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New aspects of the cobalt-dioxygen complex chemistry opened by hydrotris(pyrazoly)borate ligands ($\mathrm{Tp^R}$): unique properties of $\mathrm{Tp^RCo}$-dioxygen complexes

Shiro Hikichi *, Munetaka Akita, Yoshihiko Moro-oka

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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* Corresponding author. Tel.: +81-45-924-5230; fax: +81-45-924-5226.
E-mail address: shikichi@res.titech.ac.jp (S. Hikichi)

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Abstract

Recent advances in the chemistry of cobalt-dioxygen and related complexes supported by hydrotris(pyrazolyl)borate ligands (Tp^R) are reviewed. The unique properties of inorganic and organometallic Tp^RCo complexes clearly indicate that hindered Tp^R ligands carrying alkyl substituents on the pyrazolyl groups can stabilize the coordinatively unsaturated, low valent cobalt species, and that the reactivity of the coordinatively unsaturated species is influenced by steric hindrance of Tp^R. The unusual low-valent metal-peroxo and high-valent metal-oxo species such as Co^{II}-superoxo, -alkylperoxo and dinuclear Co^{III}-bis(μ-oxo) complexes are characterized. The high-valent metal-oxo species, $[Tp^RCo^{III}]_2(\mu\text{-}O)_2$, are capable of abstracting the H atom from the alkyl groups proximal to the bimetallic bis(μ-oxo) core. In the hydrotris(3,5-diisopropyl-1-pyrazolyl)borate ligand system ($Tp^{Pr^i_2}$), oxygenation of the proximal isopropyl substituents on $Tp^{Pr^i_2}$ is mediated by the Co_2^{III}-$(\mu\text{-}O)_2$ and Co^{II}–OOX (X = alkyl, H) species. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dioxygen complex; Cobalt; Hydrotris(pyrazolyl)borate; O–O bond activation; Aliphatic C–H bond activation

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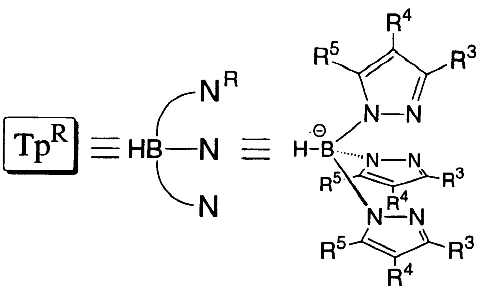
1. Introduction

The synthesis and characterization of transition metal-dioxygen complexes are long-standing attractive subjects, because metal-peroxo (M–OOX; X = none, metal, H, alkyl, acyl) and related high-valent metal-oxo (M=O) species take part in various synthetic and biological oxidation processes as key reaction intermediates [1]. From the viewpoint of bioinorganic chemistry, the structural and physicochemical properties and reactivity of the dioxygen complex have been investigated in order to understand the mechanism of oxygen metabolism such as O_2 transport, storage and activation, which are essential events for life [2]. Interest in the oxidative transformation of various organic compounds mediated by metalloenzymes containing transition metal in their active sites has recently grown from the standpoint not only of bioinorganic but also synthetic and catalytic chemistry, because such biological reactions proceed under relatively mild conditions and will be able to solve economical and environmental problems.

Cobalt has been the most studied element in synthetic metal-dioxygen complexes [3]. In fact, the first structurally determined transition metal-dioxygen complex was the dinuclear Co^{III}-μ-superoxo complex, $\{[(H_3N)_5Co^{III}]_2(\mu\text{-}O_2^-)\}^{5+}$, reported in 1966. In cobalt-dioxygen complex chemistry, it is known that the common oxidation state of the metal center is +3, which is kinetically very stable. Many Co^{III}-dioxygen complexes are formed via oxidative addition of O_2 to the corresponding Co^{II} precursors. In addition to the analogy of their oxidation behavior, Co is a neighbor of Fe in the periodic table. Therefore Co dioxygen complexes have been studied as synthetic models for O_2 metabolic Fe proteins, although neither a cobalt-dependent O_2 carrier nor oxygenase/oxidase is known so far. In the early biomimetic investigations, the relatively stable Co^{III}-dioxygen complexes provided much information on the structural and physicochemical properties of transition metal-dioxygen species relevant to the biological system [2a]. However, recent advances in instruments and techniques for handling unstable compounds allows us to study more reactive compounds such as Fe and Cu dioxygen complexes which are more closely related to the O_2-metabolic metalloproteins. In contrast to the Fe and Cu compounds, Co^{III} complexes (except some Co^{III}-alkylperoxo complexes, which can oxidize the external hydrocarbyl substrates,) do not exhibit remarkable oxidation capability due to their electrical disadvantage for further O–O bond activation. This is because further electron donation from Co^{III} to the antibonding σ^* orbital (LUMO) of the peroxide to cleave the O–O bond is difficult.

Cobalt catalysts are utilized for industrial catalytic oxidation processes such as the *p*-xylene oxidation giving terephthalic acid (Mid-Century/Amoco) and the adipic acid synthesis from cyclohexane (DuPont). It is believed that these catalytic processes involve Co^{III}-alkylperoxo intermediates, which assist autoxidation reactions (i.e. degradation of the alkylhydroperoxides to induce radical chain reaction). Because these oxidation reactions are carried out under high pressure and temperature, development of an efficient catalyst, which can generate radicals via O–O or Co–O bond homolysis under mild conditions (moderate temperature and pressure), is expected [4].

In contrast to the relatively stable Co^{III} dioxygen species, only a limited number of Co^{II} dioxygen complexes have been characterized. Especially, a family of the hydrotris(pyrazolyl)borate ligands (Tp^R; R denotes substituents of the pyrazolyl rings: see Chart 1) makes the unusual low-valent metal-dioxygen species isolable [5]. Actually, mono- and dinuclear superoxo and alkylperoxo complexes bearing Tp^R have been structurally characterized. Moreover, intramolecular aliphatic C–H bond oxidation has also been mediated by dinuclear Co^{III}-bis(μ-oxo) species resulting from O–O homolysis of a peroxide ligand. Such a new aspect of Co-dioxygen complex chemistry is opened by the unique properties of the Tp^R ligands. In this review article, we describe recent advances in Tp^RCo-dioxygen complexes and the related chemistry.

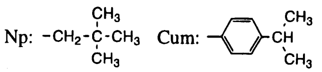


Tp^{R} ligands used for Co-dioxygen complexes

	R^3	R^4	R^5
Tp^{Me_3}	Me	Me	Me
Tp$^{Pr^i,Me}$	Pr^i	H	Me
Tp$^{Pr^i_2}$	Pr^i	H	Pr^i
Tp$^{Bu^t,Me}$	Bu^t	H	Me
Tp$^{Bu^t,Pr^i}$	Bu^t	H	Pr^i

Other Tp^{R} ligands appearing in this review

	R^3	R^4	R^5
Tp^{H_2}	H	H	H
Tp^{Me_2}	Me	H	Me
Tp^{Np}	Np	H	H
Tp$^{Bu^t}$	Bu^t	H	H
Tp^{Ph}	Ph	H	H
Tp^{Cum,Me}	Cum	H	Me


Np: $-CH_2-C(CH_3)_2-CH_3$

(Chart 1)

2. Coordination chemistry of the Tp^{R}Co system

A family of hydrotris(pyrazolyl)borate, Tp^{R}, ligands has been widely used as supporting ligands for various inorganic and organometallic compounds for three decades [5]. Its unique structural (i.e. facially capping tridentate ligand) and electronic characteristics (6e$^-$ donating monoanionic ligand) are similar to those of the family of cyclopentadienyl (Cp^{R}) ligands, which are the most commonly adopted ligands in organometallic chemistry. One of advantages of the tris(pyrazolyl)borate ligands is the ease of controlling the properties of the resulting metal complexes (coordination environment and reactivity of metal centers, solubility in organic solvents, facility of crystallization, etc.) by introduction of various substituents onto the pyrazole rings. It is notable that highly sterically demanding hydrotris(pyrazolyl)borate ligands containing bulky substituents at the 3-position of the pyrazole rings can stabilize a coordinatively unsaturated metal center and provide a vacant site for substrate binding. In addition, a hydrophobic shading pocket formed by the bulky substituents surrounding the metal center may kinetically stabilize unstable functional groups such as O–O and metal–carbon bond moieties.

Before discussion of the chemistry of the dioxygen complexes, we review some inorganic and organometallic Tp^{R}Co complexes in order to reveal their unique properties arising from the characteristics of Tp^R. This information may be helpful for understanding Co-dioxygen chemistry with Tp^R described later.

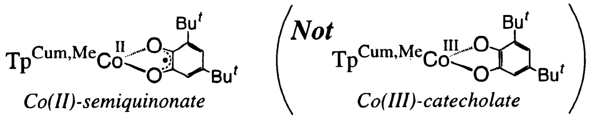
2.1. Inorganic chemistry of the Tp^RCo system

In general, the stable oxidation state for the cobalt ion is $+2$ or $+3$ [6]. In fact, a large number of Tp^RCo^{II} complexes have been synthesized and characterized to date, although Tp^RCo^{III} complexes are scarce.

2.1.1. Inorganic chemistry of Co^{II} and Co^{III} complexes

It is known that the Co^{II} ion takes various coordination numbers and geometries. To date, Trofimenko et al. and others have reported molecular structures of several $Tp^RCo^{II}(L)$ complexes with four-coordinated tetrahedral ($L =$ monodentate ligands such as I^- and NCS^-), five-coordinated square-pyramidal ($L = \kappa^2$-bis(pyrazolyl)borate) or trigonal-bipyramidal ($L = \kappa^2$-semiquinonate (see below)), and six-coordinated octahedral geometries ($L =$ less hindered κ^3-Tp^R ligand) [5a,7]. In the case of the coordinatively unsaturated species (i.e. four and five-coordinated Co^{II} complexes), coordination of σ-donating solvents such as MeCN and THF was observed. For example, a five-coordinated trigonal-bipyramidal NCS complex involving a THF solvate, $Tp^{Ph}Co^{II}(NCS)(THF)$ [7a], and an MeCN-adduct of the κ^2-NO_3 complex, $Tp^{Me_3}Co(\kappa^2\text{-}NO_3)(NCMe)$ [7i], were structurally characterized, whereas the non-solvated isothiocyanato and nitrato complexes with Tp^{Bu^t} contained the tetrahedral ($Tp^{Bu^t}Co^{II}(NCS)$ [7a]) and the distorted trigonal-bipyramidal cobalt centers ($Tp^{Bu^t}Co^{II}(\kappa^2\text{-}NO_3)$; see below), respectively.

Only a limited number of Tp^RCo^{III} complexes have been reported [8]. Remarkably, the metal centers of the structurally characterized Co^{III} complexes, except for our Co_2^{III}-$(\mu\text{-}O^{2-})_2$ complex (see below), are supported by the less hindered non-substituted Tp^{H_2} ligand. Co^{III} ion (d^6) strongly favors an octahedral geometry with a low-spin ($S = 0$) state [6] and, therefore, the substituted Tp^R ligands would distort the structure from an ideal octahedral geometry. For example, Pierpont et al. reported the very stable Co^{II}-semiquinonato complex with $Tp^{Cum,Me}$ (Chart 2), while the isoelectronic phosphine or Cp* ligands systems produced the corresponding Co^{III}-catecholato complexes [9]. The unusual stability of the divalent state of the Co center in the $Tp^{Cum,Me}$-semiquinonate complex is ascribed to the bulky three cumenyl substituents which prevent the formation of the stable octahedral coordination geometry.



Co(II)-semiquinonate

Co(III)-catecholate

(Chart 2)

2.1.2. Tp^RCo complexes relevant to bioinorganic chemistry

From the bioinorganic standpoint, the trigonally capping Tp^R can mimic the coordination environment made by three histidyl residues often found in metalloproteins (Fig. 1). Therefore, the Tp^{R} ligands have been applied to the studies of bioinorganic chemistry and various complexes of Mn, Fe, Cu and Zn have been investigated [5b,10].

The cobalt ion is an essential element for life, although it does not participate in O_2 metabolism. One of the topics of the bioinorganic chemistry of Co is a family of vitamin B_{12} that catalyzes *trans*-alkylation and isomerization via $\mathrm{Co}^{\mathrm{III}}$-alkyl intermediates [2a]. However, their Co centers are supported by a 15-membered macrocyclic corin ligand with a planar N_4-donor set similar to porphyrin, and so far the tripodal Tp^{R} ligands have not been used for the synthetic model study of vitamin B_{12}. Therefore, the bioinorganic approach to use $\mathrm{Tp}^{\mathrm{R}}\mathrm{Co}$ complexes has been focused on modeling the Co-substituted form of Cu or Zn metalloproteins. One example of a bioinorganic $\mathrm{Tp}^{\mathrm{R}}\mathrm{Co}$ complex is a tetrahedral thiolato complex, $\mathrm{Tp}^{\mathrm{Me}_2}\mathrm{Co}^{\mathrm{II}}(\mathrm{SC}_6\mathrm{F}_5)$, prepared as the structural model for the Co-substituted type I copper proteins which take part in electron transfer [11]. Another biologically important $\mathrm{Tp}^{\mathrm{R}}\mathrm{Co}$ species is related to carbonic anhydrase, which catalyzes the reversible conversion between CO_2 and H_2CO_3. It should be noted that Tp^{R} reproduces the coordination environment of the Zn center (i.e. facially capping three histidyl nitrogen donors) of carbonic anhydrase. In addition, $\mathrm{Co}^{\mathrm{II}}$ can replace the $\mathrm{Zn}^{\mathrm{II}}$ center of this enzyme while retaining enzymatic activity [12]. We [13] and Parkin et al. [14] have investigated the structural and functional model complexes of $\mathrm{Zn}^{\mathrm{II}}$ and $\mathrm{Co}^{\mathrm{II}}$ in order to gain insight into the role of the metal ion in carbonic anhydrase. Parkin and his coworkers prepared nitrato (NO_3^-) complexes of $\mathrm{Zn}^{\mathrm{II}}$, $\mathrm{Cu}^{\mathrm{II}}$, $\mathrm{Ni}^{\mathrm{II}}$ and $\mathrm{Co}^{\mathrm{II}}$ with $\mathrm{Tp}^{\mathrm{Bu}^t}$ as structural models for the substrate binding state of the enzyme; the coordination modes of the nitrate ligand (NO_3^-), which is isoelectronic with bicarbonate (HCO_3^-), depend on the kind of metal centers as shown in Fig. 2 [14a].

During the course of our model study for carbonic anhydrase, we found some interesting characteristics of the $\mathrm{Tp}^{\mathrm{R}}\mathrm{Co}^{\mathrm{II}}$ system. A dinuclear $\mathrm{Co}^{\mathrm{II}}$ bis(μ-hydroxo) complex, $[\mathrm{Tp}^{\mathrm{Pr}^i_2}\mathrm{Co}^{\mathrm{II}}]_2(\mu\text{-OH})_2$ (**1a**), readily reacted with atmospheric CO_2 to give a μ-carbonato complex, $[\mathrm{Tp}^{\mathrm{Pr}^i_2}\mathrm{Co}^{\mathrm{II}}]_2(\mu\text{-CO}_3)$ (Eq. 1) [13]. This observation implies

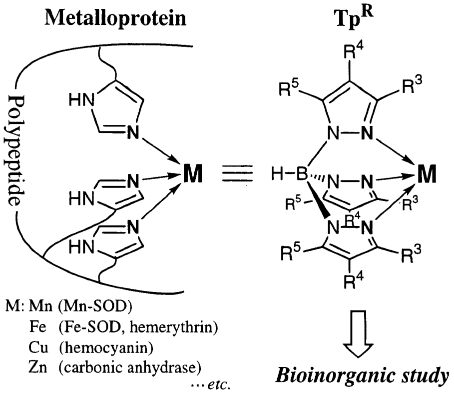


Fig. 1. Concept of the application of Tp^{R} to bioinorganic chemistry.

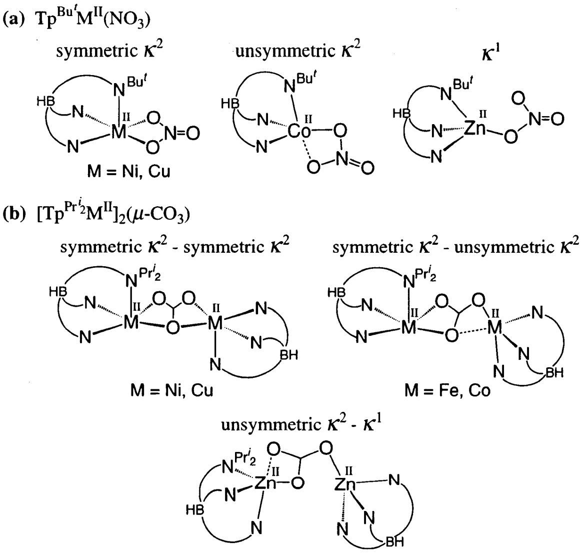
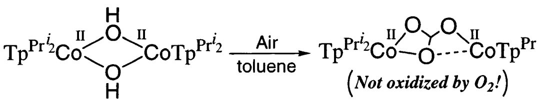


Fig. 2. Variation of the coordination modes of NO_3^- (a) and CO_3^{2-} (b) ligands depending on the metal ions.

that the hydroxo complex **1a** is (1) nucleophilic enough to react with CO_2 in the air, and (2) stable toward O_2, although the analogous Fe^{II}- and Mn^{II}-hydroxo complexes, $[Tp^{Pr^i_2}M^{II}]_2(\mu\text{-}OH)_2$ (M = Fe, Mn), are extremely O_2 sensitive [15]. On the basis of the first observation, we have successfully prepared Co-dioxygen species via dehydrative condensation with XOOH (X = H, alkyl; vide infra). The second observation may be a remarkable property upon application of Tp^R to Co-dioxygen chemistry. As we mentioned in Section 1, the most common route to the Co-dioxygen species is oxidative addition of O_2 appropriate Co^{II} compounds; in fact, the similar trigonally capping $TACN^{Me_3}$ system ($TACN^{Me_3}$ = 1,4,7-trimethyl-1,4,7-triazacyclononane) yields the dinuclear Co^{III} μ-peroxo complex via O_2-oxidative addition to the Co^{II} acetylacetonato complex [16]. The O_2-insensitivity of **1** might be attributed to the stabilization of the lower oxidation state derived by the sterically demanding Tp^R ligands.

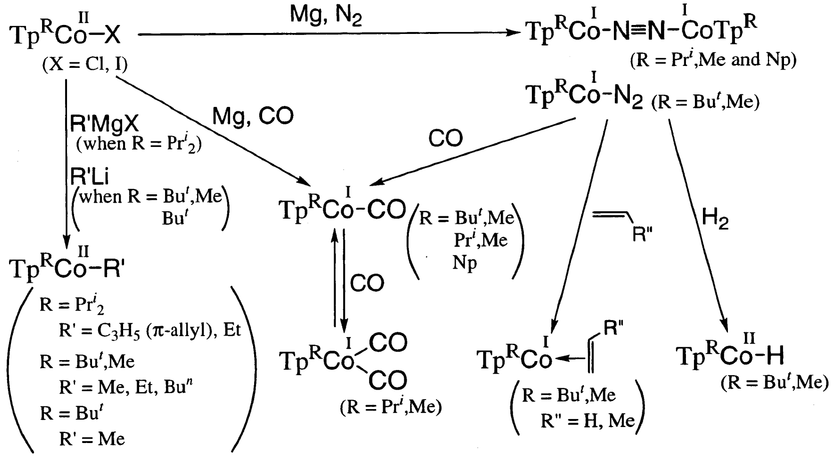


1a

(1)

2.2. Organometallic chemistry of Tp^RCo system

Research interest in organometallic compounds Tp^RCo(L), where L denotes CO, alkene, alkyl, allyl, H and N_2 (Scheme 1), has also been rapidly growing because the hindered Tp^R ligands can stabilize the coordinatively unsaturated species, which are expected to show unique reactivity [17–24].

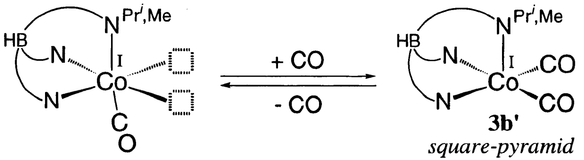


Scheme 1.

2.2.1. Co^I complexes

Halide complexes of Co^{II} supported by the sterically demanding Tp^R ligands, $Tp^RCo^{II}X$ (X = Cl, I), were reduced by Mg under a N_2 atmosphere to give the corresponding dinitrogen complexes as reported by Theopold et al. Molecular structures of the $Tp^{Pr^i,Me}$ (**2b**) [17] and Tp^{Np} [22] derivatives were determined by X-ray crystallography; the neutral N_2 ligand bridged the two Tp^RCo^I fragments in a μ-η^1:η^1 fashion to give a dinuclear structure. In the case of the highly sterically demanding $Tp^{Bu^t,Me}$ system, the resulting N_2 complex **2a** had a mononuclear structure as was derived by measurement of the amount of N_2 uptake (i.e. the $Tp^{Bu^t,Me}Co$ fragment reacted with one equivalent of N_2) [18].

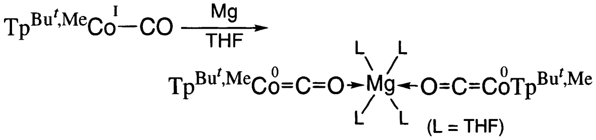
The N_2 complexes **2** are versatile starting materials for various complexes due to the lability of the N_2 ligand; reactions with CO and alkene afforded the corresponding Co^I-carbonyl and alkene complexes, respectively, and moreover, the $Tp^{Bu^t,Me}$ complex **2a** yielded Co^{II}-hydrido [19] and superoxo [18] complexes via oxidative addition of H_2 and O_2 to the Co^I centers, respectively (vide infra). For the CO complexes, the steric bulkiness of the Tp^R substituents affected the composition of the complexes; the relatively hindered $Tp^{Bu^t,Me}$ and Tp^{Np} yielded the monocarbonyl complexes, $Tp^RCo^I(CO)$ [18,19,22], while the less hindered $Tp^{Pr^i,Me}$ ligand system gave the mono- and dicarbonyl complexes, which were in the equilibrium in the presence of CO (Eq. 2) [21]. The $Tp^{Bu^t,Me}$ complex **2a** could be reduced by Mg to give a trinuclear $Co(0)_2Mg^{II}$ μ-carbonyl complex, $Mg^{II}\{[Tp^{Bu^t,Me}Co^0]_2(\mu\text{-}CO)\}_2(THF)_4$ (Eq. 3) [22]. Upon exposure to O_2, $Tp^RCo(CO)$ were transformed to Co^{II}-superoxo (when $Tp^{Bu^t,Me}$ and $Tp^{Pr^i,Me}$) complexes as described below. It is notable that all of the above mentioned 16e Co^I complexes of N_2, CO and alkene, except the 18e dicarbonyl complex bearing $Tp^{Pr^i,Me}$, are paramagnetic due to the highly distorted unsymmetrical geometry of their Co^I centers; the geometry of the four-coordinated Co^I centers is best described as 'octahedral containing two adjacent vacant sites (*cis*-divacant octahedron)' rather than 'distorted tetrahedron (C_{3v} symmetric structure as found for the halide and alkyl complexes of Tp^RCo^{II})' as is judged from the deviation of the B–Co–L angles (L = C (where CO complex) or N (N_2 complex)) from 180°.



3b
cis-divacant octahedron
16e, paramagnetic

3b'
square-pyramid
18e, diamagnetic

(2)

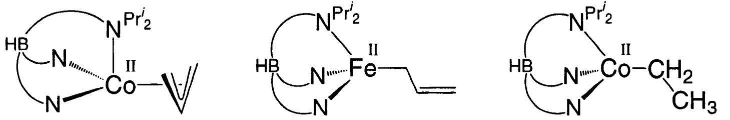


$$Tp^{Bu^t,Me}\overset{I}{Co}{-}CO \xrightarrow[THF]{Mg} Tp^{Bu^t,Me}\overset{0}{Co}{=}C{=}O{\rightarrow}MgL_4{\leftarrow}O{=}C{=}\overset{0}{Co}Tp^{Bu^t,Me} \quad (L = THF) \tag{3}$$

2.2.2. Co^{II}-R′ (alkyl, allyl) complexes

Treatment of Co^{II}-halide complexes, $Tp^{Pr^i_2}Co^{II}Cl$, $Tp^{Bu^t}Co^{II}I$ and $Tp^{Bu^t,Me}Co^{II}I$, with alkylation reagents such as R′MgX (for the $Tp^{Pr^i_2}$ system) and R′Li (Tp^{Bu^t} and $Tp^{Bu^t,Me}$) afforded the corresponding $Tp^RCo^{II}R'$ complexes, but the reactivities of the resulting alkyl complexes varied depending on the Tp^R ligands.

By using the $Tp^{Pr^i_2}$ ligand, we synthesized the Co^{II}-allyl and alkyl complexes, $Tp^{Pr^i_2}Co^{II}(\eta^3\text{-}C_3H_5)$ [23] and $Tp^{Pr^i_2}Co^{II}(Et)$ [24], and their structures were determined by X-ray crystallography (Chart 3). In the allyl complex, the Co^{II} center is supported by the κ^3-$Tp^{Pr^i_2}$ and η^3-allyl ligands resulting in a square-pyramidal geometry when the coordination number of the allyl ligand is assumed to be two. It is remarkable that the Co^{II}-η^3-allyl complex (Chart 3(a)) is a 17e species, closer to the coordinatively saturated 18e-configuration, whereas an Fe analogue involves a η^1-allyl ligand (Chart 3(b)) resulting in a more electron deficient 14e species [23].



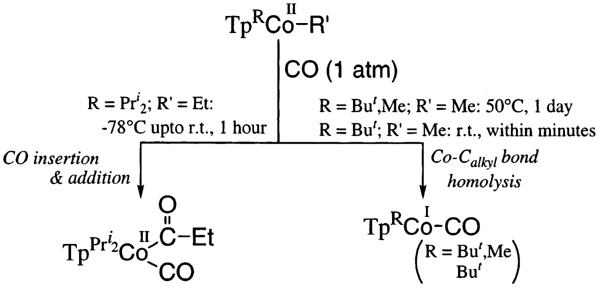
(a) $Tp^{Pr^i_2}Co^{II}(\eta^3\text{–}C_3H_5)$ — *square pyramid, 17e*

(b) $Tp^{Pr^i_2}Fe^{II}(\eta^1\text{–}C_3H_5)$ — *pseudo tetrahedron, 14e*

(c) $Tp^{Pr^i_2}Co^{II}(Et)$ — *pseudo tetrahedron, 15e*

(Chart 3)

The ethyl complex with $Tp^{Pr^i_2}$ involves a four-coordinated pseudo-tetrahedral (C_{3v}) Co^{II} center (Chart 3 (c)), and the methyl complex with Tp^{Bu^t}, reported by Theopold et al. exhibits similar structural characteristics [19]. Theopold and coworkers also prepared a series of the alkyl (Me, Et, Bu^n) complexes by using the more sterically demanding $Tp^{Bu^t,Me}$ ligand. The most remarkable characteristic of these alkyl complexes is their thermal stability and resistance to β-hydride elimination, although they are coordinatively unsaturated 15e species [19,24]. Interestingly, their reactivity toward carbonylation is regulated by the steric hindrance of the Tp^R ligands (Scheme 2). Stirring a toluene solution of our $Tp^{Pr^i_2}$ complex under 1 atm CO at room temperature resulted in immediate formation of an acyl complex, $Tp^{Pr^i_2}Co^{II}[C(=O)Et](CO)$, via a migratory insertion mechanism [24]. In contrast, the more hindered Tp^{Bu^t} and $Tp^{Bu^t,Me}$ derivatives yielded the corresponding Co^I-carbonyl complexes, which must be formed via Co–C(alkyl) bond homolysis [19]. A similar steric effect for reactivity toward carbonylation was observed for the alkyl-iron complexes, $Tp^{Pr^i_2}Fe^{II}(Et)$ [24] and $[PhB(Pz^{Bu^t})_3]Fe^{II}(Me)$ ($PhB(Pz^{Bu^t})_3$ = phenyltris(3-*tert*-butyl-1-pyrazolyl)borate) [25], reported by us and Parkin et al., respectively.



Scheme 2.

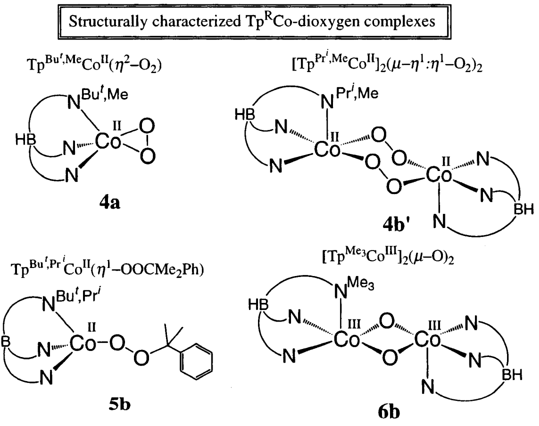
2.3. Remarks on characteristics of the Tp^RCo system

The above review of inorganic and organometallic Tp^RCo chemistry reveals several characteristics of these Tp^RCo species. The following points are especially important for the Tp^RCo-dioxygen complexes chemistry presented in the next section.

1. The sterically hindered Tp^R ligands can stabilize the +2 or lower oxidation state of Co. As a result, Tp^RCo^{II} species are not oxidized by O_2.
2. The hydroxo complex of Co^{II} supported by $Tp^{Pr^i_2}$ (**1**) is highly basic (enough to react with atmospheric CO_2).
3. The hydrophobic shading pocket around the metal center formed by the bulky substituents hinders the approach of the protic substrate toward reactive moieties such as a metal–carbon bond (and probably an O–O bond), and this results in stabilization of the reactive species. Reactivity of the coordinatively unsaturated species is influenced by the steric hindrance of Tp^R (e.g. carbonylation of the Co^{II}-alkyl complexes).

3. Dioxygen complexes of the Tp^RCo system

The chemistry of Co^{II}–OOX (X = none, alkyl) and Co^{III}-oxo species supported by Tp^R (see Chart 4) has been studied extensively and new aspects of transition metal-dioxygen chemistry have been revealed. In Section 3, the structural and physicochemical characteristics, and reactivities of $Tp^{R}Co$-dioxygen complexes will be described.



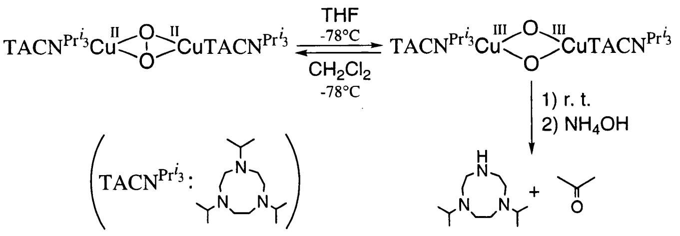
(Chart 4)

3.1. Background

The pioneer of $Tp^{R}Co$-dioxygen chemistry was Theopold and coworkers. In 1990, the first structural determination of Co^{II}–O_2 was reported [18]. They adopted the highly hindered tris(pyrazolyl)borate ligand $Tp^{Bu^t,Me}$ in order to generate the coordinatively unsaturated species, which might show the different reactivity of the relatively stable octahedral Co^{III}-peroxo species. As a result, oxidative addition of a dioxygen molecule to the $Tp^{Bu^t,Me}Co^{I}$ fragment yielded not a Co^{III}–O_2^{2-} but the Co^{II}–O_2^{-} complex **4a** shown above.

In our laboratory, Cu-, Fe- and Mn-dioxygen complexes with Tp^{R} ligands have been investigated as biomimetic models [5b]. One remarkable result is the isolation and structural characterization of the first example of the Cu_2^{II}-μ-η^2:η^2-peroxo complex with $Tp^{Pr^i_2}$, which fully reproduces the spectroscopic characteristics of oxyhemocyanin. It is notable that the unusual low ν(O–O) values for the model complex and the proteins are associated with the μ-η^2:η^2 coordination mode of the peroxide ligand [26]. More recently, Tolman et al. have reported an equilibrium between the Cu_2^{II}-μ-η^2:η^2-peroxo and Cu_2^{III}-bis(μ-oxo) cores for the $TACN^{Pr^i_3}$-copper complex ($TACN^{Pr^i_3}$ denotes 1,4,7-triisopropyl-1,4,7-triazacyclononane) containing a tripodal N_3M skeleton. $TACN^{R_3}$ is an N_3 donor similar to the Tp^{R} ligands. In addition, the resulting high-valent metal-oxo species promotes intramolecular ligand oxidation (Scheme 3) [27]. These observations suggest that the electronic and coordination environment of metal centers tuned by the supporting ligands is a key factor for O_2-activation mediated by metal complexes, and motivate us to investigate the metal-dioxygen complexes systematically by using a series of Tp^{R} ligands.

Recently we have extended our synthetic targets to dioxygen complexes of various metal ions ranging from the early transition metals (V, Cr) to the biologically irrelevant first- and second-row late transition metals (Co, Ni, Ru, Rh, Pd; i.e.



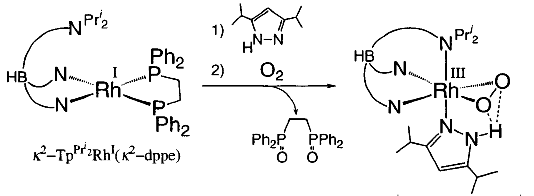
Scheme 3.

they do not participate in O_2 metabolism, although Co and Ni are essential for life) [28]. Systematic investigation of the various metal-dioxygen complexes having the same Tp^R ligand may provide insight into the reaction mechanisms, the role of the metal ions and the effect of the supporting ligands in various biological and synthetic oxidation reactions, and directions for oxidation catalyst design, etc. Especially, the formation of dioxygen complexes of Co and Ni and their tremendous oxidation ability toward alkyl groups are remarkable [29]. Of course, our objective to elucidate the transition metal-dioxygen chemistry based on the Tp^R system is still in progress.

3.2. Synthesis and characterization of Tp^RCo-dioxygen complexes

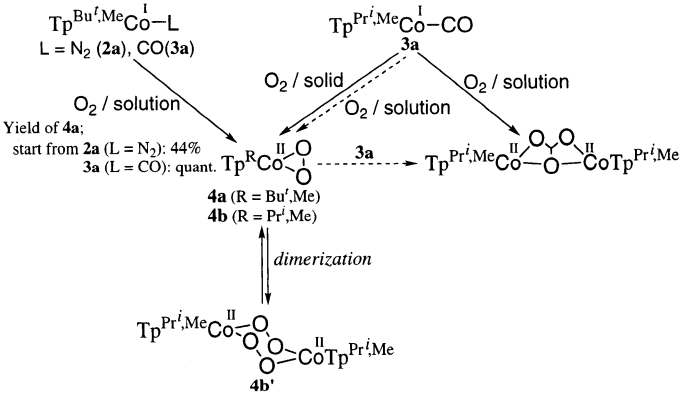
3.2.1. Co^{II}-superoxo complexes

The Co^{II}-superoxo complexes with Tp^R were obtained by oxidative addition of O_2 to the appropriate Co^I precursors (Scheme 4). In contrast to the Co system, oxygenation of coordinatively unsaturated Rh^I species supported by $Tp^{Pr^i_2}$ or Tp^{H_2} resulted in the formation of the corresponding Rh^{III}-peroxo complexes, $Tp^{Pr^i_2}Rh^{III}(\eta^2\text{-}O_2)(Pz^{Pr^i_2}H)$ and $Tp^{H_2}Rh^{III}(\eta^2\text{-}O_2)(PPh_3)$, recently discovered by us (Eq. 4) [28g] and Hill et al. [30], respectively. Although Co and Rh are classified into the same Group 9 transition metals, the energy levels of the d-orbitals of Rh are higher than that of Co and that may be a reason for the different behavior of the monovalent metal complexes toward oxygenation.



(4)

3.2.1.1. $Tp^{Bu^t,Me}$ system. As described in Section 2.2, the dinitrogen complex with $Tp^{Bu^t,Me}$ (**2a**) reacted with the various substrates including CO, alkene, H_2 [19]. As was expected from the labile nature of the N_2 ligand, reaction with O_2 resulted in



Scheme 4.

the formation of the relatively stable O_2 complex **4a** in a moderate yield (44%) [18]. The somewhat low yield of the dioxygen complex is attributed to occurrence of further reaction of the resulting dioxygen complex with the coordinatively unsaturated $Tp^{Bu^t,Me}Co^I$ fragment formed by the dissociation of the N_2 ligand of **2a** (see below). This dioxygen complex **4a** was also obtained by reaction of a solution of the Co^I-carbonyl complex **3a** with O_2; in contrast to the N_2 complex **2a**, **3a** was transformed to **4a** quantitatively [17].

X-ray crystallography as well as spectroscopy characterized the resulting dioxygen complex **4a**. The dioxygen ligand is coordinated to the Co center with side-on (η^2) fashion and the O–O bond length is 1.262(8) Å which falls in the range of the previously reported O–O bond lengths of superoxide anion (O_2^-) ligands. The effective magnetic moment of 3.88 μ_B (at 298K) implies the ground state of **4a** is $S = 1$ resulting from the antiferromagnetic coupling of the high-spin Co^{II} center ($S = 3/2$) and the superoxide anion radical ($S = 1/2$). On the basis of these observations, the dioxygen complex **4a** has been identified as an η^2-superoxo complex of Co^{II}, $Tp^{Bu^t,Me}Co^{II}(\eta^2\text{-}O_2^-)$. This Co^{II}–O_2^- complex is not only the first structurally determined Co^{II}-dioxygen complex but also the first observation of the η^2-binding of superoxide ligand in transition metal complexes. A similar η^2-superoxo structure is observed for the analogous Cu^{II} complex with the more hindered Tp^{Bu^t,Pr^i} ligand, $Tp^{Bu^t,Pr^i}Cu^{II}(\eta^2\text{-}O_2^-)$ [31]. The ν(O–O) value of 961 cm^{-1} observed for **4a** is in the middle of the previously reported values for the superoxide (1200–1070 cm^{-1}) and the peroxide (930–720 cm^{-1}). Such an unusual low frequency for the superoxide ligand in **4a** may arise from the contribution of the back-donation from the Co^{II} center.

3.2.1.2. $Tp^{Pr^i,Me}$ system. The sterically less hindered ligand, $Tp^{Pr^i,Me}$, has been also applied to Co-dioxygen complex chemistry [17,20,32]. However, the oxygenation patterns of the carbonyl and dinitrogen complexes with $Tp^{Pr^i,Me}$ are different from those found for the $Tp^{Bu^t,Me}$ system (see above) [17,18]. Treatment of a solution of

$Tp^{Pr^i,Me}Co^I(CO)$ (**3b**) with O_2 produced a dinuclear Co^{II}-μ-carbonato (CO_3^{2-}) complex, which should be formed via migratory insertion of the CO ligand of **3b** into an O–O bond of an initially formed dioxygen complex. Instead, exposure of a solid sample of **3b** to O_2 allowed the isolation of the dioxygen complex. On the basis of the similarity of the spectroscopic characteristics between the $Tp^{Pr^i,Me}$ and $Tp^{Bu^t,Me}$ derivatives (paramagnetic at room temperature and low ν(O–O) frequency), the resulting $Tp^{Pr^i,Me}$ complex was assumed to be an analog of the $Tp^{Bu^t,Me}$ complex **4a** (i.e., mononuclear Co^{II}-η^2-superoxo complex, $Tp^{Pr^i,Me}Co^{II}(\eta^2\text{-}O_2^-)$ (**4b**)).

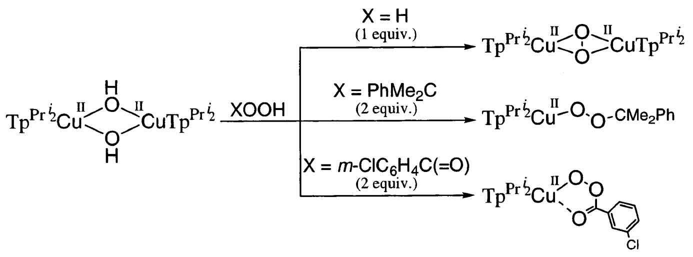
In the solution state, **4b** exhibited a temperature-dependent equilibrium between monomeric and dimeric forms as was judged from its thermochromic behavior; the brown solution at 270 K turned to dark green at 220 K. The molecular structure of the green isomer of the Co^{II}–O_2^- complex was determined by X-ray crystallography; two superoxide ligands bridge two square-pyramidal Co^{II} centers in a *trans*-μ-η^1:η^1 mode resulting in the dimeric complex formulated as $[Tp^{Pr^i,Me}Co^{II}]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2^-)_2$ (**4b′**). This dimeric form of the Co^{II}-superoxo complex shows unique structural and physicochemical properties. The O–O bond length (1.354(5) Å) in the crystal structure is intermediate between the O–O lengths usually found for μ-superoxo (1.24–1.32 Å) and μ-peroxo (1.38–1.53 Å) complexes [3]. The dinuclear Co^{II}-bis(-*trans*-μ-η^1:η^1-superoxo) core consists of a six-membered Co–O–O–Co–O–O ring with a chair conformation, and such a structural motif is rare for metal-dioxygen complexes. This dimeric form is a diamagnetic species arising from strong antiferromagnetic coupling of the low-spin Co^{II} center ($S = 1/2$) with the superoxide ligand ($S = 1/2$), while the ground state of the monomeric isomer is $S = 1$ arising from the magnetically coupled high-spin Co^{II} ($S = 3/2$) and O_2^- core [32]. In summary, reduction of the steric hindrance of the substituents of Tp^R (i.e. Bu^t to Pr^i) provides access for the two Co centers of the monomers to produce the dimeric isomer of the Co^{II}-superoxo species.

It is also notable that the reaction of the dinuclear Co^I-μ-N_2 complex, $[Tp^{Pr^i,Me}Co^I]_2(\mu\text{-}N_2)$ (**2b**), with O_2 does not yield the Co^{II}-superoxo species but another dioxygen complex, which is assumed as a dinuclear Co^{III}-bis(μ-oxo) species (see below) [17,21], although the $Tp^{Bu^t,Me}Co^{II}$-superoxo complex **4a** has been formed from the corresponding Co^I–N_2 complex **2a**.

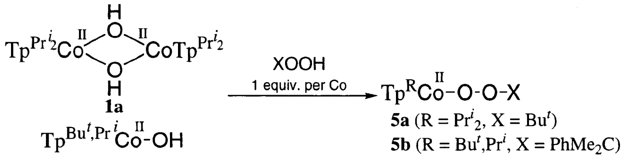
3.2.2. *Co^{II}-alkylperoxo complexes*

Several examples of alkylperoxo complexes of Co^{III} have been reported to date [4,33]. In general, such Co^{III}-alkylperoxo complexes were prepared by treatment of the appropriate Co^{II} precursors with XOOH (X = alkyl); the Co^{II} precursor might be oxidized by XOOH initially, yielding the Co^{III} compound, while the following ligand displacement with XOO^- gave the Co^{III}-alkylperoxo complex. However, no alkylperoxo complex of Co^{II} had been characterized before our complexes **5** described below.

We have established the synthetic method for the dioxygen complexes via dehydrative condensation of divalent metal-hydroxo complexes with XOOH (X = H, alkyl, acyl). The relatively basic hydroxide moiety is protonated by various protic substrates HA [A^- = conjugated base such as carboxylate, phenoxide, thiolate, peroxide (= XOO; X = H, alkyl, acyl), etc.] and the subsequent ligand displacement from the resulting H_2O to A^- results in the formation of a M–A bond. The formal charge of the metal center does not change during the reaction. In fact, a series of Cu^{II}-dioxygen complexes bearing the $Tp^{Pr^i_2}$ ligand, $Tp^{Pr^i_2}Cu^{II}$–OO–X [X = $Cu^{II}Tp^{Pr^i_2}$ (μ-η^2:η^2-peroxo), Bu^t and CMe_2Ph (alkylperoxo), $C(=O)C_6H_4Cl$ (acylperoxo)], has been obtained by reaction of the dinuclear Cu^{II} hydroxo complex, $[Tp^{Pr^i_2}Cu^{II}]_2(\mu\text{-}OH)_2$, with the corresponding hydroperoxides (XOOH; where X = H, alkyl, acyl) (Scheme 5) [26]. As we described above, the dinuclear Co^{II} bis(μ-hydroxo) complex, $[Tp^{Pr^i_2}Co^{II}]_2(\mu\text{-}OH)_2$ (**1**), is also basic enough to react with atmospheric CO_2 [13]. When two equivalents of Bu^tOOH was added to a pentane solution of the hydroxo complex at − 78°C, the color of the pentane layer immediately turned from red to blue, which was characteristic of the tetrahedral Co^{II} species arising from d–d transition around 600 nm (Eq. 5) [6]. We thus assigned this blue species to a mononuclear tetrahedral Co^{II}-alkylperoxo complex, but it decomposed even at − 78°C to induce the ligand oxygenation (see below) and this alkylperoxo complex **5a** was not fully characterized.



Scheme 5.



(5)

Then we attempted isolation of the alkylperoxo species by using the sterically more hindered ligand Tp^{Bu^t,Pr^i}. The Tp^{Bu^t,Pr^i} derivative of a hydroxo complex, $Tp^{Bu^t,Pr^i}Co^{II}(OH)$, reacted with an equimolar amount of cumyl hydroperoxide at − 40°C to yield the corresponding Co^{II}-cumylperoxo complex, $Tp^{Bu^t,Pr^i}Co^{II}(OOCMe_2Ph)$ (**5b**), and its structure was determined by X-ray crystallography (see Chart 4) [29a]. A unit cell of **5b** contained two crystallographically independent molecules with essentially the same structures. The geometry of the Co^{II} ions in **5b** is best described as a slightly distorted tetrahedron coordinated by the oxygen atom of the end-on (η^1) bound alkylperoxide ligand and the three pyrazolyl nitrogen atoms. The relatively small M–O–O bending angle (Co2–O21–O22; 108.1(6)°) and the somewhat short interatomic distance from the

Co to distal oxygen atoms (Co2···O22; 2.650(9) Å) in one of the two crystallographically independent molecules may imply the contribution of a weak π-bonding interaction of the alkylperoxide to the Co center. A similar weak π-interaction of the alkylperoxide to the metal center is suggested for the Mn^{II} analog bearing the same Tp^{Bu^t,Pr^i} ligand reported by us [28c]. The shorter O–O lengths (O11–O12; 1.36(1) and O21–O22; 1.42(1) Å, mean 1.39 Å) compared to the O–O lengths in the previously reported Co^{III} alkylperoxo complexes (1.42–1.52 Å) [4,33] may be attributed to the weaker Lewis acidity of the divalent cobalt ion, although the values of O–O bond lengths in **5b** also fall in the typical range of the O–O bond lengths of the transition metal-alkylperoxo complexes [28g,34].

3.2.3. Dinuclear Co^{III}-bis(μ-oxo) complexes

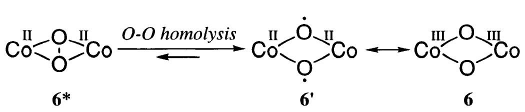
As we mentioned above, the hydroxo complex with $Tp^{Pr^i_2}$, $[Tp^{Pr^i_2}Co^{II}]_2(\mu\text{-}OH)_2$ (**1**), reacted with alkylhydroperoxide stoichiometrically to give the highly reactive Co^{II}-alkylperoxo species **5a** [29a]. Then we have also examined the reaction of **1** with an equivalent of H_2O_2, because H_2O_2 is more acidic than alkylhydroperoxides (the pK_a values of peroxides in H_2O at 25°C: H_2O_2; 11.58, $PhMe_2COOH$; 12.60, Bu^tOOH; 12.80) and therefore the dehydrative condensation with H_2O_2 is expected to occur. Indeed, treatment of the hydroxo complex with one equivalent of H_2O_2 (at -50°C) resulted in the formation of a thermally unstable dark brown species **6a**. We originally assigned **6a** as a dinuclear Co^{II}-μ-η^2:η^2-peroxo complex on the basis of the analogy to the $Cu^{II}_2\text{-}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2^{2-})$ complex bearing the same $Tp^{Pr^i_2}$ [35]. Although **6a** is moderately stable at -78°C, our attempts to prepare single crystals suitable for X-ray analysis so far have not met with success. Moreover, its intramolecular ligand oxidation reaction (i.e. oxygenation of the proximal Pr^i group at room temperature, see below) hinders complete characterization.

In order to prevent oxygenation of the Pr^i methine part, the Pr^i substituents were replaced by methyl groups which are much more resistant to oxidation due to the higher C–H bond energy. As a result, use of hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate, Tp^{Me_3}, led to the successful isolation and structural determination of the brown species. Reaction of a red Co^{II} hydroxo complex, $[Tp^{Me_3}Co^{II}]_2(\mu\text{-}OH)_2$ (**1b**), and one equivalent of H_2O_2 in CH_2Cl_2 at -50°C yielded a brown *meta*-stable complex (**6b**) which exhibited characteristic UV–vis feature ($\lambda_{max} = 360$ ($\varepsilon = 7600$), 490 (1500) and 614 (800) nm) similar to that of the above commented $Tp^{Pr^i_2}$ complex **6a** [35]. X-ray crystallography revealed a dinuclear structure of **6b**; two slightly distorted square pyramidal Co centers are bridged by two oxygen atoms, and the O···O separation (2.33 Å) clearly indicates a non-bonding interaction between them. The Co···Co, Co–O, $Co\text{–}N_{av.}$ distances are shorter than those of the starting dinuclear Co^{II} bis(μ-hydroxo) complex **1b**. These structural features are quite similar to those of Tolman's $TACN^{R_3}$-Cu complexes [27]. On the basis of these observations, we conclude that the *meta*-stable brown complex **6b** is a five-coordinate dinuclear Co^{III} bis(μ-oxo) complex, $[Tp^{Me_3}Co^{III}]_2(\mu\text{-}O)_2$ [29b]. A more reactive Ni^{III} analog, $[Tp^{Me_3}Ni^{III}]_2(\mu\text{-}O)_2$, has also been characterized successfully. Both of the Co^{III} and Ni^{III} bis(μ-oxo) complexes were obtained from the reactions of the corresponding M^{II}-hydroxo precursors with H_2O_2, whereas reactions with other oxidizing reagents such as alkylhydroperoxides, MCPBA and $KMnO_4$ did not give such M^{III}-oxo species. Therefore, dehydrative condensation of the dimeric M^{II}–OH precursors with one equivalent of H_2O_2 must occur at the initial stage giving the μ-peroxo intermediates and the subsequent O–O bond cleavage via 2e donation from the two metal centers yields the M_2^{III}-(μ-O)$_2$ complexes [29b]. In Tolman's TACN$^{Pr^i_3}$Cu system, a solvent-dependent equilibrium between the Cu_2^{II}-(μ-η^2;η^2-O_2) and Cu_2^{III}-(μ-O)$_2$ isomers was observed [27]. More recently, Karlin et al. have also reported a similar isomerization in the tripodal N_3 ligand Cu system [36]. In our Tp^{R}Co system, no significant change of the spectral features (UV–vis, ^{1}H-NMR) are detected in any solvent. However, very rapid interconversion between the Co_2^{III}-(μ-O)$_2$ and Co_2^{II}-(μ-O_2) isomers (Chart 5) cannot be entirely excluded at this stage.

It is known that Co^{III} ions (d^6) strongly favor an octahedral geometry with low-spin ($S = 0$) state, and only a limited number of structurally characterized five-coordinate paramagnetic Co^{III} species are known [37]. Because **6b** contains two five-coordinate Co^{III} centers having a slightly distorted square pyramidal geometry, it is not diamagnetic as is indicated for its paramagnetically-shifted ^{1}H-NMR spectrum. To date, cubane type tetranuclear $[(Co^{III}\text{-oxo})_4]^{4+}$ and trinuclear Co^{III}-(μ$_3$-oxo) complexes with low-spin, six-coordinate octahedral Co^{III} centers have been reported [38].

Formation of a similar unstable species in the Tp$^{Pr^i,Me}$ ligand system has also been observed by Theopold et al. Mixing of the isolated Co^{II}-superoxo complex **4b** and half an equivalent of the dinuclear Co^{I}-dinitrogen complex **2b**, or exposure of the solid sample of **2b** to O_2 yielded the thermally unstable brown compound **6c**. They also originally assigned this brown species **6c** as a dinuclear Co^{II} μ-peroxo complex [20], but DFT calculation result suggested that a Co_2^{III}-bis(μ-oxo) structure was more plausible. Surprisingly, structural parameters of the Co_2^{III}-(μ-O)$_2$ core optimized by their calculation is in good agreement with those found in our X-ray structure of **6b** [17].

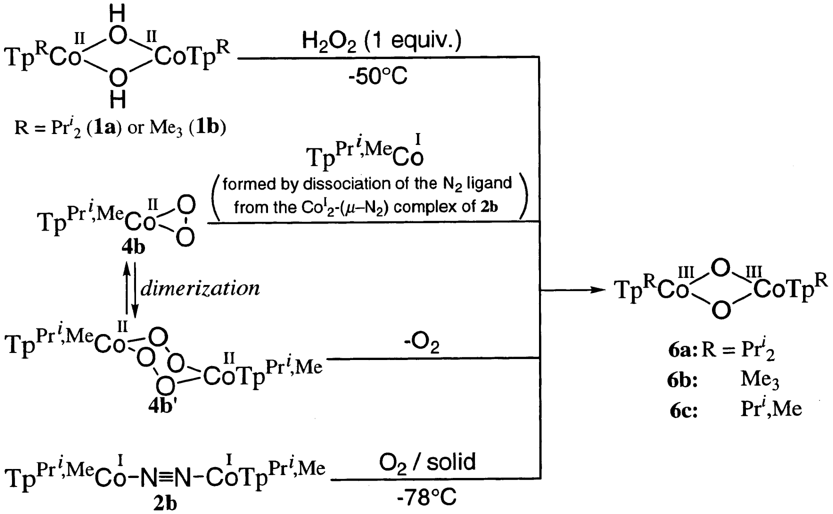
As summarized in Scheme 6, the less hindered Tp^R ligand systems (i.e. the substituent proximal to the metal center (3-R group) is smaller than *tert*-butyl) give the thermally unstable dinucler Co^{III}-bis(μ-oxo) species **6**, which must be formed via O–O bond homolysis of the dinuclear Co^{II}-μ-peroxo isomer **6*** (Chart 5).



(Chart 5)

3.3. Reactivity of the Tp^{R}Co-dioxygen complexes

Some of the Co^{III}-peroxo (especially Co^{III}-alkylperoxo) complexes are known to show hydrocarbon oxidation ability, but such oxidation reactions proceed at

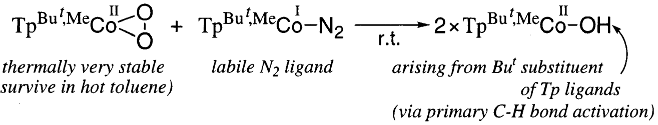


Scheme 6.

slightly higher temperature (ca. 50°C). In contrast, all of the above Tp^RCo-dioxygen complexes can oxidize the alkyl substituents of Tp^R which are proximal to the Co centers even below room temperature! In this section, we will review the O–O and aliphatic C–H bond activation processes mediated by the Tp^RCo complexes.

3.3.1. Reactivity of the Co^{II}-superoxo complexes

*3.3.1.1. $Tp^{Bu^t,Me}$ complex (**4a**).* The mononuclear Co^{II}-superoxo complex bearing the highly hindered $Tp^{Bu^t,Me}$ ligand **4a** was thermally very stable in the absence of any other Co^I species; surprisingly, it could be crystallized from a hot toluene solution and did not react with olefins or even PPh_3 [17]. The thermal stability of **4a** may be attributed to the substituent effect of the highly bulky *tert*-butyl groups, which form a 'deep' shading pocket surrounding the Co-(η^2-O_2) moiety. Moreover, extensive electron donation from metal ions or ligands (e.g. porphyrins) should be required to activate the O–O bond; i.e. in order to cleave the O–O bond of superoxide, three more electrons are requisite (so called 'reductive' activation). Actually, this superoxo complex **4a** reacted with the mononuclear Co^I–N_2 complex **2a** immediately to give two equivalents of a mononuclear Co^{II}-hydroxo complex, $Tp^{Bu^t,Me}Co^{II}(OH)$ (Eq. 6). When this reaction was carried out in deuterated solvent (toluene-d_8), deuterium was not incorporated in the resulting hydroxo group; this fact implies that the hydrogen atom of the *tert*-butyl substituent must be abstracted by a highly reactive species postulated as a mononuclear Co^{II}–$O^\bullet$ or Co^{III}=O giving the OH moiety of the product. The active species might result from O–O bond cleavage of a dinuclear μ-peroxo intermediate formed via nucleophilic attack of the superoxo complex to the $Tp^{Bu^t,Me}Co^I$ fragment. However, no intermediates were detected in the $Tp^{Bu^t,Me}Co$ system [17,18].



$$Tp^{Bu^t,Me}\overset{II}{Co}O_2 + Tp^{Bu^t,Me}\overset{I}{Co}{-}N_2 \xrightarrow[r.t.]{} 2\times Tp^{Bu^t,Me}\overset{II}{Co}{-}OH \quad (6)$$

3.3.1.2. $Tp^{Pr^i,Me}$ complex (4b and 4b′)

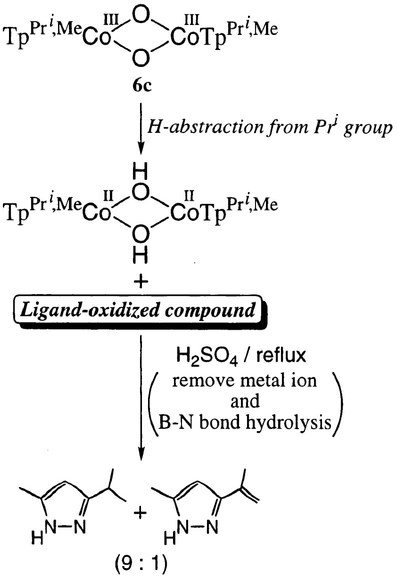
The superoxo complex of the $Tp^{Pr^i,Me}$ derivative is dimerized at low temperature due to a decrease in the steric hindrance of the proximal substituent (vide supra) [32], and its thermal stability is reduced. Whereas the monomeric isomer **4b** was relatively stable, the dimeric form (= $[Tp^{Pr^i,Me}Co^{II}]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2)_2$, **4b**′) was unstable even in the solid state and it decomposed spontaneously to give a dinuclear Co^{II} bis(μ-hydroxo) species, which must be formed via H-abstraction from the methine part of the Pr^i substituent by the dinuclear Co^{III} bis(μ-oxo) intermediate **6c**. Loss of one molecule of O_2 from **4b**′ might yield the dinuclear Co^{II}-μ-peroxo intermediate **6c*** (i.e. disproportionation of the two O_2^- to O_2^{2-} and O_2) following two electron-donation from each Co^{II} center to the O_2^{2-} ligand resulted in O–O bond homolysis giving the reactive Co_2^{III}-(μ-O)$_2$ species, whereas the μ-peroxo intermediate **6c*** had not been detected. As mentioned above, reaction of **4b** (monomeric isomer) with the coordinatively unsaturated $Tp^{Pr^i,Me}Co^I$ species, which was generated by dissociation of N_2 from the dinuclear Co^I μ-dinitrogen complex **1b**, also yielded **6c** [20]. These results clearly indicate that formation of the bimetallic core is essential for the dioxygen activation by multi-electronic reduction.

3.3.2. Hydrogen atom abstraction ability of the dinuclear Co^{III} bis(μ-oxo) complexes

The thermally unstable dinuclear Co^{III} bis(μ-oxo) species **6** are the practical active species for the ligand oxidation reaction.

As commented above, the Co^{II}–OH species, in which the hydrogen atom of OH came from the proximal alkyl substituents on Tp^R, were formed from the Co^{II}-superoxo complexes **4** via bimetallic O–O activation. In the $Tp^{Pr^i,Me}$ system, the reactive bimetallic intermediate **6c** was detected and was assigned as the dinuclear Co^{III}-bis(μ-oxo) complex on the basis of the DFT calculation result (vide supra) [17]. Subsequent thermal decomposition of **6c** gave a mixture of products, one of which was a dinuclear Co^{II} bis(μ-hydroxo) complex, $[Tp^{Pr^i,Me}Co^{II}]_2(\mu\text{-}OH)_2$. Moreover, hydrolysis of the reaction mixture under acidic condition yielded not only 3-isopropyl-5-methylpyrazole (90%) but also 3-isopropenyl-5-methylpyrazole (10%) (Scheme 7); the isopropenyl substituent was suggested to be formed via disproportionation of the isopropyl radicals, which were generated by H-atom abstraction from the proximal Pr^i substituent at the initial stage. Kinetic analysis of the decomposition process of **6c** revealed that H-abstraction from the methine part of

Pr^i was rate-determining step as was suggested from a large kinetic isotope effect ($k_H/k_D = 22$ at 281 K) [20].



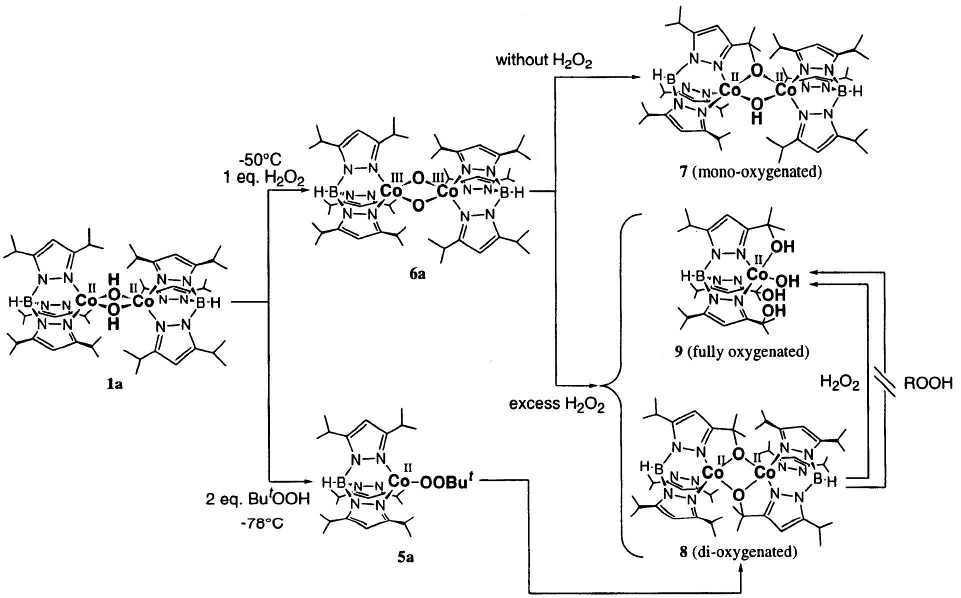
Scheme 7.

The hydrogen atom abstraction ability of the Co_2^{III}-(μ-O)$_2$ species is revealed concretely by our investigation for the reactivity of the structurally determined $[Tp^{Me_3}Co^{III}]_2(\mu\text{-}O)_2$ (**6b**). In contrast to the $Tp^{Pr^i_2}$ derivative **6a** which decomposed at ambient temperature to give a ligand-mono-oxygenated complex (see below) [29a], **6b** was reasonably stable due to absence of the reactive tertiary C–H bond, but it also decomposed slowly even at room temperature. As observed for the Theopold's $Tp^{Pr^i,Me}$ system, a large k_H/k_D value obtained from the first-order decomposition rates of the Tp^{Me_3} and $Tp^{(CD_3)_2,4\text{-}Me}$ derivatives ($k_H/k_D = 9$ at 343 K) evidently indicates that the rate-determining H-abstraction from the primary C–H bond of Me is mediated by the Co_2^{III}-(μ-O)$_2$ species. However, the nickel analog of the dinuclear trivalent metal-bis(μ-oxo) complex, $[Tp^{Me_3}Ni^{III}]_2(\mu\text{-}O)_2$, shows ca. 10^3 times greater reactivity toward H-abstraction from the proximal Me substituent of Tp^{Me_3} [39].

3.3.3. *Aliphatic C–H bond oxygenation by the $Tp^{Pr^i_2}$Co-dioxygen complexes*

In the $Tp^{Pr^i_2}$ system, reaction of the dinuclear Co^{II} bis(μ-hydroxo) complex **1** with an equivalent of H_2O_2 yielded the brown species **6a** which should now be identified as the Co_2^{III}-(μ-O)$_2$ complex (or mixture of the Co_2^{III}-(μ-O)$_2$ and Co_2^{II}-(μ-O$_2$) isomers [36]) on the basis of its characteristic UV–vis spectral feature similar to that of the structure-determined **6b** [29b, 35]. In addition, the mononuclear Co^{II}-alkylperoxo complex **5a** was detected at − 78°C, when **1** reacted with the two equivalents of

Bu^{t}OOH [29a]. Both $\mathrm{Co_2^{III}}$-(μ-O)$_2$ (**6a**) and Co$^{\mathrm{II}}$–OOBu^t (**5a**) complexes were thermally very unstable due to facile H-abstraction from the reactive tertiary C–H bonds which are located proximal to the metal center (i.e. 3-Pr^i groups of Tp$^{\mathrm{Pr}^i_2}$). Interestingly, spontaneous decomposition of **6a** and **5a** resulted in the oxygenation of the Pr^i substituent on the pyrazolyl ligands as confirmed by X-ray crystallographic analysis of the products, and the number of the incorporated oxygen atoms into the products depended on the kind of the dioxygen species (i.e. bis(μ-oxo), alkylperoxo, hydroperoxo) and the reaction conditions (Scheme 8) [29a,c].



Scheme 8.

3.3.3.1. Characterization of the ligand-oxygenated products. In the absence of H$_2$O$_2$, a ligand mono-oxygenated compound **7** was produced from the bis(μ-oxo) complex **6a**. X-ray crystallography revealed the unique structure of **7**, described as a μ-alkoxo-μ-hydroxo dinuclear Co$^{\mathrm{II}}$ complex, Co$_2$(μ-OH)[HB(μ-3-OCMe$_2$-5-Pr^{i}pz)(3,5-Pr$^i_2$pz)$_2$](Tp$^{\mathrm{Pr}^i_2}$), in which one of the six methine groups in the isopropyl substituents proximal to the metal centers is oxygenated and the resulting alkoxide functional group bridges the two Co$^{\mathrm{II}}$ centers.

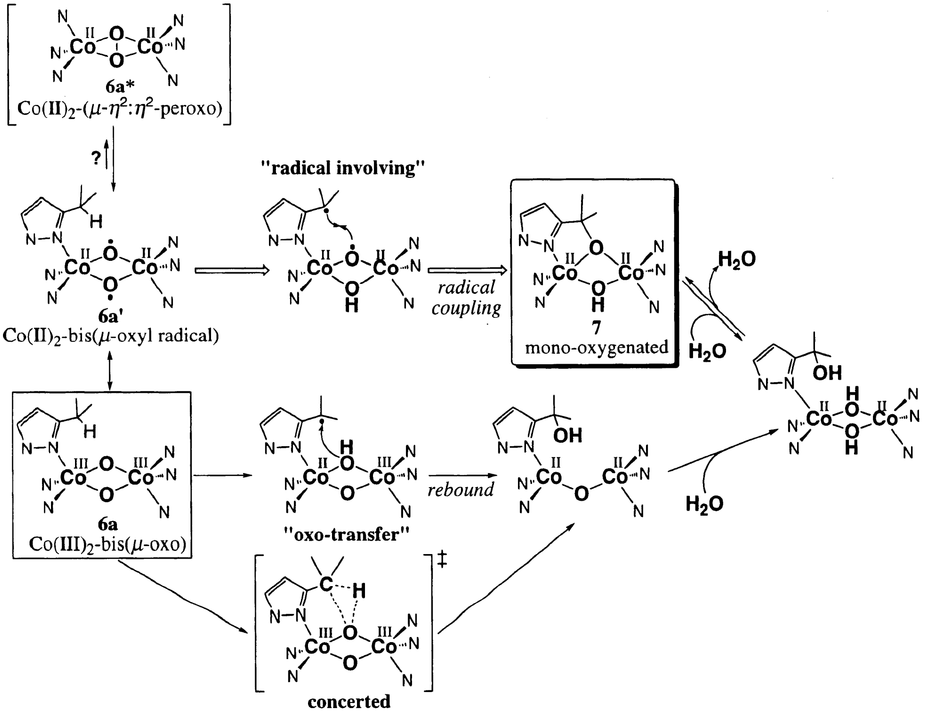
Decomposition of **6a** in the presence of excess H$_2$O$_2$ resulted in the formation of a mixture of two further oxygenated products. In a deep blue–green product {Co[HB(μ-3-OCMe$_2$-5-Pr^{i}pz)(3,5-Pr$^i_2$pz)$_2$]}$_2$ (**8**) two of the six methine carbon atoms in the isopropyl groups proximal to the Co centers are oxygenated, and the resultant chelating alkoxide ligands bridge the two Co$^{\mathrm{II}}$ ions to give the dimeric structure. In contrast to the structures of **7** and **8**, another pale brown product **9** is a mononuclear $\mathrm{Co^{II}}$ hydroxo alcohol complex, $\overline{\mathrm{Co(OH)[HB(3\text{-}Me_2C}}\mathrm{OH\text{-}5\text{-}Pr^{\mathit{i}}pz)(3\text{-}Me_2COH\text{-}5\text{-}Pr^{\mathit{i}}pz)_2]}$. The most striking structural feature is that all the proximal methine sites of the Pr^i groups are hydroxylated to give the chelating alcohol ligand and two free alcohol functional groups.

The alkylperoxo complex **5a** also decomposed to give the di-oxygenated bis(μ-alkoxo) compound **8**. However, the fully oxygenated compound **9** was never formed even in the presence of a large excess of alkylhydroperoxide. Reaction of **8** with $\mathrm{Bu}^t\mathrm{OOH}$ did not yield **9**, whereas **8** with $\mathrm{H_2O_2}$ did give **9**.

3.3.3.2. Reaction mechanism. In all the ligand oxygenated complexes, only the isopropyl methine part proximal to the Co centers was oxygenated and no functionalized distal Pr^i substituents were observed. We thus conclude that the present ligand oxygenation reactions must proceed within the coordination sphere of the Co centers.

As described above, the dinuclear $\mathrm{Co^{III}}$-bis(μ-oxo) species **6** exhibited the ability for H-atom abstraction from the alkyl substituent of $\mathrm{Tp^R}$ proximal to the metal centers. Therefore, formation of the mono-oxygenated complex might be initiated by H-abstraction from the methine part of a 3-Pr^i substituent. Plausible reaction mechanisms are summarized in Scheme 9. One possible 'radical involving' mechanism including a dinuclear $\mathrm{Co^{II}}$-bis(μ-oxyl radical) intermediate **6a**′, which is an alternative resonance structure of the $\mathrm{Co_2^{III}\text{-}(\mu\text{-}O)_2}$ compound, consists of the following steps; (1) abstraction of the methine hydrogen atom in the proximal Pr^i group with $\mathrm{Co^{II}\text{–}O^{\bullet}}$ generates the *tert*-alkyl radical center, and (2) coupling of the resulting *tert*-alkyl radical center with the remaining $\mathrm{Co\text{–}O^{\bullet}}$ moiety to furnish the chelating alkoxide structure. In this process, not only the mono-oxygenated compound but also the bis(μ-hydroxo) complex **1**, in which the Pr^i groups are unfunctionalized, are obtained, but the di-oxygenated bis(μ-alkoxo) complex **8** is not detected. Therefore formation of the μ-alkoxo-μ-hydroxo core of **7** may proceed with retention of the bimetallic structure. Another possible mechanism is so called 'oxo-transfer' mechanism mediated by the dinuclear $\mathrm{Co^{III}}$-bis(μ-oxo) species, and a similar oxygenation mechanism is proposed for Tolman's $\mathrm{TACN^{R_3}}$-Cu system [27a,40]. The proximal H atom is abstracted by the $\mathrm{Co^{III}}$-oxo species, and 'rebound' between the resulting tertiary alkyl radical and the OH radical to yield a $\mathrm{Co^{II}}$-μ-oxo species containing a hydroxylated Pr^i group. Hydration of this μ-oxo species followed by dehydrative condensation of the resulting alcohol and hydroxide furnishes the final product **7**. In the case of this mechanism, concerted oxygen atom transfer via a transition state in which the oxo group interacts with both the carbon and hydrogen atoms of the Pr^i-methine group should also be taken into consideration.

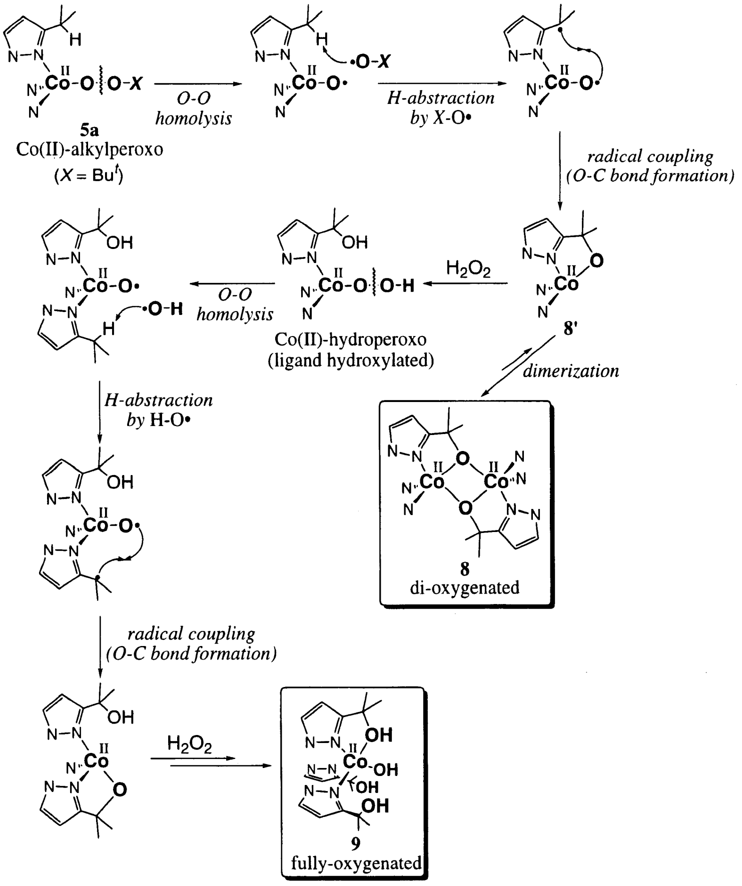
In contrast, the alkylperoxo complex **5a** is monomeric, thus the decomposition of **5a** may proceed via a monomeric intermediate. At first, O–O bond homolysis gives $\mathrm{RO^{\bullet}}$ and $\mathrm{Co^{II}\text{–}O^{\bullet}}$ and then, a proximal methine-H atom is abstracted by $\mathrm{RO^{\bullet}}$.



Scheme 9.

Coupling of the resulting *tert*-alkyl radical and Co–O$^\bullet$ yielding an alkoxo moiety and final dimerization leads to the stable five-coordinated structure of the bis(μ-alkoxo) complex **8** (Scheme 10). As found in the decomposition of **6a**, the non-functionalized bis(μ-hydroxo) complex **1** is also formed, but the mono-oxygenated complex **7** is not obtained from **5a**. These results imply that scrambling of the hydroxo complex **1** with the monomeric alkoxo intermediate **7**′ can be excluded.

The decomposition of the Co_2^{III}-(μ-O)$_2$ complex **6a** in the presence of excess H_2O_2 yielded the di-oxygenated bis(μ-alkoxo) complex **8** and the fully-oxygenated hydroxo-alcohol complex **9**. Species **9** was also obtained by the reaction of the isolated di-oxygenated bis(μ-alkoxo) complex **8** with H_2O_2, but the reaction of **1** or **8** with alkyl hydroperoxides under various conditions failed in full oxygenation. These observations imply that the present oxygenation giving the fully-oxygenated complex **9** may proceed via Co^{II}–OOH intermediates in a stepwise manner as presented in Scheme 10. H_2O_2, which is more acidic than alkylhydroperoxides XOOH (X = Bu^t, PhMe$_2$C), replaces the alkoxide ligand in the monomeric alkoxo compound **8**′ to form the hydroperoxo intermediate, by which another proximal Pr^i group is oxygenated to give a monomeric di-oxygenated product. Repetition of the oxygenation process would furnish **9** after coordination of one of the resulting alcohol groups and the hydroxide.



Scheme 10.

4. Concluding remarks

The sterically demanding 3,5-dialkyl substituted Tp^R ligands make the isolation of the Co^{II}-dioxygen complexes such as Co^{II}-superoxo and -alkylperoxo possible. In addition, these Co^{II}-dioxygen species are reactive compared to the previously reported Co^{III}-peroxo compounds even at low temperature. This result implies that a lower oxidation state metal center is more effective for O–O bond activation due to the high electron donating ability of the metal center to the peroxide. The LUMO of the peroxide anion is a σ^* orbital and therefore back-donation from the metal center to the antibonding σ^* orbital weakens the O–O bond.

A recent advance in metal-dioxygen complex chemistry reveals that a high-valent metal oxo (O^{2-}) species is formed via O–O bond cleavage of the O_2^{2-} ligand of the metal-peroxo complex and works as an active intermediate for C–H bond oxygenation. Especially, bimetallic M_2^{n+}-$(\mu\text{-}O)_2$ species of Cu(III/III) [27,36,40,41], Fe(III/

IV) and Fe(IV/IV) [42], which are the isomers of the corresponding μ-peroxo compounds $M_2^{(n-1)+}$-(μ-O_2), take part in biological and chemical oxidation processes of aliphatic C–H bond. Discovery of the C–H bond activating Co_2^{III}-(μ-O)$_2$ species, which must be formed via O–O cleavage of the dinuclear Co^{II} μ-peroxo isomer, suggests that such M_2-(μ-O)$_2$ species of the high-valent metal ions are emerging as a common reactive intermediate of the oxidation process mediated by first-row late transition metal complexes, and their reactivity can be controlled by tuning of the coordination environment of the metal centers.

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Appendix A. Abbreviations

Tp^R	hydrotris(3,4,5-substituted-1-pyrazolyl)borate (see Chart 1)
Cp	cyclopentadienyl
$TACN^{R_3}$	1,4,7-trialkyl-1,4,7-triazacyclononane
$TACN^{Me_3}$	1,4,7-trimethyl-1,4,7-triazacyclononane
$TACN^{Pr^i_3}$	1,4,7-triisopropyl-1,4,7-triazacyclononane
$PhB(Pz^{Bu^t})_3$	phenyltris(3-*tert*-butyl-1-pyrazolyl)borate
Bu^tOOH	*tert*-butlyhydroperoxide

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