Oxygenation of Saturated Hydrocarbyl Groups in the Dinuclear Ni(III) Bis(μ-oxo) Complexes with the Hydrotris(pyrazolyl)borate Ligands Tp^R (R = Me_3 and Pr^i_2)

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(Received June 16, 1999; CL-990517)

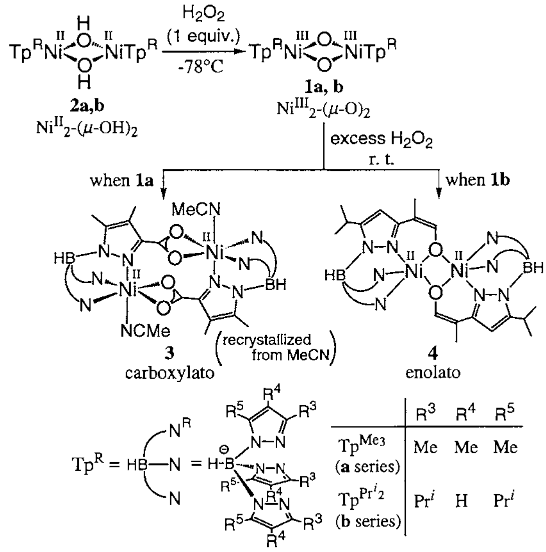
Intramolecular oxygenation of the Me and Pr^i substituents of Tp^R to give the carboxylate ($-CO_2^-$) and enolate ($-CMe=CHO^-$) groups, respectively, is mediated by the Ni(III)$_2$-bis(μ-oxo) complexes in the presence of an excess amount of H_2O_2.

Elucidation of the reactivity of transition metal coordinated active oxygen species (O_2^-, O_2^{2-}, OOH^-, OOR^- and O^{2-}) toward C-H bond oxidation is essential to understand the synthetic, catalytic and biological oxidation mechanisms.[1] In order to get comprehensive insights into the role of transition metal ions and reaction mechanisms in various oxidation processes, we have been investigating chemistry of the first- and second-row transition metal-dioxygen complexes with the tripodal N_3-donating hydrotris(pyrazolyl)borate ligands (= Tp^R).[2] Very recently, the bimetallic bis(μ-oxo) complexes of Ni(III) and Co(III) with the Tp^{Me_3} ligand (Tp^{Me_3} = hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate), which are closely related to the biologically important high-valent M(μ-O)$_2$M complexes of Cu [3] and Fe,[4] have been synthesized and characterized by X-ray crystallography.[2a] In addition, intramolecular oxygenation of the isopropyl substituents on the $Tp^{Pr^i_2}$ (= hydrotris(3,5-diisopropyl-1-pyrazolyl)borate) ligand via metal-dioxygen species have been observed for the manganese [5] and cobalt [2b] complexes. In this communication, we report unique oxygenation of saturated hydrocarbyl groups mediated by the highly reactive dinuclear Ni(III)-bis(μ-oxo) species, $Tp^RNi^{III}(\mu\text{-}O)_2Ni^{III}Tp^R$ (**1**: Tp^R = Tp^{Me_3} (**1a**), $Tp^{Pr^i_2}$ (**1b**)) in the presence of the excess amount of H_2O_2.[6,7]

The Ni(III)$_2$-bis(μ-oxo) complex with the Tp^{Me_3} ligand (**1a**) was reasonably stable to allow the structural characterization at low temperature but decomposed within an hour at room temperature in a solution state.[2a] A dinuclear Ni(II) bis(μ-hydroxo) complex bearing the $Tp^{Pr^i_2}$ ligand, $Tp^{Pr^i_2}Ni^{II}(\mu\text{-}OH)_2Ni^{II}Tp^{Pr^i_2}$ (**2b**), [8] also reacted with 1 equiv. of aqueous H_2O_2 (30 wt%) at -78 °C to give an extremely thermally unstable Ni^{III}_2-bis(μ-oxo) species **1b** (Scheme 1), which exhibited two intense absorption bands at 300 and 400 nm similar to the Tp^{Me_3} derivative **1a**.[9] But the $Tp^{Pr^i_2}$ derivative **1b** was too unstable to be isolated and a brown pentane solution of **1b** turned to green one within a minute even at -50 °C.

Interestingly, treatment of the bis(μ-oxo) complexes **1** with an excess amount of H_2O_2 resulted in oxygenation of the proximal alkyl substituents of Tp^R, but the reaction patterns are slightly different from that observed for the analogous $Tp^{Pr^i_2}$–cobalt system.[2b] Upon standing of a CH_2Cl_2 solution of the Tp^{Me_3} complex **1a** at room temperature in the presence of an excess amount of aqueous H_2O_2, the solution color turned from brown to blue within 2 h. X-Ray analysis of blue crystals **3** (obtained by recrystallization from a THF/MeCN solution) revealed the molecular structure formulated as $\{Ni^{II}[HB(3\text{-}(\kappa^2\text{-}O_2C)\text{-}4,5\text{-}Me_2pz)(3,4,5\text{-}Me_3pz)_2](NCMe)\}_2$ (Figure 1, top)[10,11]; one of the three 3-Me substituents on Tp^{Me_3} was oxygenated to give the corresponding carboxylate group ($-CO_2^-$), which was coordinated

Scheme 1



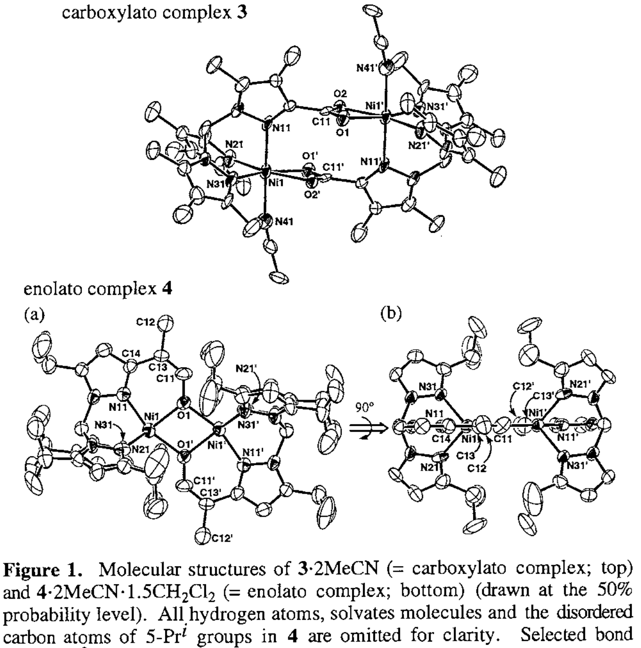


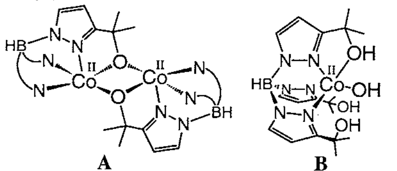
Figure 1. Molecular structures of **3**·2MeCN (= carboxylato complex; top) and **4**·2MeCN·1.5CH_2Cl_2 (= enolato complex; bottom) (drawn at the 50% probability level). All hydrogen atoms, solvates molecules and the disordered carbon atoms of 5-Pr^i groups in **4** are omitted for clarity. Selected bond lengths (Å) and angles (deg); for **3** (top), Ni1-O1, 2.175(6); Ni1-O2, 2.102(6); Ni1-N11, 2.076(6); Ni1-N21, 2.033(8); Ni1-N31, 2.063(8); Ni1-N41, 2.106(9); O1-C11, 1.24(1); O2-C11, 1.26(1); Ni1---Ni1', 5.443(3); O1-Ni1-O2, 61.3(2); N11-Ni1-N41, 177.8(4). for **4** (bottom); one of the two crystallographically independent molecules is presented: (a) side-view, (b) 90° rotated along the Ni1---Ni1' axis (All 5-Pr^i groups are omitted), Ni1-O1, 2.014(6); Ni1-O1', 1.997(6); Ni1-N11, 1.988(8); Ni1-N21, 2.052(8); Ni1-N31, 2.057(7); O1-C11, 1.32(1); C11-C13, 1.30(1); C12-C13, 1.47(1); C13-C14, 1.48(1); Ni1---Ni1', 3.179(2); C11-C13-C12, 122.2(9); C11-C13-C14, 122.0(9); C12-C13-C14, 115.8(8).

to the other Ni center to form the dimeric structure. The Ni centers were supported by an N_4O_2 ligand donor set composed of three pyrazolyl nitrogen atoms of the κ^3-Tp^R moiety, the chelating κ^2-carboxylate oxygen atoms coming from the other oxidized Tp^R, and the MeCN molecule. Existence of the metal-coordinating carboxylate group was supported by the observation of the strong absorption at 1570 cm^{-1} in its IR spectrum. Remarkably, the remaining Me substituents on the functionalized Tp^R ligands were not oxidized. The present carboxylation reaction may proceed via sequential oxidation of the one of the three 3-Me substituents on Tp^{Me_3} to the corresponding primary alcohol ($-CH_2OH$) and the aldehyde ($-C(=O)H$) intermediates, although the reaction mechanism remains to be studied.

In the case of the $Tp^{Pr^i_2}$ system, very unique oxidation reaction of the 3-Pr^i group was observed. Decomposition of **1b** in the presence of an excess amount of H_2O_2 (at r.t.) brought about not only oxygenation but also dehydrogenation of the Pr^i groups[12] to give an enolato complex, $\{Ni^{II}[HB(3\text{-}(\mu\text{-}OCH{=}CMe)\text{-}5\text{-}Pr^i pz)(3,5\text{-}Pr^i{}_2pz)_2]\}_2$ (**4**).[13] In its IR spectrum, strong absorption was observed at 1616 cm^{-1} which was assigned as the C=C vibration. The determination of its molecular structure by X-ray crystallography was also accomplished successfully as presented in the bottom of Figure 1.[11] Complex **4** is a dimeric compound in which the chelating enolate ligands bridge the two Ni centers. Hybridization of the C13 and C13' atoms is sp^2 judging from the bond angles around them and the resulting oxygenated isopropenyl groups are coplanar with respect to the adjacent pyrazolyl rings. Six-membered nickelacycle (i.e. chelation through the pyrazolyl nitrogen and enolate oxygen atoms) may be highly stabilized by the extended π-electron-conjugation system over the functionalized pyrazolyl-enolato moiety.

The oxidation of the alkyl substituents of Tp^R observed for the present Ni system is slightly different from that observed for the analogous cobalt system (Chart 1). The decomposition of **1** in the presence of the excess amount of H_2O_2 results in further oxidation of the Me and Pr^i substituents on Tp^R to give the carboxylato (**3**) and enolato (**4**) complexes instead of di- and fully-oxygenated complexes like **A** and **B**, which should be furnished via the mononuclear Co–OOX (X = alkyl, H) species.[2b] It should be notable that treatment of the dinuclear Ni(II) bis(μ-hydroxo) complexes **2** with alkylhydroperoxides yielded neither the oxo species **1** nor the ligand oxygenated complexes **3** and **4**. These observations suggest that not mononuclear but dinuclear intermediates (presumably reactive $Ni^{III}{}_2$–bis(μ-oxo) species) repetitiously oxidize the same alkyl substituents.[14]

Chart 1



A *di-oxygenated* **B** *fully-oxygenated*

(All unfunctionalized part of the Tp ligands are omitted (5-Pr^i groups) or abbreviated for clarity.)

In conclusion, oxygenation of the Me and Pr^i substituents of Tp^R to give the carboxylate ($-CO_2^-$) and enolate ($-CMe{=}CHO^-$) groups, respectively, was mediated by the Ni(III)-bis(μ-oxo) complexes in the presence of the excess amount of H_2O_2.

We are grateful to the Ministry of Education, Science, Sports, and Culture of the Japanese Government for financial support of this research (Grant-in-Aid for Scientific Research 08102006).

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7 Abbreviations used in this paper: Tp^{Me_3}, hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate; $Tp^{Pr^i_2}$, hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; 3,4,5-Me_3pzH, 3,4,5-trimethylpyrazole; 3,5-$Pr^i{}_2pzH$, 3,5-diisopropylpyrazole.

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9 When 1 equiv. of aqueous H_2O_2 was added to an Et_2O solution of the Ni(II) hydroxo complex **2b** at -78 °C, the green solution changed to a dark brown one. UV-vis (Et_2O, -78 °C, nm, $\varepsilon/M^{-1}cm^{-1}$): 304 (12000), 404 (10500), 495 (sh, 3000), 570 (sh, 2200).

10 20 equiv. of aqueous H_2O_2 (30 wt%) was added to a CH_2Cl_2 solution of **1a**. Upon being stirred for 2h at room temperature, the brown solution turned to pale green. After removal of remaining H_2O_2 and H_2O, the solvent was evaporated under vacuum. Recrystallization from THF/MeCN (-30 °C) afforded the pale blue crystalline solids of **3** in 71% isolated yield (based on **1a**). Selected spectroscopic data for **3**: IR (KBr pellet, ν/cm^{-1}): 2515 (BH), 1570 (COO). UV-vis (toluene, 23 °C, nm, $\varepsilon/M^{-1}cm^{-1}$): 405 (110), 678 (30). FD-MS (m/z): 854 (**3**-2MeCN).

11 Crystal data; for **3**·2MeCN: $C_{44}H_{62}B_2N_{16}Ni_2O_4$, f.w. = 1018, monoclinic space group $P2_1/a$ (# 14), $a = 13.882(3)$ Å, $b = 12.697(3)$ Å, $c = 15.12(1)$ Å, $\beta = 105.28(2)°$, $V = 2570(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.32$ gcm^{-3}, μ(Mo Kα) = 7.89 cm^{-1}, $R(Rw) = 8.81(8.50)\%$ for 2571 reflections ($I > 3\sigma(I)$) with 308 parameters. for **4**·2MeCN·1.5CH_2Cl_2: $C_{59.5}H_{95}B_2Cl_3N_{12}Ni_2O_2$ f.w. = 1284, triclinic, space group $P\overline{1}$ (# 2), $a = 15.354(10)$ Å, $b = 18.706(2)$ Å, $c = 13.101(2)$ Å, $\alpha = 100.71(1)°$, $\beta = 105.84(2)°$, $\gamma = 81.56(1)°$, $V = 3538(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.21$ gcm^{-3}, μ(Mo Kα) = 6.94 cm^{-1}, $R(Rw) = 8.99(8.91)\%$ for 6058 reflections ($I > 5\sigma(I)$) with 790 parameters. A unit cell of **4**·2MeCN·1.5CH_2Cl_2 contained two crystallographically independent molecules of **4** with essentially the same structures.

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13 When 5 equiv. of aqueous H_2O_2 was added to a toluene solution of **2b** at -78 °C, the green solution changed to a dark brown one. After being stirred for 1h at -78 °C, the reaction mixture was warmed up to room temperature then the solvent was removed in vacuo. The resulting yellow green solid was washed with MeCN to afford **4** (43% yield based on **2b**). Recrystallization from a MeCN/CH_2Cl_2 solution afforded yellow green single crystals of **4**. Selected spectroscopic data for **4**: IR (KBr pellet, ν/cm^{-1}): 2533 (BH), 1616 (C=C). UV-vis (toluene, 23 °C, nm, $\varepsilon/M^{-1}cm^{-1}$): 417 (1020), 440 (sh, 800), 460 (sh, 550), 640 (46), 772 (480), 865 (30). FD-MS (m/z): 537, 1074 (M^+).

14 We could not determine the oxygen atom source in **3** and **4** due to exchange of the oxo ligands of **1** for O atom of exogeneous H_2O.[2a] Moreover, **3** and **4** could not be detected when **1** decomposed in the absence of excess amount of H_2O_2 under O_2 (1 atm).