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Structural Characterization and Oxidation Reactivity of a Nickel(II) Acylperoxo Complex

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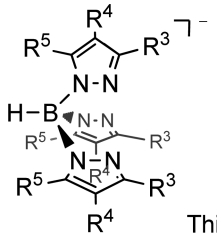
Supporting Information

ABSTRACT: The nickel(II)–acylperoxo complex [Ni(Tp^{CF_3Me})(κ^2-*m*CPBA)] ($\mathbf{1}^{CF_3Me}$) [Tp^{CF_3Me} = hydrotris(3-trifluoromethyl-5-methylpyrazolyl)borate, *m*CPBA = *m*-chloroperbenzoate] was isolated and fully characterized. The electrophilic oxygenation ability of $\mathbf{1}^{CF_3Me}$ toward sulfides and olefins was confirmed. The Michaelis–Menten-type behavior of thioanisole oxygenation indicates the existence of a pre-equilibrium of substrate association in the reaction. In addition, $\mathbf{1}^{CF_3Me}$ retains H-atom abstraction ability for hydrocarbons with activated methylene C–H bonds (e.g., fluorene). The oxidations of styrenes and these readily oxidizable hydrocarbons follow second-order kinetics, first-order each with respect to $\mathbf{1}^{CF_3Me}$ and substrate. The lack of clear acceleration in the decay of $\mathbf{1}^{CF_3Me}$ in the presence of substrates with high C–H bond dissociation energies (e.g., cyclohexane) suggests that another reaction pathway contributes through the O–O-cleaved intermediate.

Organic peroxycarboxylic acids, such as *m*-chloroperbenzoic acid (H*m*CPBA) and peracetic acid, are versatile oxidants and extensively utilized reagents for organic substrate oxygenation. H*m*CPBA has enough reactivity for O-atom transfer toward various organic compounds, including non-activated hydrocarbons, without the use of a catalyst. However, the combination of a transition-metal catalyst and H*m*CPBA leads to regio- and chemoselective oxygenation. In the catalytic process, it is considered that an initially formed metal–acylperoxo complex is a precursor to the actual active oxidants, namely, high-valent metal–oxo species formed via homolytic or heterolytic O–O bond cleavages.[1] In the case of heme iron complexes, the metal–acylperoxo species themselves also work as O-atom transfer reagents toward olefins.[2,3] As a result, the chemical properties of *m*CPBA complexes of redox-active transition metals have attracted much attention. To date, fully characterized *m*CPBA complexes are still scarce. Especially, the substrate-oxidizing abilities of non-heme metal–*m*CPBA complexes remain to be clarified. The transfer of O atoms from Cu–*m*CPBA complexes to phosphine has been reported. However, these copper complexes are not very reactive.[4]

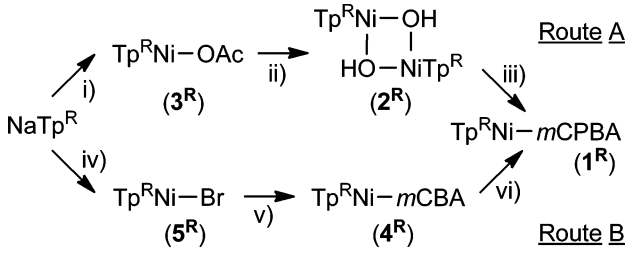
Recently, the selective hydroxylation of cyclohexane catalyzed by Ni(II) complexes with H*m*CPBA has been reported.[5] While we were examining the reactivity of the active oxygen complexes of nickel with tridentate Tp^R ligands, where Tp^R denotes a substituted hydrotris(pyrazolyl)borate and R lists the non-hydrogen substituents (R = iPr_2, iPr_2Br, Me_2, and Me_2Br; see Chart 1), we detected thermally unstable Ni(II)–acylperoxo intermediates [$Ni^{II}(Tp^R)$(*m*CPBA)] ($\mathbf{1}^R$).[6] The acylperoxo complexes $\mathbf{1}^R$ were formed by reaction of the dinuclear bis(μ-hydroxo)nickel(II) complexes [$(Ni^{II}Tp^R)_2(\mu$-$OH)_2$] ($\mathbf{2}^R$) with stoichiometric amounts of H*m*CPBA (Scheme 1, route A). The thermal stability of $\mathbf{1}^R$ depends on the electronic nature of the R^4 group on the Tp ligand: the complex $\mathbf{1}^{Me_2Br}$ bearing the electron-withdrawing bromine group is more stable than the nonbrominated derivative $\mathbf{1}^{Me_2}$. Interestingly, the acylperoxo species $\mathbf{1}^R$ have the potential to abstract a hydrogen atom from the aliphatic C–H group, as evidenced by the kinetic isotope effect during the self-decomposition of $\mathbf{1}^R$ in CH_2Cl_2/CD_2Cl_2. We have not been able to isolate $\mathbf{1}^R$ to date. Not only does its structure remain to be characterized, but the nature of its oxidizing abilities toward various external substrates other than alkanes remains to be clarified. In this work, we characterized in detail the molecular

Chart 1. Abbreviations for the Tp^R Ligands



	Tp^R	R^3	R^4	R^5
	Tp^{iPr2}	iPr	H	iPr
	Tp^{iPr2Br}	iPr	Br	iPr
	Tp^{Me2}	Me	H	Me
	Tp^{Me2Br}	Me	Br	Me
This work	Tp^{CF3Me}	CF_3	H	Me

Scheme 1. Preparation of Tp^RNi^{II} Complexes[a]



[a] *m*CBA and *m*CPBA indicate *m*-chlorobenzoate and *m*-chloroperbenzoate, respectively. Reaction conditions: (i) $Ni(OAc)_2$; (ii) NaOH; (iii) H*m*CPBA; (iv) $NiBr_2$; (v) K*m*CBA; (vi) H*m*CPBA.

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structure and external substrate oxidizing behavior of a Ni(II)−*m*CPBA complex.

Our strategy for the isolation of a Ni(II)−*m*CPBA complex involved controlling the properties of the Ni-supporting Tp^R ligand. As mentioned above, the incorporation of electron-withdrawing groups (EWGs) on the pyrazolyl rings of Tp^R enhances the stability of **1**. In addition, steric hindrance and chemical stability (i.e., resistance to oxidation) of the substituent groups on Tp^R are critical. Bulky alkyl groups (e.g., isopropyl groups) at the R^3 position of the pyrazolyl rings wrap the O−O moiety of the metal-bound acylperoxide, stabilizing **1** and hindering the reaction with external substrates. Moreover, C−H bonds of the R^3 substituents are oxidized by a proximal oxidant (i.e., metal-bound acylperoxide or further activated species generated via O−O breaking) through intramolecular reaction. Therefore, in this study hydrotris(3-trifluoromethyl-5-methylpyrazolyl)borate (Tp^{CF_3Me}) was employed as the Ni-supporting ligand because the proximal trifluoromethyl groups exhibit an electron-withdrawing nature, high oxidation resistance, and moderate steric hindrance. The versatility of Tp^{CF_3Me} for the stabilization of metal−dioxygen species was revealed by the $Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)$ complex reported by Gorun and co-workers.[7]

Our first attempt to synthesize an acylperoxo complex with Tp^{CF_3Me} ($\mathbf{1}^{CF_3Me}$) in a manner similar to that used to form the reported $\mathbf{1}^{R}$ (i.e., dehydrative condensation between the Ni(II)−hydroxo species and H*m*CPBA; route A in Scheme 1)[6] failed because of the insolubility of the putative Ni(II)−hydroxo complex $\mathbf{2}^{CF_3Me}$ formed by the reaction of the Ni(II)−acetato complex [$Ni^{II}(Tp^{CF_3Me})(OAc)$] ($\mathbf{3}^{CF_3Me}$) with aqueous NaOH. Therefore, we selected an *m*-chlorobenzoate (*m*CBA) complex, [$Ni^{II}(Tp^{CF_3Me})(m$CBA)] ($\mathbf{4}^{CF_3Me}$), as a precursor to $\mathbf{1}^{CF_3Me}$ because exchange of the *m*CBA ligand with *m*CPBA on the Ni(II) center might occur during the turnover process in catalytic alkane oxidation by Ni/*m*CPBA systems (route B in Scheme 1).[5] $\mathbf{4}^{CF_3Me}$ was prepared from bromido complex $\mathbf{5}^{CF_3Me}$ by ligand exchange with K*m*CBA.[8] As we expected, the reaction of $\mathbf{4}^{CF_3Me}$ with a small excess (∼2 equiv) of H*m*CPBA in CH_2Cl_2 at −40 °C allowed a perfect conversion to $\mathbf{1}^{CF_3Me}$. Monitoring of the UV−vis spectral changes revealed an increase in absorbance at 375 nm, which was attributed to $\mathbf{1}^{CF_3Me}$, as the 408 nm band of $\mathbf{4}^{CF_3Me}$ decreased with an isosbestic point at 395 nm. Surprisingly, this titration experiment was reproducible at room temperature, indicating the high thermal stability of the formed $\mathbf{1}^{CF_3Me}$ [Figure S2 in the Supporting Information (SI)].

After the volatiles were removed from the reaction mixture of H*m*CPBA (2.7 equiv) and $\mathbf{4}^{CF_3Me}$ in CH_2Cl_2, the dissociated H*m*CBA and the remaining excess H*m*CPBA were washed out with H_2O and EtOH. The agreement between the UV−vis spectra of the redissolved isolated solid and the final species in the above-mentioned titration in CH_2Cl_2 suggests that isolation was achieved (Figure S4). Recrystallization of the resulting green-blue solid from CH_2Cl_2/*n*-hexane yielded a single crystal of $\mathbf{1}^{CF_3Me}$ suitable for X-ray analysis (Figure 1 and Table S3 in the SI).[8,9] The oxidation state of the Ni center is +2, and $\mathbf{1}^{CF_3Me}$ is a neutral complex, as evidenced by the absence of any counterions in the crystal lattice. The Ni center in $\mathbf{1}^{CF_3Me}$ is supported by a donor set containing three N atoms and two O atoms. The O−O bond length [1.443(3) Å] falls in the typical range for peroxide O−O lengths (Figure S4).[3,4a,10] The coordination mode of *m*CPBA is κ^2, as indicated by the bond lengths of the percarboxylate moiety [Ni1−O1, Ni−O3, and O3═C16 = 1.914(2), 2.040(2), and 1.223(3) Å, respectively]. The Ni−N(Tp) lengths in $\mathbf{1}^{CF_3Me}$ [Ni1−N1, Ni1−N3, and Ni1−N5 = 2.037(2), 2.041(2), and 2.058(2) Å, respectively] are comparable to those in $\mathbf{4}^{CF_3Me}$, where the Ni center is supported by the tridentate Tp^{CF_3Me} ligand and the κ^2-binding *m*CBA ligand. The geometry of the nickel center of $\mathbf{1}^{CF_3Me}$ is slightly distorted from square-pyramidal (τ = 0) toward trigonal-bipyramidal (τ = 1), as indicated by its τ value of 0.26. The Ni−*m*CPBA site is fully surrounded by CF_3 groups. These structural characteristics are consistent with the following observed spectroscopic properties:[8] Paramagnetically shifted ^{1}H NMR signals of $\mathbf{1}^{CF_3Me}$ assignable to the protons of the Tp^{CF_3Me} and *m*CPBA ligands support the high-spin configuration (S = 1) of the distorted five-coordinate Ni(II) center (Figures S5 and S6). Coordination of the carbonyl moiety of the acylperoxo ligand leads to a red shift of the $\nu_{C=O}$ vibration to 1644 cm^{-1} in the IR spectrum, as found in the previously reported Tp^R derivatives (i.e., for $\mathbf{1}^{Me2}$ in CH_2Cl_2 solution at −40 °C, $\nu_{C=O}$ = 1646 cm^{-1}) (Figures S7−S9).[4,6,11]

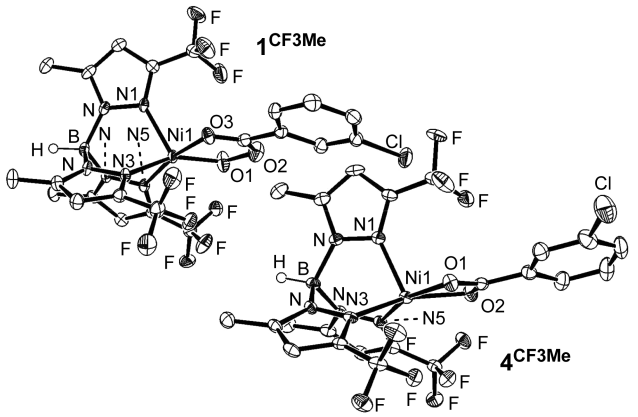

Figure 1. ORTEP diagrams of the complexes $\mathbf{1}^{CF_3Me}$ and $\mathbf{4}^{CF_3Me}$ with 50% thermal ellipsoids. H atoms on the carbon backbones have been omitted for clarity.

The oxidation reactivity of the isolated Ni(II)−acylperoxo complex $\mathbf{1}^{CF_3Me}$ for external substrates in aprotic solvents ($CF_3C_6H_5$, toluene, benzene) was studied by kinetic analysis using UV−vis spectroscopy and product analysis using GC (Scheme 2).[8] Without any substrate, the complex $\mathbf{1}^{CF_3Me}$ was thermally robust even at 70 °C in benzene (first-order rate constant = 1.63 × 10^{-5} s^{-1}), while $\mathbf{1}^{Me2}$ decomposed below −20 °C.[12] This thermal stability of $\mathbf{1}^{CF_3Me}$ is a result of the steric protection around the Ni center and the electron-withdrawing nature of the CF_3 groups in the Tp^{CF_3Me} ligand. However, $\mathbf{1}^{CF_3Me}$ behaved as an O-atom transfer reagent toward nucleophiles such as phosphine and sulfide under mild conditions. A reaction solution containing 10 equiv of thioanisole stoichiometrically formed MeS(═O)Ph (96%) and $MeS(=O)_2Ph$ (1%), and the use of 10 equiv of PPh_3 gave O═PPh_3 (103%), as determined by GC analyses (yields based on $\mathbf{1}^{CF_3Me}$; Table S4). In fact, the decay of $\mathbf{1}^{CF_3Me}$ was accelerated even at −40 °C in the presence of excess thioanisole. The pseudo-first-order reaction rate constant (k_{obs}) for the decay of $\mathbf{1}^{CF_3Me}$ became saturated as the concentration of thioanisole increased, implying that the reaction of $\mathbf{1}^{CF_3Me}$ and thioanisole proceeds through a Michaelis−Menten-type mechanism (Scheme 2 and Figures S10−S12).[13] A Lineweaver−Burk-type plot (1/[thioanisole] vs $1/k_{obs}$) gave values of the association equilibrium constant K_{on}

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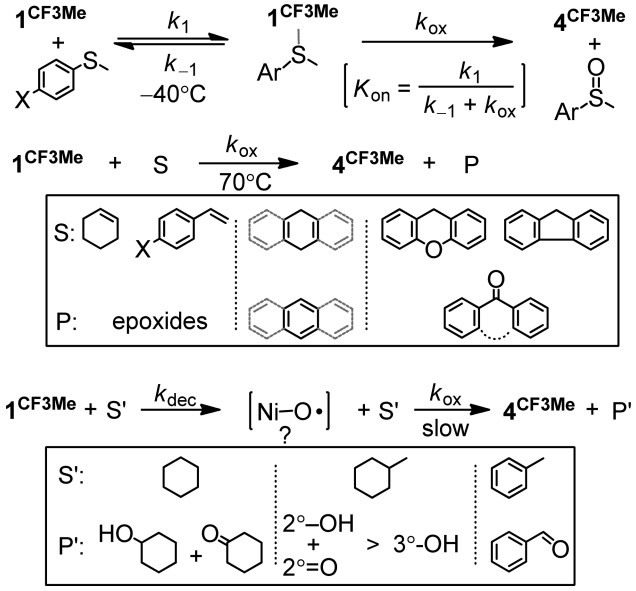
Scheme 2. Oxidation of Various Substrates Using $\mathbf{1}^{CF_3Me}$ as the Stoichiometric Oxidant



for the formation of a substrate adduct of $\mathbf{1}^{CF_3Me}$ and the rate constant k_{ox} for the subsequent sulfoxide formation (Figure 2a).

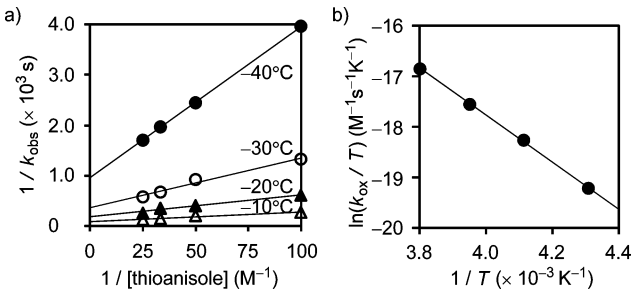


Figure 2. Plots of (a) $1/k_{ox}$ vs $1/[\text{thioanisole}]$ (Lineweaver–Burk plot) and (b) $\ln(k_{ox}/T)$ vs $1/T$ (Eyring plot) for the reaction of $\mathbf{1}^{CF_3Me}$ (1 mM) with thioanisole (5–40 mM) at −40 to −10 °C in toluene under Ar. The Eyring plot gave $\Delta H^{\ddagger}$ = 38.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −191 J K^{-1} mol^{-1}.

The negative value of $\Delta S^{\ddagger}$ (−191 J K^{-1} mol^{-1}) derived from the Eyring plot suggested that the O-atom transfer from the Ni-bound acylperoxide to the S atom occurs directly (Figure 2b). The reactions of $\mathbf{1}^{CF_3Me}$ with other para-substituted thioanisoles ($MeSC_6H_4$–X; X = Br, Me, OMe) exhibited similar reaction profiles. Linear correlations between the substituent constants σ and the K_{on} and k_{ox} values, with negative values of the Hammett reaction constants ρ, indicated that the higher Lewis basicity of the substrate enhances the formation of the $\mathbf{1}^{CF_3Me}$·$MeSC_6H_4$–X adduct and that the Ni-bound acylperoxide shows an electrophilic nature (Figures S13 and S14).

The Ni(II)–acylperoxide complex $\mathbf{1}^{CF_3Me}$ also behaves as an electrophilic O-atom transfer reagent toward alkenes. Reactions of $\mathbf{1}^{CF_3Me}$ with 10 equiv of cyclohexene and styrene in $CF_3C_6H_5$ at 70 °C yielded the corresponding epoxides in 66 and 92% yield, respectively. The formation of small amounts of 2-cyclohexen-1-ol (4%)/2-cyclohexen-1-one (6%) and benzaldehyde (3%), respectively, might suggest the involvement of a small extent of H-atom abstraction (Table S4). The reactions of $\mathbf{1}^{CF_3Me}$ with a series of para-substituted styrenes (H_2C=CHC_6H_4–X; X = Br, H, Me, OMe) exhibited second-order kinetics (Figures S15–S20). The negative value of $\Delta S^{\ddagger}$ (−110 J K^{-1} mol^{-1}) for the oxidation of styrene (X = H) indicates that the reaction proceeds through an associative transition state. The time course of changes in the UV–vis spectral pattern showed an isosbestic point, which may imply conversion from $\mathbf{1}^{CF_3Me}$ to $\mathbf{4}^{CF_3Me}$ without any intermediate. Also, the electrophilic nature of $\mathbf{1}^{CF_3Me}$ was evidenced by a negative ρ value (−1.35) derived from the Hammett plot of σ versus log k_{ox} (k_{ox} = second-order rate constant) at 90 °C.

Remarkably, $\mathbf{1}^{CF_3Me}$ can oxidize hydrocarbon substrates with activated methylene C–H bonds, such as 1,4-cyclohexadiene (CHD), 9,10-dihydroanthracene (DHA), xanthene, and fluorene, obeying second-order kinetics (Figures S21–S28). In the UV–vis spectrum of $\mathbf{1}^{CF_3Me}$ in the presence of a large excess of CHD, the $\mathbf{4}^{CF_3Me}$ band at 408 nm increased concomitantly with the consumption of $\mathbf{1}^{CF_3Me}$. No significant features were found at around 800 nm in our system; we attribute this result to the absence of putative high-valent Ni–O species arising from the cleavage of the acylperoxide O–O bond.[14] The negative $\Delta S^{\ddagger}$ values for the reactions of the compounds with activated methylene C–H bonds indicated that $\mathbf{1}^{CF_3Me}$ works as the direct oxidant without an O–O-bond-cleaved intermediate (Figures S29–S32). The values of the second-order rate constants and C–H bond dissociation energies (BDEs) of these substrates are not correlated, which might be attributable to the steric effects of the CF_3 groups around the Ni center of $\mathbf{1}^{CF_3Me}$: less hindered CHD is more easily accessible to the acylperoxide ligand of $\mathbf{1}^{CF_3Me}$, leading to a faster reaction than with hindered DHA, although the latter has a lower BDE (Figure S33). It must be noted that no clear acceleration of the decay of **1** was observed in the presence of 1000 equiv of cyclohexane in benzene. The product analysis of the reaction of $\mathbf{1}^{CF_3Me}$ and methylcyclohexane indicated that the reaction proceeded in the somewhat sterically crowded coordination sphere of the Ni center (Table S4).[6] Therefore, in the case of large-BDE substrates such as cyclohexane, another reaction pathway through the O–O-cleaved intermediates [i.e., high-valent Ni–O or Ni(II)–oxyl species] is dominant.

In conclusion, we have succeeded in fully characterizing the Ni(II)–acylperoxo complex. This thermally robust acylperoxide compound works as an O-atom transfer reagent toward nucleophilic sulfides and olefins and also is a genuine oxidant toward activated aliphatic C–H bonds.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) See the Supporting Information.

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(12) The thermal stability of $\mathbf{1}^{CF_3Me}$ is comparable to that of H*m*CPBA.

(13) Ligand exchange with the terminal O atom of *m*CPBA during the initial association process can be excluded because no immediate decrease in the peroxide-to-Ni ligand-to-metal charge-transfer band of $\mathbf{1}^{CF_3Me}$ at 375 nm was observed in the UV−vis spectrum after the addition of thioanisole.

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