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Dioxygen Activation and Substrate Oxygenation by a *p*-Nitrothiophenolatonickel Complex: Unique Effects of an Acetonitrile Solvent and the *p*-Nitro Group of the Ligand

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Supporting Information

ABSTRACT: The nickel(II) complex [Ni(Tp^{Me2})($SC_6H_4NO_2$)] [**1a**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazol-1-yl)borate] reacts with O_2 to form the ligand oxygenation product $ArSO_2^-$ in MeCN, and also **1a** catalyzes the oxygenation of external substrates such as triphenylphosphine. The reactivity may correlate to the unique quinoid-like resonance structure of the thiophenolate ligand. The structure is stabilized by a *p*-nitro group and induced by coordination of MeCN.

Recently, interest in nickel−dioxygen (O_2) complexes chemistry has been growing from a biomimetic viewpoint,[1] because various organic substrate oxidations are promoted by nickel complexes through O_2 or peroxide activation under mild conditions.[2] In terms of O_2 activation, a lower-valent (zero or 1+ charge) nickel center in comparison to nickel(II) often causes the oxidative addition of O_2 to smoothly yield corresponding O_2 adducts such as nickel(II) or nickel(III) peroxo and nickel(II) superoxo species.[3] A few cases of nickel(II) complexes with strong electron-donating ligands such as amide, oximate, thioether group-containing Schiff base, and N-heterocyclic carbene can react with O_2 because of stabilization of the high-valent nickel(III) state.[4] In addition, some nickel(II) complexes with thiolate ligands also react with O_2 to cause oxygenation on sulfur-donor moieties.[5] In this study, we have investigated O_2 activation on a nickel complex with a *p*-nitro-substituted thiophenolate ligand, [$Ni^{II}(Tp^{Me2})(SC_6H_4NO_2)$] [**1a**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazol-1-yl)borate; see Scheme 1]. Complex **1a** exhibits selective oxygen-atom-transfer activity toward the sulfur center of the thiophenolate ligand. Moreover, **1a** catalyzes the aerobic oxygenation of external nucleophilic substrates in MeCN-containing solvents.

Complex **1a** was synthesized from a dinuclear di-μ-hydroxonickel(II) complex, [$(NiTp^{Me2})_2(\mu\text{-}OH)_2$] (**2**), with *p*-nitrothiophenol.[6−8] When an MeCN solution of **1a** was exposed to O_2 (1 atm), decolorization of a dark-brown-orange solution occurred within 20 min at room temperature. Recrystallization of the resulting compound mixture by slow evaporation of the MeCN/$CHCl_3$ solution gave pale-green-blue crystals of [Ni(Tp^{Me2})$(OH_2)_3$]$(NO_2C_6H_4SO_2)$ (**3a**), in which *p*-nitrosulfinate existed as a counteranion (Figure S1 and Tables S1−S3 in the Supporting Information, SI), in 92% isolated yield.[8]

Interestingly, quantitative high-performance liquid chromatography analysis of the oxidized products derived from a *p*-nitrothiophenolate ligand revealed that only 1% of nonoxygenated disulfide (**6a**), 99% of the sulfur-oxygenated products (94% of *p*-nitrophenylsulfinate (**5a**), and 5% of the corresponding sulfonate (**4a**)) were formed under these reaction conditions (see Scheme 1 and Figures S2−S4 in the SI).[7e,f,9] Such selective sulfur oxygenation occurs only in the case of the reaction of **1a** with O_2 in MeCN, while oxidations in other aprotic solvents [acetone, tetrahydrofuran (THF), and CH_2Cl_2] yield product mixtures with the majority of **6** (53−77%). Moreover, a para-unsubstituted analogue of **1a**, namely, [Ni(Tp^{Me2})(SC_6H_5)] (**1b**),[7b,c] also reacts with O_2, but the major product of the oxidized thiophenolate ligand is disulfide even in MeCN. The source of two oxygen atoms of **5a** derived from oxygenation of **1a** in MeCN was external O_2, as was confirmed by an $^{18}O_2$-labeling experiment (Figures S5 and S6 in the SI). The reaction proceeded without scrambling between the oxygen atoms originating from O_2 and $H_2{}^*O$, as was evidenced by the fact that the mixed-labeled **5a** [i.e., ArS(O)(*O)] did not form, while the incorporation of one *O atom into **4a** occurred through hydrolysis of the initially formed **5a** by $H_2{}^*O$. However, oxygenation under $^{16}O_2/^{18}O_2$ mixed gas yielded $ArS(^{16}O)(^{18}O)^-$. This fact indicates that the present ligand oxidation is proceeded by two steps via a sulfenate [=$ArS(O)^-$] intermediate and direct dioxygenation on the sulfur atom does not occur.

Kinetic analyses of the reaction of **1** with O_2 at 25 °C by UV−vis absorption spectra also revealed the unique behavior of the MeCN solution of **1a**. In a typical nonpolar solvent such as toluene and dichloromethane, complex **1** decreased slowly with pseudo-first-order kinetics without any observations of intermediate species (Table S4 and Figure S7 in the SI). The half-lifetimes of the decays of **1a** and **1b** are quite different [11.4 days (**1a**) and 7.4 h (**1b**) in toluene]. The correlation between the order of the reaction rates and the oxidation potentials of complexes **1** [E_{ox} = 1.0 (**1a**) and 0.66 (**1b**) V vs Fc/Fc^+ in CH_2Cl_2; see Figures S8 and S9 in the SI] suggests that the rate-determinating step of the reaction includes one-electron oxidation of thiophenolate ligands. On the other hand, both complexes

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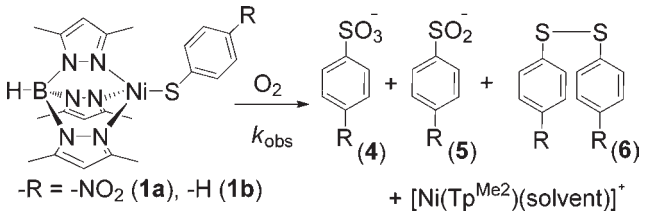
decay quickly within 20 min in MeCN, and one reason for the acceleration may be the solvation effect of the polar solvent.[10] Notably, the reaction of **1a** in MeCN follows second-order kinetics on the complex concentration, while **1b** follows first-order kinetics. The result indicates that the reaction pathway of oxygenation of **1a** in MeCN is different from the other cases of simple one-electron transfer. More interestingly, an electron-withdrawing bromine-containing Tp analogue of **1a**, [$Ni^{II}(Tp^{Me2,Br})(SC_6H_4NO_2)$] [**1c**; where $Tp^{Me2,Br}$ denotes hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate], reacts with O_2 faster than **1a**, although both complexes show the same kinetic behavior (i.e., second-order decays in MeCN and first-order decays in other solvents).[8] Acceleration of the reaction with O_2 on **1c** seems to be caused by decreasing electron donation from the Tp ligand, and this implies that the electronic property of the nickel center is dominant.

To reveal the origin of the unique reactivity of **1a** in MeCN, the coordination properties of **1** depending on the solvent and substituent groups on the thiophenolate ligands were compared. X-ray crystallographic analyses of **1** revealed that MeCN-recrystallized **1a** (**1a′**; Figure S10) takes a octahedral coordination structure with two MeCN and a quinoid-type thiophenolate ligand, despite of the tetrahedral geometry of toluene-recrystallized **1a**, MeCN-recrystallized **1b**, and all other related [$Ni^{II}(Tp^{R})(SAr)$] complexes[7b−d] (Figure S10 and Tables S1−S3 in the SI). The contribution of the quinoid-type resonance form of the $SC_6H_4NO_2$ moiety is observed as follows: The S−C_{Ar} length in **1a′** (1.734 Å) is slightly shorter than the general single bond length of coordinating S^- thiophenolate observed in **1a** (1.767 Å, and also **1b**).[11] An enlarged Ni−S−C_{Ar} angle (113.27° in **1a′** vs 101.59° in **1a**) and a smaller Ni−S−Ar_{plane} torsion angle (14° in **1a′** vs 32° in **1a**) also support the sp^2-like hybridization of the sulfur-atom orbital. In solution, the unique structural change of the **1a**/MeCN system was evident by ^1H NMR and UV−vis spectral studies of both complexes **1a** and **1b** in various solvents (Figures S11−S14 and Table S4 in the SI).[7b,c,8]

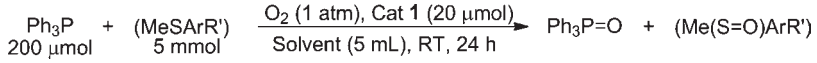
Scheme 1. Ligand Oxidation of the Thiophenolato Complexes 1 with O_2 in Solution at Room Temperature



The catalytic aerobic oxidation of Ph_3P (10 equiv) has been investigated to prove O_2 activation on the nickel center and the external substrate oxidation ability of **1a** (Table 1 and Figure S16 in the SI). Full conversion to $Ph_3P{=}O$ was observed only in the case of **1a** under the presence of MeCN (entry 1), whereas **1a** in acetone or **1b** exhibited no significant effect compared to the control run (entries 2 and 3).[12] These results clearly show that the **1a**/MeCN system holds the catalytic oxygen-atom-transfer ability toward the external substrate. The substrate oxidizing potential of the **1a**/MeCN system is not high, as has been suggested by the fact that catalytic oxygenation does not occur when thioanisole (=MeSArH) or cyclohexene is used as the sole substrate instead of Ph_3P. However, aerobic oxygenation of thioanisole proceeded only in the presence of **1a** and Ph_3P as cosubstrates (entry 4, Figure S17 in the SI). The oxygen atoms of both $Ph_3P{=}O$ and MeS(=O)ArH are from O_2, as has been evidenced by isotope-labeling experiments (Figure S18 in the SI). In the oxidation of para-substituted thioanisoles (MeSArR′, where R′ = Br, MeO) under the same conditions as those of MeSArH, yields of the corresponding sulfoxide products increase upon the introduction of an electron-donating group to the substrate, indicating that the real active oxidant has electrophilic character (entries 4−6). The lower yield of sulfoxide than $Ph_3P{=}O$ may imply that the reaction proceeds via oxygen-atom transfer rather electron transfer.[13]

We suppose a mechanism for O_2 activation on **1a** in MeCN (Scheme 2). The quinoid-type resonance structure of *p*-nitrothiophenolate in **1a′** might be essential.[7i,14] Acceleration of the reaction rate with O_2 by reducing the electron density on the nickel center (i.e., reaction of O_2 with **1c**) indicates that a nickel(I) radical ligand species (**1a″**) is partially formed via intramolecular electron transfer.[8,15] In **1a″**, the radical ligand may be stabilized as a semiquinoid-type resonance form by the electron-withdrawing *p*-NO_2 group and that is the reason for the prevention of thiyl radical dissociation from nickel. The nickel(I) center of **1a″** may react with O_2 to give the putative nickel(II) superoxo species **7**. The second-order kinetics of the reaction of **1a′** with O_2 in MeCN suggests that a bimolecular reaction between the nickel(II) superoxo species **7** and another **1a′** will occur without the external substrate: A plausible explanation is that **7** attacks the sulfur center of **1a′**, giving **3a** through the sulfenate intermediate, although the formation of dinuclear nickel μ-peroxo species (through attack of the nickel center) cannot be excluded at this moment. In the presence of the

Table 1. Aerobic Oxidation of External Substrates Catalyzed by 1



entry	cat./solv.	MeSArR′ R′ = para-substituents	$Ph_3P{=}O$ yield (%)	MeS(=O)ArR′ yield (μmol)
1	**1a**/mix[a]	no[b]	>99[c]	
2	**1b**/mix[a]	no[b]	12[c]	
3	**1a**/acetone	no[b]	35[d]	
4	**1a**/mix[a]	yes (H)	>99	27[e]
5	**1a**/mix[a]	yes (MeO)	>99	31[e]
6	**1a**/mix[a]	yes (Br)	>99	24[e]

[a] CH_2Cl_2 (2.5 mL) and MeCN (2.5 mL). [b] Without thioanisoles. [c] 12% yield without catalyst. [d] After 50 h. [e] <2 μmol yield without catalyst **1a** or Ph_3P.

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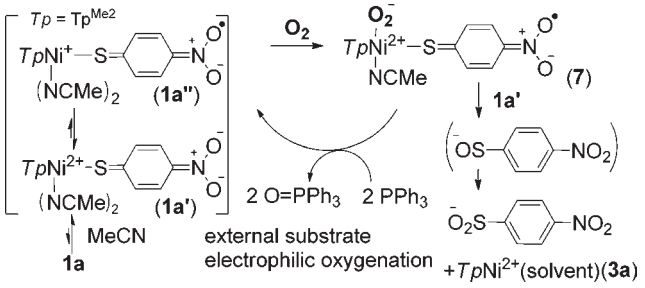
Scheme 2. Plausible Mechanism for O_2 Activation by 1a in MeCN



external substrates, **7** works as a weak electrophilic oxidant to cause oxygen-atom transfer to Ph_3P, and that may yield a more reactive Ni^{III}=O (or $Ni^{II}O^{\bullet}$) species, which shows oxygenation activity toward the sulfides.[16]

In summary, we have revealed that the nickel(II) complex having the *p*-nitrothiophenolato ligand activates O_2 in MeCN to yield quantitative oxygenation of the sulfur atom of the ligand and also catalyzes oxygenation of the external substrates. This O_2 activation capability emerges by the prevention of the thiyl radical elimination from the nickel center due to the semiquinoid-type resonance structure stabilized by the *p*-nitro group. Our results demonstrate that the appropriate combination of the "noninnocent" ligand[11a] with a redox-active metal center is a versatile approach to an O_2-activating system.

■ ASSOCIATED CONTENT

Supporting Information. Syntheses, crystallographic data, and reactivity studies of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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