the H atom capturing by the radical ligand and an electron transfer from the substrate to the copper(II) center giving a copper(I) species.[3, 24]

An aerobic oxidation of benzyl alcohol to benzaldehyde was mediated by **1** (eq. 1). A Michaelis-Menten type kinetics, as was evidenced by dependence of the initial reaction rate on the catalyst condensation and a liner Lineweaver-Burk plot (Fig. S9), suggest that this reaction proceeds through the catalyst-alcohol complex intermediate. The yield of acetophenone derived from oxidation of 1-phenylethanol (secondary alcohol) was lower than that of benzaldehyde from benzylalcohol (Fig. 3), and this result also supports the mechanism through the the catalyst-alcohol complex because of the steric hindrance of benzylacohol is lower than that of 1-phenylethanol.[26] Oxidation of Ph_3P occurred on the co-substrates system (Fig. S10) and that suggests the concomitant H_2O_2 generation as found in the hydroquinone/Ph_3P system. However, the reaction rate was not so high and the reaction was terminated before the turn over numbers of catalyst **1** reached to 2 under any conditions. Moreover, the alcohol oxidation did not occur in the absence of O_2. Thus, **1** itself could not work as $2e^-$ oxidant, and the reaction mechanism of the alcohol oxidation mediated by **1** might be diffent from that mediated by the enzyme. In the enzymatic process, both copper(II) center and the phenoxy radical of the cysteine-cross linked tyrosine ligand play as a $1e^-$ acceptor, and that leads to complete $2e^-$ oxidation of alcohol to aldehyde. In contrast, the cobalt(II) center of **1** cannot work as a $1e^-$ acceptor, and therefore, O_2 is essential to oxidize cobalt(II) to cobalt(III). Several examples of alcohol oxidation by radical ligand-containing copper complexes have been reported so far.[25] To our knowledge, the present result is the first example of Co(II)-semiquinonato complex mediated reaction, although the reaction mechanism is not clear.



(eq. 1)

[Figure 3]

Conclusion

The cobalt(II)-semiquinonate complex **1** can be synthesized by oxidation of the cobalt(II)-catecholato species generated by reaction of the cobalt(II)-OH precursor with catechol, or anaerobic reaction of the cobalt(III)-oxo species with catechol. Compound **1** shows affinity toward O_2. Moreover, compound **1** exhibits catecholase rather catechol dioxygenase activity. During the catalytic oxidation of hydroquinones to benzoquinones mediated by **1**, concomitant H_2O_2 generation occurs. Such O_2 activating and catecholase like behaviours of **1** are similar to those of the previously reported iridium-catecholato complex. Biomimetic monooxygenase-type oxygenation process can be composed by combination of the hydroquinone oxidation catalyzed by **1** with another appropriate H_2O_2 activating system. The cobalt-based radical ligand complex **1** also promoted the O_2 oxidation of alcohols to the corresponding carbonyl compounds, although catalytic performance is low. Our findings demonstrate the redox active dioxolene ligand plays important roles for the emergence of oxidation catalyses.

Experimental Section

General

All manipulations were performed under argon by standard Schlenk techniques. Solvents used in this study (CH_2Cl_2, toluene, MeCN) were purified by Glass Counter System by Grubbs' method. The other reagents of the highest grade commercially available were used without further purification. The starting materials of **1**, i.e. cobalt(II)-hydroxo complex **2** and dinuclear cobalt(III)-bis(μ-oxo) complex **3**,[11] and the olefin epoxidation catalyst, $K_2[\{W(=O)(\eta^2\text{-}O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$ (**6**),[21] were prepared by the methods described previously. IR measurements were carried out as KBr pellets using JASCO FT/IR-4200 spectrometer. IR spectra of the solution samples were recorded using a Mettler Toledo ReactIR iC10. ^{1}H NMR spectra were recorded on JEOL JNM EX-270 spectrometer. Chemical shifts (δ) were reported in ppm downfield from internal $SiMe_4$. UV-vis spectra were recorded on JASCO V-670 spectrometer. Gas chromatographic (GC) analyses were carried out on Shimadzu GC-2010 instrument with a flame ionization detector equipped with RESTEK Rtx-1 or Rtx-1701 (30 m, 0.25 mmID, 0.25 μmdf) capillary columns. GC-MS analyses were carried out on Shimadzu PARVUM2 system equipped with RESTEK Rxi-5MS (30 m, 0.25 mmID, 0.25 μmdf) capillary column.

Synthesis of the Co(II)-semiquinonato complex [Co^{II}(DTBSQ)(Tp^{Me2})] (1)

The hydroxo complex **2** (82 mg; 0.11 mmol) was dissolved in 30 mL of CH_2Cl_2 under argon. To this solution, toluene solution (10 mL) of $DTBCH_2$ (51 mg; 0.23 mmol) was added. The reaction mixture was exposed to O_2 (1 atm) and stirred for 2 h. The voletiles were evaporated under vacuum, then recrystallization of the resulting solid from MeCN at 243 K afforded the dark green powder of **1** (72 mg; 0.12 mmol; 55% yield based on **2**). Anal. Calcd for $C_{29}H_{42}N_6O_2BCo$ (**1**): C, 60.43; H, 7.34; N, 14.58.

Found: C, 59.95; H, 6.83; N, 14.08. IR (KBr, ν/cm^{-1}): 2508 (BH). UV-vis (CH_2Cl_2, r.t., nm, ε/M^{-1}cm^{-1}): 305 (2990), 329 (sh, 2220), 379 (2100), 596 (180). ^{1}H NMR ($CDCl_3$, r.t.): δ_H –61.8 (9H), –2.9 (9H), 9.8 (9H), 37.5 (3H), 39.2 (9H), 61.2 (1H).

Catalytic oxidation

Catalyst **1** (10 μmol), substrate (hydroquinones and alcohols; 1.0 mmol) and decane (an internal standard for quantitative analysis by GC; 0.10 mmol) were dissolved in MeCN (4 mL) under argon atmosphere and then degassed by freeze-pump-thaw cycles (twice). This degassed reaction solution was exposed to O_2 (1 atm) and stirred at 305 K, and analyzed by gas chromatography.

H_2O_2 detection experiment

Generated H_2O_2 (derived from $DTBCH_2$ oxidation) was directly detected by extraction to water. $DTBCH_2$ (1.0 mmol) and 1 mol % of **1** (10 μmol) were dissolved in toluene (2.0 mL) under argon atmosphere. Acetate buffer solution (pH 4.4; 2.0 mL) was added to this toluene solution and then degassed by freeze-pump-thaw cycles (twice). This degassed reaction solution was exposed to O_2 (1 atm) and stirred at 313 K for 24 h. The organic phase was analyzed by gas chromatography with internal standard, and the yield of DTBQ was 77 % (0.77 mmol; based on initial $DTBCH_2$). The concentration of H_2O_2 in aqueous phase was 0.13 mol/L determined by iodometry.

Co-oxidation of para-hydroquinone and Ph_3P with O_2 catalyzed by 1

Catalysts **1** (10 μmol), *para*-hydroquinone (100 μmol), and Ph_3P (100 μmol) were dissolved in the mixture of MeCN (2.0 mL) and CH_2Cl_2 (2.0 mL) under argon and then degassed by freeze-pump-thaw cycles (twice). This degassed reaction solution was exposed to O_2 (1 atm) and stirred at 305 K for 90 min. The organic products were analyzed by GC. The final yields of products: benzoquinone, 87 μmol; $Ph_3P=O$, 64 μmol.

Co-oxidation of $DTBCH_2$ and allylalcohol with O_2

Catalysts **1** (10 μmol) and the potassium salt of **6** (=$K_2[\{W(=O)(\eta^2\text{-}O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$; 5.0 μmol), $DTBCH_2$ (1.0 mmol), and allylalcohol (2.5 mmol) were dissolved in the mixture of toluene (2.0 mL) and acetate buffer solution (pH 4.4; 2.0 mL) under argon and then degassed by freeze-pump-thaw cycles (twice). This degassed reaction solution was exposed to O_2 (1 atm) and stirred at 313 K for 24 h. The organic products were analyzed by GC. The yields of products: DTBQ, 0.17 mmol; glysidol, 0.13 mmol.

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Frediani, A. Meli and F. Vizza, *Inorg. Chem.*, 1992, **31**, 1523 – 1529; (*d*) S. Dutta, S.-M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2000, **39**, 2231 – 2234; (*e*) A. Bencini, E. Bill, F. Mariotti, F. Totti, A. Scozzafava and A. Vargas, *Inorg. Chem.*, 2000, **39**, 1418 – 1425.

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Angew. Chem. Int. Ed., 2007, **46**, 3567 – 3570.

25 (*a*) F. Thomas, *Eur. J. Inorg. Chem.*, 2007, 2379 – 2404, and references cited therein ; (*b*) S. Itoh, M. Taki, S. Takayama, S. Nagatomo, T. Kitagawa, N. Sakurada, R. Arakawa and S. Fukuzumi, *Angem. Chem. Int. Ed.*, 1999, **38**, 2774 – 2776.

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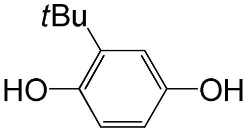
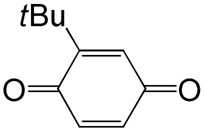
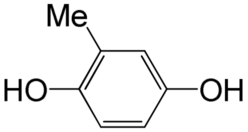
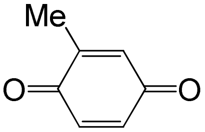
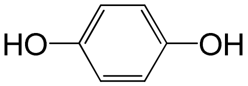
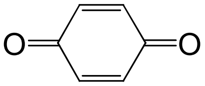
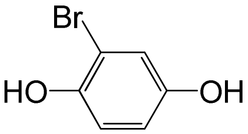
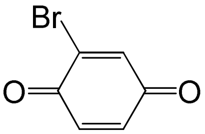
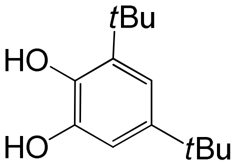
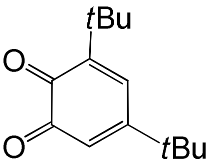
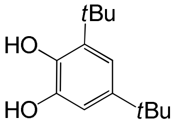
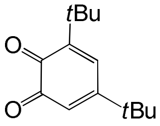
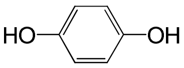
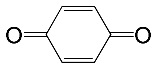
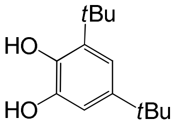
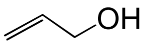
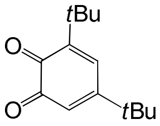
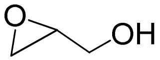
Table 1. Oxidation of hydroquinones with O_2 catalyzed by **1**

Entry	Substrate	Product	Reaction time [min]	Yield [%]
1			15	>98
2			60	98
3			120	88
4			180	14
5			1440	52

Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 1.0 mmol; O_2, 1 atm; solvent (MeCN), 4.0 mL; reaction temperature, 315 K. The yields were determined by gas chromatography.

Table 2. Trapping of H_2O_2 generating through the catalytic O_2 oxidation of hydroquinones by **1**. [a]

Entry	Solvents (condition)	Hydroquinone (amount / mmol)	Substrate (amount / mmol)	Benzoquinone (amount / mmol)	Product (amount / mmol; yield based on benzoquinone)
1	Toluene/acetate buffer (biphase)	 (1.0 mmol)	none	 (0.77 mmol)	H_2O_2 (0.26 mmol; 34 %)
2	MeCN / CH_2Cl_2 (homogeneous)	 (0.10 mmol)	Ph_3P (0.10 mmol)	 (0.087 mmol)	$Ph_3P{=}O$ (0.064 mmol; 74 %)
3	Toluene/acetate buffer (biphase)	 (1.0 mmol)	 (2.5 mmol)	 (0.17 mmol)	 (0.13 mmol; 76 %)

[a] Detail reaction conditions are stated in experimental section.

List of the Legends of Schemes and Figures

Scheme 1 Synthesis of **1**.

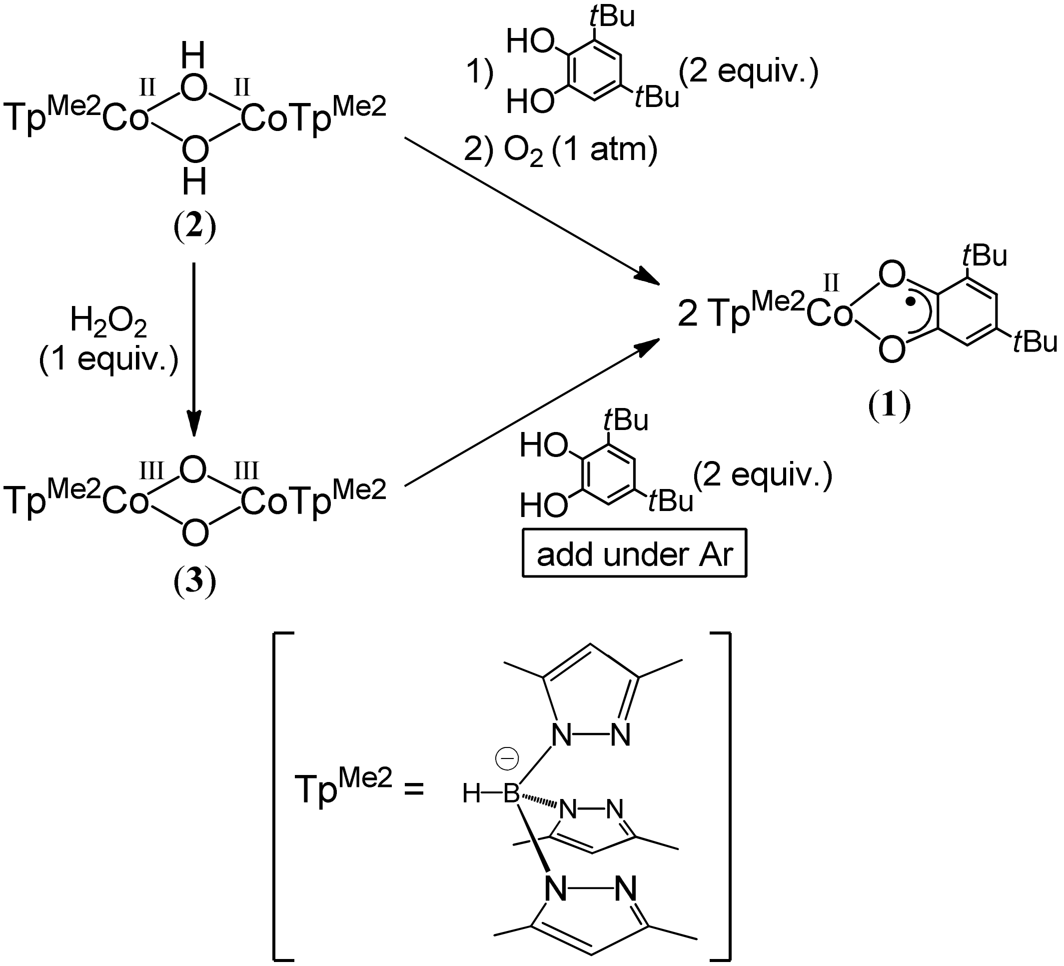
Scheme 2 Reaction of **1** with O_2.

Scheme 3 Biphasic system composed of **1** and peroxotungstate catalyst (**5**) for O_2 epoxidation of allyl alcohol.

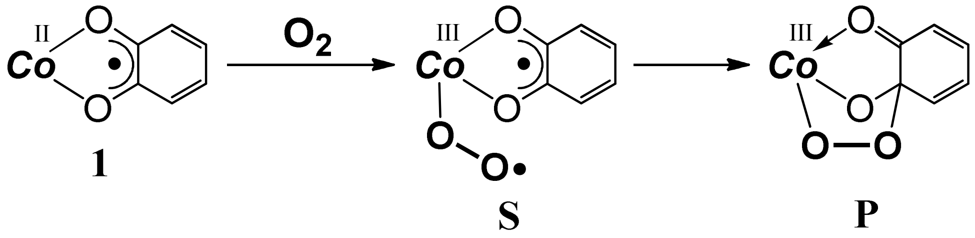
Fig. 1 UV-vis spectra of a CH_2Cl_2 solution of **1** and *in situ*-generated dioxygen adduct of **1** (= **1**•O_2) recorded at 203 K. (a: solid line) spectrum of **1** under argon atmosphere (b: gray line) spectrum of **1**•O_2 under O_2 atmosphere.

Fig. 2 Time course for the co-oxidation of *para*-hydroquinone and triphenylphosphine with O_2 catalyzed by **1**. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 100 μmol; O_2, 1 atm; solvent (1:1 mixture of CH_2Cl_2 and MeCN), 4.0 mL, Reaction temperature, 305 K.

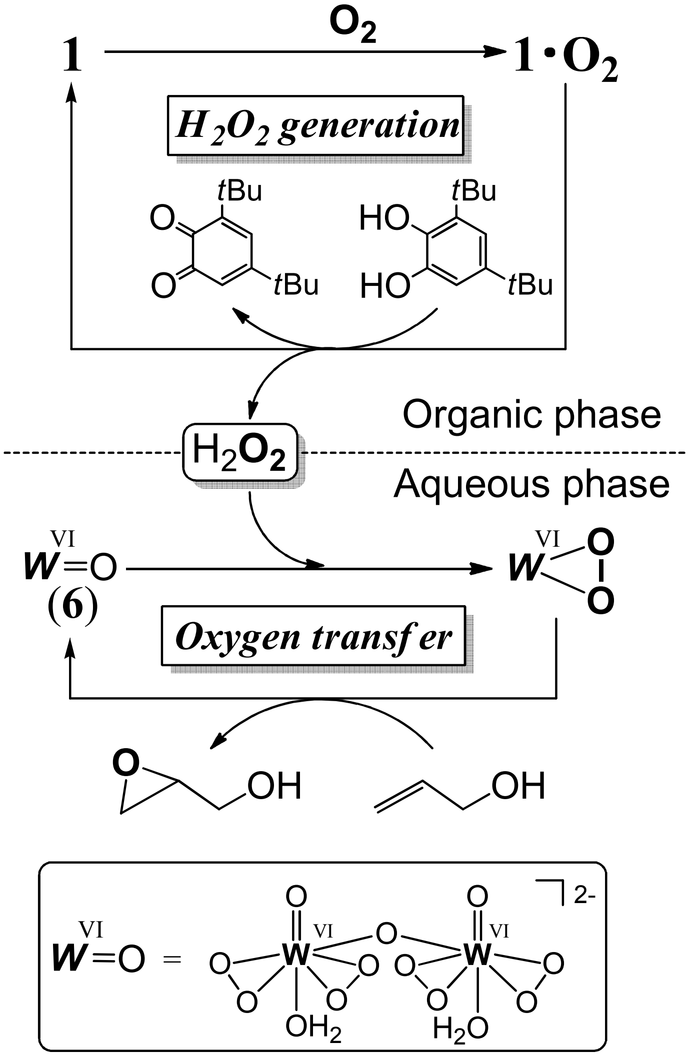
Fig. 3 Time course for the aerobic oxidation of primary and secondary alcohols mediated by **1**. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 100 μmol; O_2, 1 atm; solvent (1:1 mixture of CH_2Cl_2 and MeCN), 4.0 mL, Reaction temperature, 305 K. The yields were determined by gas chromatography.



Scheme 1 Synthesis of **1**.



Scheme 2 Reaction of **1** with O_2.



Scheme 3 Biphasic system composed of **1** and peroxotungstate catalyst (**6**) for O_2 epoxidation of allyl alcohol.

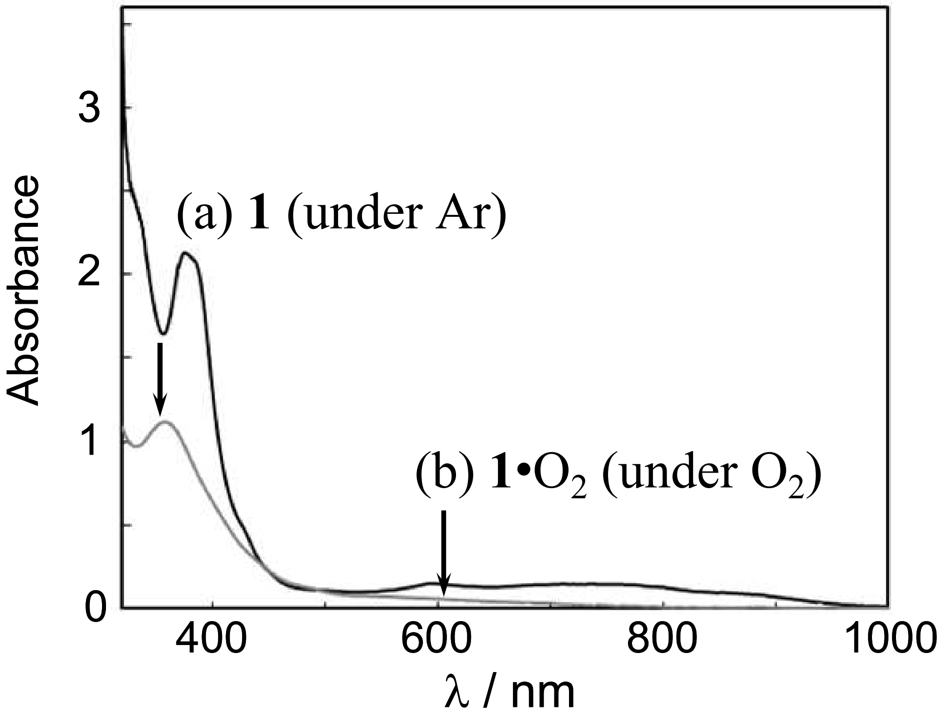


Fig. 1 UV-vis spectra of a CH_2Cl_2 solution of **1** and *in situ* generated dioxygen adduct of **1** (= **1**•O_2) recorded at 203 K. (a: solid line) spectrum of **1** under argon atmosphere (b: gray line) *in situ* generated **1**•O_2 under O_2 atmosphere.

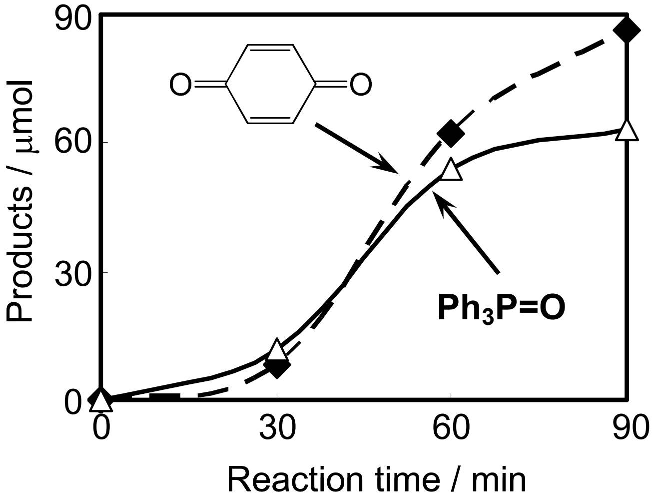


Fig. 2 Time course for the co-oxidation of *para*-hydroquinone and triphenylphosphine with O_2 catalyzed by **1**. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 100 μmol; O_2, 1 atm; solvent (1:1 mixture of CH_2Cl_2 and MeCN), 4.0 mL, Reaction temperature, 305 K.

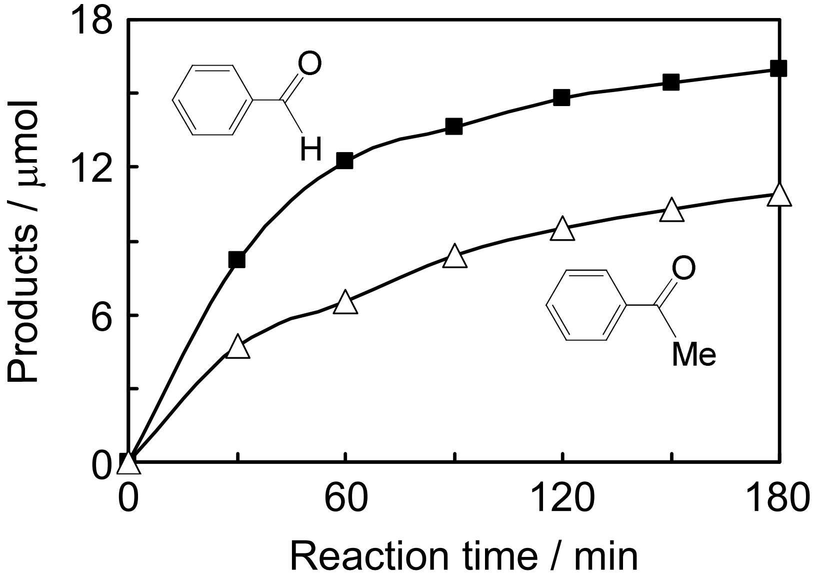


Fig. 3 Time course for the aerobic oxidation of primary and secondary alcohols mediated by **1**. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 100 μmol; O_2, 1 atm; solvent (1:1 mixture of CH_2Cl_2 and MeCN), 4.0 mL, Reaction temperature, 305 K. The yields were determined by gas chromatography.