Peroxonickel Complexes

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Structural Characterization and Oxidation Activity of a Nickel(II) Alkylperoxo Complex**

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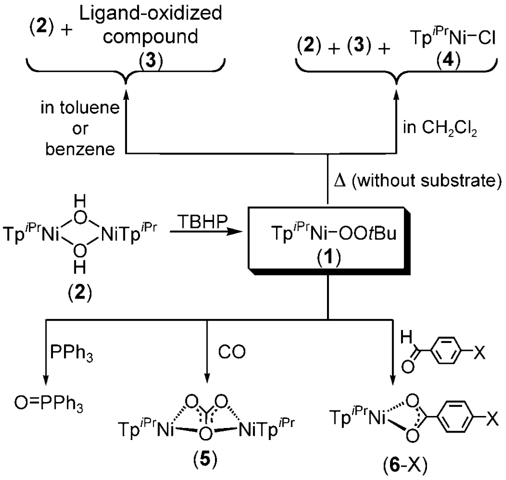
Transition-metal alkylperoxo species (M-OOR′; R′ denotes alkyl group) are postulated as reactive intermediates in various oxidation reactions ranging from industrial processes to biological systems.[1] The alkylperoxo complexes of d^0 early transition-metal ions (groups 4–6), in particular, have attracted much attention, owing to their potential as oxygenating reagents for organic compounds (for example, olefin epoxidation).[2–5] Interest in the alkylperoxo complexes of late transition metals is also growing because of their industrial significance and biological relevance.[6–8]

Nickel is recognized as one of the most useful metals in promoting various organic transformation reactions, owing its intrinsic redox properties. Recent developments in the chemistry of nickel dioxygen complexes have shed light on the applicability of nickel species as oxidizing agents. For example, dinuclear nickel(III) bis(μ-oxo) compounds exhibit H-abstraction of aliphatic hydrocarbyl species, in a similar fashion to the $M_2(\mu\text{-}O)_2$ species of high-valent Fe and Cu.[9] Furthermore, several nickel dioxygen complexes[9b,10] and peroxide-based catalytic oxidation reactions with nickel complexes[11] have been reported. An nickel(II) alkylperoxo complex, reported by Suzuki and coworkers, was formed by O_2 oxygenation of the alkyl radical center on the metal-supporting ligand, which was itself generated through H-abstraction by the $Ni_2(\mu\text{-}O)_2$ species.[9a,12] However, the structure and reactivity of nickel alkylperoxo complexes remains to be studied, to afford an insight into the interaction between nickel compounds and peroxides, the intrinsic reactivity of the resulting nickel peroxo species, and the properties of catalytic intermediates. Herein we report the molecular structure and the oxidizing activity of a nickel(II) alkylperoxo complex, $[Ni^{II}(OOtBu)(Tp^{iPr})]$ (**1**; Tp^{iPr} = hydrotris(3,5-di-2-propylpyrazolyl)borate).

Compound **1** was synthesized by the dehydrative condensation of a nickel(II) hydroxo complex, $[(Ni^{II}Tp^{iPr})_2(\mu\text{-}OH)_2]$ (**2**, Scheme 1),[13] with a stoichiometric amount of *tert*-butylhydroperoxide (TBHP). Addition of two equivalents of TBHP at 0 °C to a pentane solution of **2** resulted in an immediate change in the color of the solution, from green to orange, and the appearance of a strong band in the absorption spectrum at around 370 nm ($\varepsilon = 1400\ \mathrm{cm^{-1}M^{-1}}$). The molecular structure of **1** was revealed by single-crystal X-ray diffraction (Figure 1). The nickel center of **1** is coordinated by three donor nitrogen atoms from the Tp^{iPr} ligand. The



Scheme 1. Synthesis and reactions of **1**. TBHP = *tert*-butylhydroperoxide; Tp^{iPr} = hydrotris(3,5-di-2-propylpyrazolyl)borate.

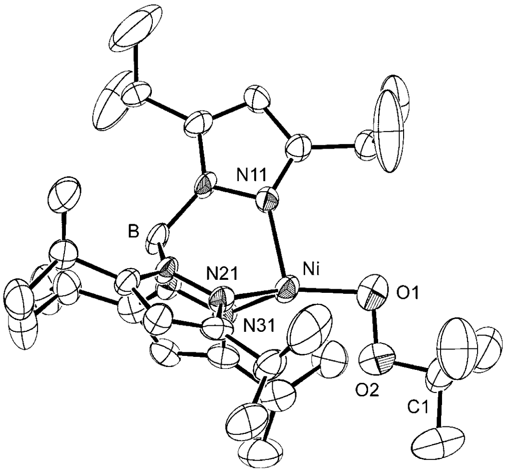


Figure 1. The molecular structure of **1**, with thermal ellipsoids set at 50% probability. All hydrogen atoms are omitted for clarity.

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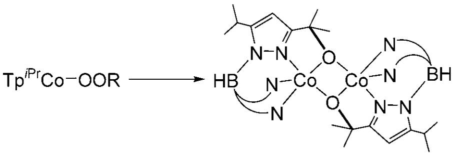
nonlinear O1-Ni-B bond angle (160.5°) indicates a deviation from C_{3v}-symmetrical pseudotetrahedral coordination geometry, which is frequently found for four-coordinate transition metal complexes with κ^3-Tp^R ligands.[14] The O−O bond length (1.440(7) Å) is within the typical range for peroxide O−O bond lengths.[3–8] The coordination mode of the OO*t*Bu ligand in **1** is intermediate between η^1 (end-on binding) and η^2 (side-on binding) coordination modes. To our knowledge, purely η^2-alkylperoxo complexes have to date only been reported for electron-deficient d^0 metal complexes (Ti^{IV} and V^V). For complex **1** the distance from the nickel center to the distal oxygen atom (O2) is relatively short (2.467(7) Å) and the Ni-O1-O2 bond angle (96.2(4)°) is the smallest reported M-O-O bond angle for η^1-OOR′ complexes. The M-O-O bond angles in η^2-OO*t*Bu complexes of titanium(IV)[3a] and vanadium(V)[5] are 83.2(2)° and 73.1(2)°, respectively. The coordinatively unsaturated nickel center, as well as the nucleophilic character of the alkylperoxide ligand, might be the cause of the weak interaction between Ni and O2 in **1**. To date, several examples of the same group 10 palladium(II) and platinum(II) alkylperoxo complexes have been reported. All of them, including our own $[Pd^{II}(OOtBu)(\kappa^2\text{-}Tp^{iPr})(py)]$, adopt low-spin ($d^8$, $S=0$) square-planar coordination geometries.[8a–c] A paramagnetically shifted ^{1}H NMR spectrum of **1** (see the Supporting Information, Figure S1) indicated a high-spin ($S=1$) electron configuration in solution, as was consistent with its nonplanar geometry revealed by single-crystal X-ray diffraction.

We examined the thermal stability of **1**. The analogous cobalt(II) derivative, $[Co^{II}(OOtBu)(Tp^{iPr})]$, decomposed spontaneously even at −78 °C, to cause the oxygenation of a proximal isopropyl substituent giving the ligand-oxygenated dinuclear cobalt(II) bis(μ-alkoxo) complex [Eq. (1)].[6b] In contrast, the nickel(II) complex **1** was relatively thermally stable in the absence of substrates (Scheme 1), and its half-life period in toluene at 298 K was approximately 2.5 h ($k_{obs} = 5.41\times10^{-5}\,s^{-1}$; also see the Supporting Information, Figure S2). Analysis of the mass spectrum revealed that the resulting green solution contained not only **2** but also another species **3** exhibiting the mass spectral peak at $m/z = 1078$, which was tentatively assigned to the nickel analogue of the ligand-oxygenated Co species.[6b,15] This tentative assignment was consistent with the complicated pattern of the ^{1}H NMR spectrum of the product mixture (see the Supporting Information, Figure S3), because the three-fold symmetry of the tris(pyrazolyl)borate ligand moiety of **3** was lost by the partial oxygenation. Therefore, complex **1**, similar to the isostructural cobalt(II) derivative, exhibits aliphatic C−H oxidation ability, although its thermal stability is markedly different. The lower energy of Ni d-orbitals, compared to that for Co, led to reduced back-donation from the nickel(II) center to the σ* orbital of the peroxide moiety, to induce O−O bond activation (presumably O−O homolysis). When **1** decomposed in CH_2Cl_2, a chloride complex, $[Ni^{II}ClTp^{iPr}]$ (**4**),[13] was also obtained (approximately 30 % yield, determined by UV/Vis spectra) in addition to **2** and **3**. Although the mechanism for the formation of **4** is not clear, a plausible explanation is that **1** decomposed through both O−O and Ni−O homolysis pathways competitively. In the case of the analogous copper(II) alkylperoxo complex, a reductive decomposition pathway, that is, Cu−O bond homolysis giving Cu^I and the alkylperoxy radical, seems to be dominant.[7f,g]



(1)

Upon the oxidation of external substrates, **1** behaved as either an electrophile or a nucleophile, depending on the substrates. Like the reported superoxo complexes of nickel(II),[10d,16] **1** exhibited weak electrophilic oxidizing properties toward triphenylphosphine and carbon monoxide, although not towards dimethylsulfide and olefins. The acceleration in consumption of **1** in the presence of excess Ph_3P ($k_{obs} = 1.82\times10^{-3}\,s^{-1}$ in the presence of 25 equivalents of Ph_3P in toluene at 298 K) indicates that the oxygenation reaction proceeded through a bimolecular mechanism. Reaction of **1** with CO resulted in the formation of a dinuclear nickel(II) μ-carbonato complex, $[(Ni^{II}Tp^{iPr})_2(\mu\text{-}\kappa^2,\kappa^2\text{-}CO_3)]$ (**5**):[13] A characteristic IR band at 1578 cm^{-1}, attributed to ν(COO), was shifted to 1538 cm^{-1} upon the reaction with ^{13}CO, which clearly indicated the oxidation of carbon monoxide. In addition, **1** showed nucleophilic reactivity. Reaction of **1** with a series of *para*-substituted benzaldehydes gave the corresponding benzoato complexes, $[Ni^{II}(\kappa^2\text{-}O_2CC_6H_4\text{-}p\text{-}X)(Tp^{iPr})]$ (**6**–X; X = OMe, Me, H, Cl), and the pseudo-first order consumption of **1** (in the presence of 25 equivalents of benzaldehyde) was accelerated by introduction of an electron-withdrawing substituent. The linear correlation of the Hammett plot ($\ln k_{obs}$ vs. σ) with a positive slope ($\rho = 4.3$; Figure 2) indicates that oxidation proceeds through a transition state stabilized by the electron-withdrawing substituent and that the nucleophilic attack of the peroxo ligand at the carbonyl carbon atom may be involved. In addition, a kinetic isotope effect (KIE) of $k^H/k^D = 1.7$ was evident when C_6H_5CDO was used in place of C_6H_5CHO (see the Supporting Information, Figure S5). The relatively small KIE value implies that the initial H abstraction of the formyl group, prior to the nucleophilic attack of the peroxo ligand at the C=O group, is improbable, although breaking of the C−H bond is a somewhat slow process.

We also examined the applicability of **1** as a catalyst for alkane oxidation. Solvent-free oxidation of cyclohexane with TBHP in the presence of a catalytic amount of **1** resulted in the formation of a mixture of cyclohexanol and cyclohexanone with low alcohol/ketone (A/K) ratio (approximately 1:2). Such a low A/K ratio suggests the contribution of radical species in this reaction, which is consistent with the thermal decomposition pathway of **1** described above.

In summary, we have succeeded in the structural characterization of the nickel alkylperoxo complex **1**. Crystallography reveals the highly distorted geometry of the nickel center coordinated by the OO*t*Bu ligand, the coordination mode of which is intermediate between η^1 and η^2. The decomposition of **1** might proceed through O−O and Ni−O

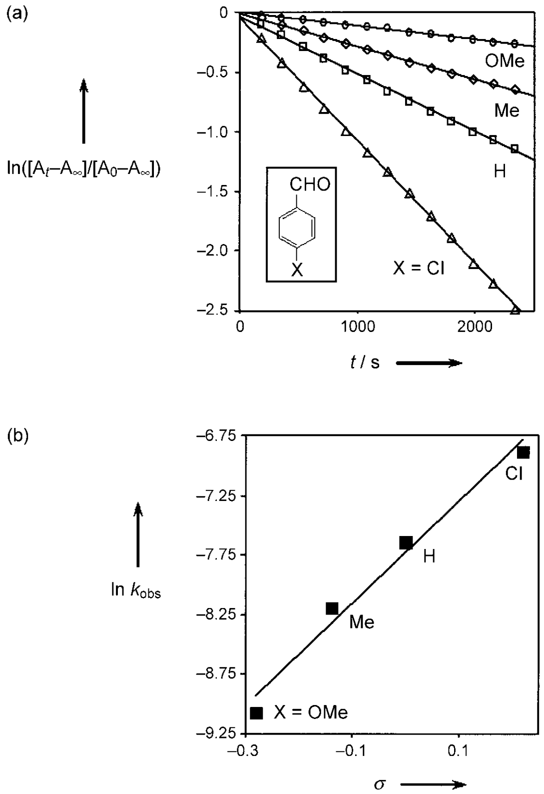


Figure 2. First-order plots (a) and Hammett plot (b) for the oxidation of a series of benzaldehydes with **1**. Conditions: **1** ((2.34 mM solution in toluene, 5 mL), benzaldehydes; (0.293 mmol, 25 equivalents), 298 K.

homolysis, and the resulting radical species would contribute to aliphatic C–H oxidation. Upon the oxidation of the external substrates, **1** behaved as either an electrophile (with Ph_3P or CO substrates) or a nucleophile (ArCHO substrate).

Experimental Section

Detail of the synthetic procedure and spectroscopic data of **1** are given in Supporting Information. CCDC 701151 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oxidation of an external substrate by **1**: The external substrate (Ph_3P or benzaldehyde, 5 equivalents) was added to the toluene solution of **1** (3 mL of a 8.48 mM solution) at ambient temperature under an argon atmosphere. Quantitative formation of $Ph_3P{=}O$ (> 98 % yield based on **1**) was confirmed by GC analysis. Characterization of a series of *para*-substituted benzoate complexes **6**–X, which were obtained by the reaction of **1** with benzaldehydes, was undertaken by comparison of the spectroscopic data of the corresponding authentic compounds (synthesized by treatment of benzoic acids with hydroxo complex **2**; see the Supporting Information). Reaction of **1** with benzaldehyde yielded **6**–H (78 % yield based on **1**) and *t*BuOH (confirmed by GC). Investigations into the reaction kinetics were carried with 25 equivalents of the substrate (pseudo-first-order conditions).**5**: Compound **1** (39 mg, 0.063 mmol) was dissolved in toluene (10 mL) and the resultant solution was degassed by means of two freeze-pump-thaw cycles. The degassed solution was exposed to carbon monoxide and stirred for 1 h. The volatile components were removed by evacuation. The resulting green compound was characterized by the comparison of the spectroscopic data with that of the authenticated carbonato complex **5**.[13] An almost quantitative yield of **5** (> 95 %) was confirmed by ^{1}H NMR spectroscopy.

Alkane oxidation catalysis: Compound **1** (26 μmol) was dissolved in cyclohexane (13 mmol) under an argon atmosphere and 29 μL of a 5.5 M decane solution of TBHP (160 μmol) was added in one portion. The reaction solution was stirred at 313 K for 2 h. Analysis by gas chromatography with an internal standard confirmed the generation of cyclohexanol (15 μmol, 9.4 % based on TBHP) and cyclohexanone (33 μmol, 41 %; because two equivalents of TBHP were consumed).

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