Conversion of a Hydroperoxo Complex, $(\mathrm{Tp}^{\mathrm{iPr2}})(\mathrm{py})\mathrm{Pd\text{-}OOH}$, into a Cyclic Alkylperoxo Complex, $[\mathrm{HB(pz}^{\mathrm{iPr2}})_2(\mathrm{pz\text{-}3\text{-}CMe_2\text{-}5\text{-}i\text{-}Pr})](\mathrm{py})\mathrm{Pd\text{-}OO}$, Catalyzed by Cu(II) Species [$\mathrm{Tp}^{\mathrm{iPr2}}$: Hydrotris(3,5-diisopropylpyrazolyl)borato]

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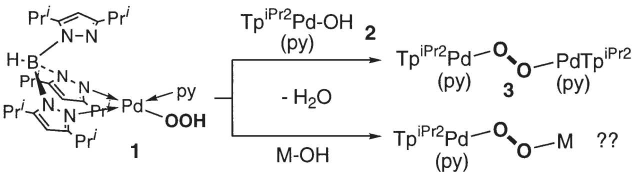
Treatment of a hydroperoxopalladium complex, $(\mathrm{Tp}^{\mathrm{iPr2}})(\mathrm{py})\mathrm{Pd\text{-}OOH}$, with a catalytic amount of a Cu(II) species resulted in peroxidation of the methine moiety of an isopropyl group proximal to the metal center to give a cyclic alkylperoxopalladium complex.

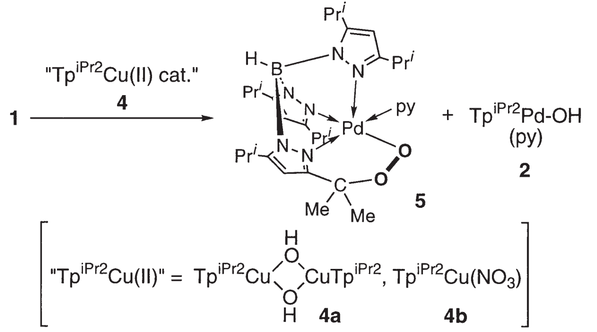
Hydroperoxo species (M-OOH) have been proposed as key intermediates of metal-catalyzed oxidation reactions of organic compounds.[1] But little information concerning M-OOH species has been accumulated so far, because they are usually thermally unstable. Only several examples are found in the CSD database and, accordingly, even their structural features have not been understood well.[2] During the course of our systematic synthetic study of dioxygen complexes containing Tp^{R} ligands [Tp^{R}= hydrotris(pyrazolyl)borato ligands][3] we found that a variety of peroxopalladium complexes, $\mathrm{Tp}^{\mathrm{R}}(\mathrm{L})\mathrm{Pd\text{-}OOX}$ [X = H, Bu^t, $\mathrm{PdTp}^{\mathrm{R}}(\mathrm{py})_n$ ($n = 0, 1$)], were stable enough to be isolated and fully characterized.[4] The successful isolation of the hydroperoxo complex, $\mathrm{Tp}^{\mathrm{iPr2}}(\mathrm{py})\mathrm{Pd\text{-}OOH}$ (**1**),[4] provided us an opportunity to examine its reactivity. Herein we wish to report a Cu-catalyzed intramolecular peroxygenation of **1**.

Previously we reported synthesis of the μ-peroxo complex, $(\mathrm{Tp}^{\mathrm{iPr2}})(\mathrm{py})\mathrm{Pd\text{-}OO\text{-}Pd}(\mathrm{Tp}^{\mathrm{iPr2}})(\mathrm{py})$ (**3**), via dehydrative condensation between **1** and the hydroxo complex, $(\mathrm{Tp}^{\mathrm{iPr2}})(\mathrm{py})\mathrm{Pd\text{-}OH}$ (**2**) (Scheme 1). This result prompted us to examine condensation of **1** with hydroxo complexes of other metals, which would produce heterometallic versions of **3**.



Scheme 1.

Attempted dehydrative condensation between **1** and the di(μ-hydroxo)dicopper complex (**4a**) in 1 : 1 ratio in $\mathrm{CH_2Cl_2}$ did not result in formation of the expected heterometallic complex but recovery of **4a** and, upon further concentration and cooling of the filtrate, an almost equimolar mixture of two pale yellow palladium complexes **2** and **5** was obtained (Scheme 2).[4] The hydroxo complex **2** was readily identified by comparison with an authentic sample[5] and the other product **5** (44% isolated yield) was characterized as the cyclic alkylperoxo species on the basis of the following spectroscopic features.[6] (i) An FD-MS spectrum revealed occurrence of dehydrogenation [m/z: 682 = 684(**1**) − 2H]. (ii) A ^{1}H-NMR spectrum with a mirror-symmetrical feature[7] containing a singlet methyl signal [δ_{H} 1.69 (6H)] revealed functionalization of the $\mathrm{Tp}^{\mathrm{iPr2}}$ ligand. (iii) A ^{13}C-NMR spectrum contained a quarternary carbon signal at δ_{C} 79.2. (iv) The ν(BH) vibration indicated κ^3-coordination of the Tp^{R} ligand. The NMR features (ii) and (iii) suggested replacement of the methine hydrogen atom of an isopropyl group by a hetero atom, most likely an oxygen atom resulting from decomposition of the OOH moiety, and the feature (i) was consistent with the cyclic alkylperoxo structure, which was confirmed by X-ray crystallography (Figure 1).[8] The structural parameters for the Pd-O-O-C linkage are comparable to those for the t-butylperoxo complex, $(\mathrm{Tp}^{\mathrm{iPr2}})(\mathrm{py})\mathrm{Pd\text{-}OOBu}^t$, previously reported by us [Pd-O: 1.988(4); O-O: 1.436(3); O-C: 1.434(6) Å].[4] Although N31···Pd separation is substantially longer than the other Pd-N distances, the lone pair electrons of N31 projecting toward the Pd center [cf. the B1-N32-N31-Pd1 dihedral angle: 0.5(5)°] revealed weak interaction between them, leading to the



Scheme 2.

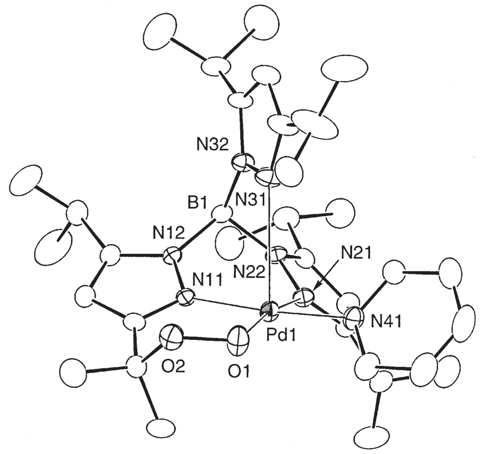


Figure 1. Molecular structure of **5** drawn with thermal ellipsoids at the 30% probability level. Selected bond lengths (in Å): Pd1-O1: 1.982(5), O1-O2: 1.479(6), O2-C14: 1.455(8), Pd1-N11: 1.991(4), Pd1-N21: 2.054(5), Pd1···N31: 2.925(5), Pd1-N41: 2.035(5).

distorted five-coordinate square-pyramidal geometry.

The recovery of the copper(II) component **4a** suggested its catalytic action in the conversion of **1**. As we expected, addition of a catalytic amount (20 mol%) of **4a** to **1** led to essentially the same result as that mentioned above. Furthermore it was found that the nitrato complex **4b**, which could not undergo dehydrative condensation, also served as a catalyst for the conversion of **1**. Thus it was concluded that the peroxygenation of **1** giving **5** did not result from decomposition of a heterometallic μ-peroxo intermediate (Scheme 1) but from a redox process mediated by the Cu(II) species **4**.

The formation of **5** and **2** is best interpreted in terms of a Kharasch-type mechanism, which accounts for formation of dialkyl peroxide from alkyl hydroperoxide and alkane in the presence of a redox-active metal catalyst ($2\ ROOH + R'\text{-}H \rightarrow ROO\text{-}R' + R\text{-}OH + H_2O$).[1] Redox decomposition of the hydroperoxide **1** by the action of a Cu catalyst (**4**) forms the peroxy (**A**) and oxy radical species (**B**). Subsequent intramolecular H-abstraction in **B** gives the alkyl radical **C**, which undergoes coupling with **A** to lead to the formation of the alkylperoxo skeleton **D**. The two Pd species **5** and **2** should be formed via reorganization of the Pd-O linkages in **D**.

When the reaction was monitored by ^{1}H-NMR (Figure 2), slow conversion was observed above $-20\,^{\circ}$C to give a mixture of products (see the spectrum observed at $0\,^{\circ}$C), which was finally converted to **2** and **5**. As can be seen from the spectra, the reaction proceeded under very mild conditions and was very clean; no other by-product could be detected. When the sample obtained at $0\,^{\circ}$C was analyzed by FD-MS, an ion peak at 1413 was observed. The m/z value is consistent with the structure **E** (Scheme 3); both **E** and **D** contain common structural features including the Pd-OO-C linkage.

The present study, a rare example of the study on chemical properties of M-OOH species, suggests that hydroperoxo species can be converted to alkylperoxo species by the action of a redox-active metal species (Scheme 4). Both of the species are key intermediates of catalytic oxidation reactions, and a new pathway from M-OOH to M-OOR associated with a C-H bond activation process has been definitely established on the basis of the present research using an isolated sample of a M-OOH species.

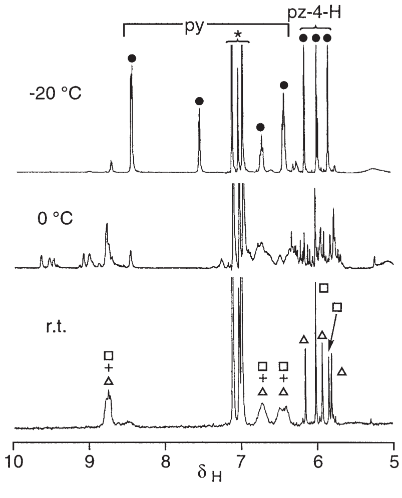
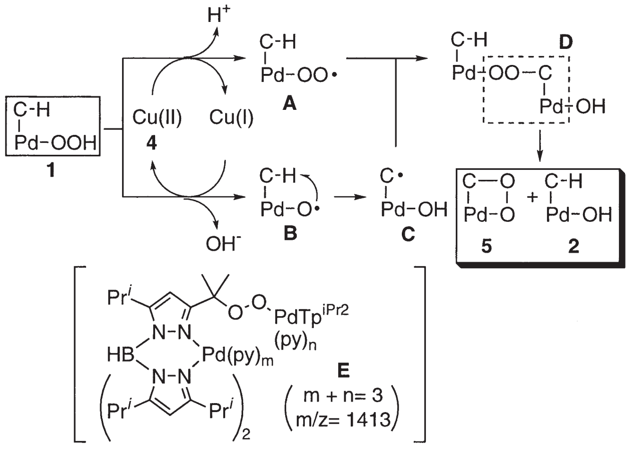


Figure 2. Reaction of **1** (•) and **4b** monitored by ^{1}H-NMR (200 MHz). **5**: □ ; **2**: △. Peaks indicated by an asterisk are for residual proton signals of toluene-d_8.



Scheme 3.

$$M\text{-}OOH + R\text{-}H \xrightarrow{\text{cat.}} M\text{-}OOR$$

Scheme 4.

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References and Notes

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[2] For structurally characterized M-OOH species, see Ref. 25 in Ref. 4(c).

[3] M. Akita and S. Hikichi, *Bull. Chem. Soc. Jpn.*, **75**, 1657 (2002). Abbreviations used in this paper: Tp$^{\mathrm{iPr2}}$: hydrotris(3,5-diisopropylpyrazolyl)borato; pz$^{\mathrm{iPr2}}$: 3,5-diisopropylpyrazolyl.

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[6] Selected spectroscopic data: **5**: IR (KBr) 2539 cm^{-1} (ν_{BH}). ^{1}H-NMR ($CDCl_3$) δ_{H} 8.81 (2H, d, $J = 5$ Hz, *o*-py), 6.63 (2H, t, $J = 8$ Hz, *p*-py), 6.32 (2H, t, $J = 7$ Hz, *m*-py), 6.06 (2H, s, 4-pz-H), 5.79 (4H, s, 4-pz-H), 3.63 (1H, sept, $J = 7$ Hz, C*H*Me$_2$), 3.44, 2.72 (2H × 2, sept, $J = 7$ Hz, C*H*Me$_2$), 1.69 (6H, s, Me$_2$COO), 1.30 – 0.99 (36H, CH*Me*$_2$). ^{13}C-NMR ($CDCl_3$) δ_{C} 159.3, 158.5, 156.0 (s, 3- or 5-pz), 152.2, (d, $J = 187$ Hz, *o*-py), 150.1 (s, 3- or 5-pz), 137.4 (dt, $J = 163$, 6 Hz, *p*-py), 124.1(dt, $J = 173$, 6 Hz, *m*-py), 98.43, 97.39 (s, $J = 169$ Hz, 4-pz), 79.2 (s, COO), 28.4 – 22.6 (i-Pr).

[7] Mirror-symmetrical NMR features were due to a fluxional process via flipping of the O-O moiety to the vacant site trans to the axial pz$^{\mathrm{iPr2}}$ ring. This process made the two diastereotopic methyl groups of the OOCMe$_2$ moiety equivalent at higher temperatures.

[8] X-ray diffraction measurement was made on a Rigaku RAXIS IV imaging plate area detector at $-90\,^{\circ}$C. Crystal data: **5**: $C_{32}H_{50}N_7O_2BPd$, $fw = 682.0$, monoclinic, space group $P2_1/n$, $a = 9.8168(4)$ Å, $b = 25.078(1)$ Å, $c = 14.0287(5)$ Å, $\beta = 98.494(2)^{\circ}$, $V = 3415.7(2)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.33$ g cm^{-3}, $R1 = 0.069$ (refined on F^2) for 5116 data ($I > 2\sigma(I)$) and 406 parameters, $wR2 = 0.193$ (all 7103 data).

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