Systematic synthesis of a series of hydroperoxo-, alkylperoxo- and μ-peroxo-palladium complexes supported by the hydrotris(3,5-diisopropylpyrazolyl)borate ligand (Tp$^{\mathrm{iPr}}$), Tp$^{\mathrm{iPr}}$Pd(py)–OOX [X = PdTp$^{\mathrm{iPr}}$(py), H, Bu$^{\mathrm{t}}$], *via* dehydrative condensation of a hydroxo complex, Tp$^{\mathrm{iPr}}$Pd(py)–OH

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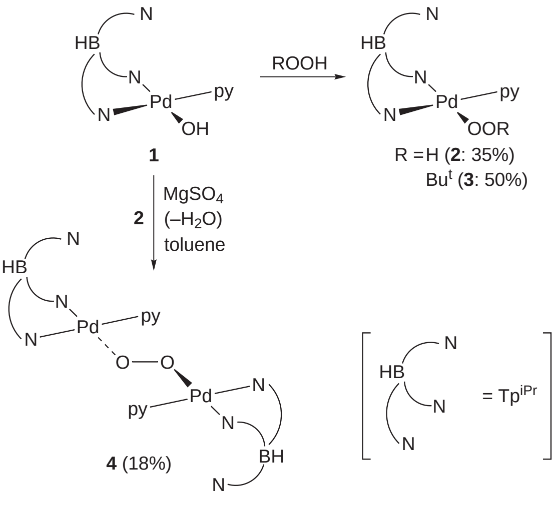
A series of hydroperoxo, *tert*-butylperoxo and μ-peroxo complexes of palladium, Tp$^{\mathrm{iPr}}$Pd(py)(OOX) [X = H, Bu$^{\mathrm{t}}$, PdTp$^{\mathrm{iPr}}$(py); Tp$^{\mathrm{iPr}}$: hydrotris(3,5-diisopropylpyrazolyl)borate] is prepared by dehydrative condensation of a hydroxo complex, Tp$^{\mathrm{iPr}}$Pd(py)(OH), with HOOX.

Transition metal peroxo, hydroperoxo and alkylperoxo species are postulated as key intermediates of catalytic oxygenations such as transition metal catalyzed oxidation of organic compounds and physiological metabolic reactions.[1] For investigation of the reaction mechanisms it is essential to characterize the structure and chemical properties of possible intermediates but well-characterized examples of peroxo complexes‡ are still rare. In our laboratory first row transition metal peroxo complexes supported by hydrotris(pyrazolyl)borate ligands (Tp$^{\mathrm{R}}$) have been studied from the bioinorganic viewpoint.[2] As for their synthetic methods, we have established that transition metal hydroxo complexes are versatile precursors for peroxo complexes *via* dehydrative condensation with ROOH. Recently our research target is extended to peroxo complexes not related to metalloproteins (Co, Ni, and the second row metals)[3] for comprehensive understanding of chemistry of transition metal dioxygen complexes based on the Tp$^{\mathrm{R}}$ ligand system. Herein we report synthesis and characterization of a series of peroxo palladium complexes, Tp$^{\mathrm{iPr}}$Pd(py)–OO–X [X = H, Bu$^{\mathrm{t}}$, PdTp$^{\mathrm{iPr}}$(py); Tp$^{\mathrm{iPr}}$: hydrotris(3,5-diisopropylpyrazolyl)borate].§

The starting hydroxo complex, (κ^2-Tp$^{\mathrm{iPr}}$)Pd(py)–OH **1**,¶ was prepared by hydrolysis of the corresponding chloro complex, (κ^2-Tp$^{\mathrm{iPr}}$)Pd(py)–Cl,‖ with aqueous NaOH solution. Complex **1** turned out to be basic enough to be condensed with various protic substrates including acetic acid, phenol, methanol and hydroperoxides (Scheme 1). Reaction with a slight excess amount of H_2O_2 (30% aqueous solution) in THF gave the hydroperoxo complex **2** as yellow solids, and the yellow *tert*-butylperoxo complex **3** was obtained *via* condensation with *tert*-butylhydroperoxide (70%; the remaining part was Bu$^{\mathrm{t}}$–OO–Bu$^{\mathrm{t}}$) in benzene. The condensation products **2** and **3** were characterized as square-planar 16e Pd$^{\mathrm{II}}$-complexes on the basis of their spectroscopic features [(*i*) the three non-equivalent pyrazolyl rings; (*ii*) the incorporation of py; (*iii*) the B–H stretching vibration appearing below 2500 cm^{-1} indicating κ^2-coordination of the Tp$^{\mathrm{iPr}}$ ligand[3b]]. Characterization of the hydroperoxo complex **2** was based on the OOH signal (^{1}H NMR) observed at δ 6.86 (*cf*. the OH signal of **1**: δ −1.79), which disappeared upon addition of a drop of D_2O, but neither ν(O–O) nor ν(O–H) stretching vibration was detected. The molecular structure of *tert*-butylperoxo complex **3** was confirmed by X-ray crystallography** (Fig. 1.)

The successful condensation reactions of **1** prompted us to examine synthesis of a dinuclear μ-peroxo complex *via* reaction



Scheme 1

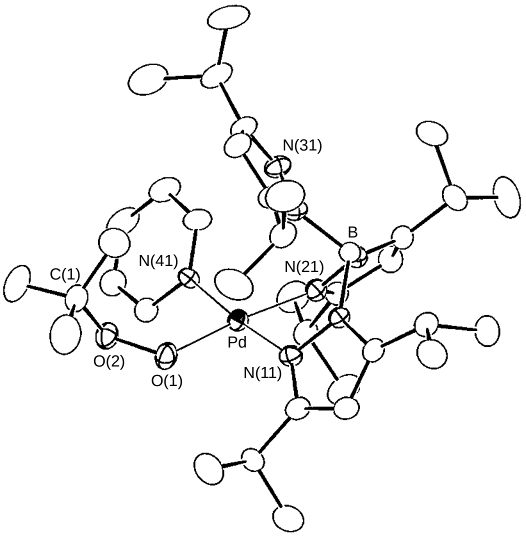


Fig. 1 Molecular structure of the *tert*-butylperoxo complex **3**. Selected interatomic distances (Å) and angles (°): O(1)–O(2) 1.440(5), O(2)–C(1) 1.439(6), Pd(1)–O(1) 1.981(4), Pd–N(11) 1.983(4), Pd–N(21) 2.021(4), Pd(1)···N(31) 3.582(5), Pd–N(41) 2.010(4); Pd–O(1)–O(2) 114.2(3), O(1)–O(2)–C(1) 109.5(4), N(21)–Pd–O(1) 174.4(1).

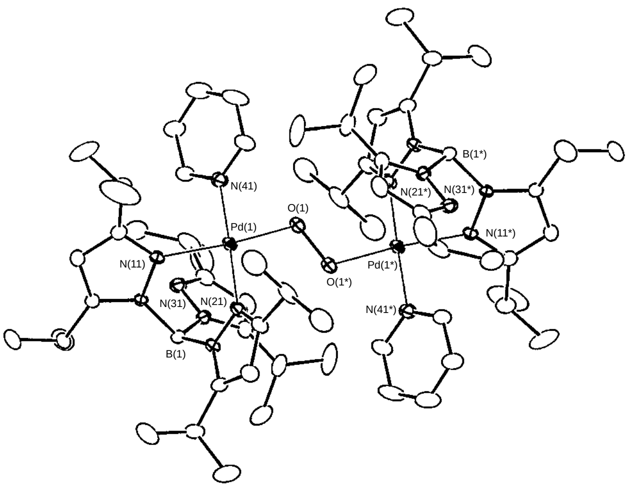


Fig. 2 Molecular structure of the μ-peroxo complex **4** drawn at the 30% probability level. Selected interatomic distances (Å) and bond angles (°). O(1)–O(1*) 1.445(5), Pd(1)–O(1) 1.971(3), Pd(1)–N(11) 2.056(3), Pd(1)–N(21) 2.020(3), Pd(1)···N(31) 3.486(3), Pd(1)–N(41) 2.035(3); Pd(1)–O(1)–O(1*) 111.8(2), N(11)–Pd(1)–O(1) 174.2(1).

with the hydroperoxo complex **2**. As was expected, stirring a mixture of **1** and **2** in toluene in the presence of $MgSO_4$ (a dehydrating reagent) gave the μ-peroxodipalladium complex **4** after crystallization from pentane–ether (Scheme 1). Because **4** was sensitive to moisture, addition of $MgSO_4$ was essential to remove water formed by the condensation. Otherwise the condensation was reversed and an equilibrated mixture of **1**, **2** and **4** was obtained. The μ-peroxo complex **4** could be also formed by condensation of **1** with 0.5 equiv. of H_2O_2, but a mixture of products containing **4** was obtained. The spectroscopic features of **4** were similar to those of **1**–**3** mentioned above, and its molecular structure was determined by X-ray crystallography** (Fig. 2).

According to the CSD database, **3** and **4** are the first examples of structurally characterized η^1-alkylperoxo and μ-peroxo complexes of palladium, respectively.[5] The four-coordinated square-planar geometry around the palladium centers is evident from the interligand N–Pd–N (or O) angles close to right angles [87.2–96.0(2)° **3**, 85.0–96.9(1)° **4**] as well as the Pd(1)···N(31) separations [3.582(5) Å **3**, 3.486(3) Å **4**] non-bonding interaction. The lone pair electrons of the N(31) atoms do not project toward the vacant axial site of the palladium centers. The O–O distances of **3** [1.440(5) Å] and **4** [1.445(5) Å] fall in the typical range of the O–O distances of organic and inorganic peroxo compounds.[1,4] Because no interaction is observed between Pd(1) and O(1*) [2.845(3) Å] in **4**, the bridging O_2 part is described as a μ-$\eta^1:\eta^1$-peroxo ligand. It is notable that the Pd–O distances of the peroxo complexes **3** [1.981(4) Å] and **4** [1.971(3) Å] are slightly shorter than that of the hydroxo complex **1′** [2.021(7) Å]. Although two diastereomeric structures are possible for the dinuclear complex **4** due to the (κ^2-Tp^{iPr})Pd(py) fragment being chiral, only one isomerically pure species (X-ray structure: *meso* form lying on a crystallographic inversion center) is present as indicated by the observation of only one set of the three CH signals for the three pyrazolyl rings in Tp^{iPr}.‖

The stability and reactivity of the square-planar peroxo complexes were considerably different from those of the first row metal complexes with tetrahedral or trigonal-bipyramidal geometry.[2–4] The peroxopalladium complexes **2**–**4** were thermally stable. The *tert*-butylperoxo complex **3** decomposed when heated at 85 °C for 3 h (in C_6D_6) in the absence of an external substrate, and the hydroperoxo (**2**) and μ-peroxo complexes (**4**) slowly (1–3 days) decomposed at ambient temperature. Addition of PPh_3, however, caused their decomposition giving the phosphine oxide ($O{=}PPh_3$) in 43% (from **2**), 71% (from **3**) and 45% yields (from **4**), although the fate of the Tp^{iPr}Pd-moieties was not clear. A complicated mixture of coordination products was merely obtained as observed by ^{1}H NMR monitoring of reaction mixtures. Preliminary experiments on reactivity of the peroxo complexes **2**–**4** toward hydrocarbons revealed that vinyl ethyl ether was converted to ethyl acetate by the action of **2**–**4** but no reaction was observed with simple alkene such as hex-1-ene.

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Notes and References

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‡ In this paper, 'peroxo complex' stands for a complex containing an M–OO fragment such as peroxo, hydroperoxo and alkylperoxo complexes.

§ Abbreviations used in this paper: Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borate; py = pyridine.

¶ The monomeric structure of the hydroxo complex was confirmed by X-ray crystallography of a derivative of **1** with the hydrotris(4-bromo-3,5-diisopropylpyrazolyl)borate ligand (**1′**).**

‖ Tp^{iPr}Pd(py)–Cl was synthesized by successive treatment of $PdCl_2(PhCN)_2$ with KTp^{iPr} and pyridine. M. Akita, T. Miyaji, N. Muroga, S. Hikichi and Y. Moro-oka, to be submitted.

** X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at −60 °C. The refinements were made on F based on the observed reflections [$I > 3\sigma(I)$]. *Crystal data*: **1′**·H_2O: $C_{32}H_{51}BBr_3N_7O_2Pd$, M_w = 922.7, triclinic, space group $P\bar{1}$, a = 11.624(5), b = 18.367(9), c = 10.057(2) Å, α = 102.47(3), β = 106.46(3), γ = 75.59(4), U = 1970(1) Å^3, Z = 2, D_c = 1.57 g cm^{-3}, μ = 36.0 cm^{-1}, $R(R_w)$ = 0.082 (0.101) for the 6091 independent reflections (of 7037 measured reflections) and 410 parameters. An ORTEP drawing is available as supplementary material. **3**: $C_{36}H_{60}BN_7O_2Pd$, M_w = 740.1, triclinic, space group $P\bar{1}$, a = 13.002(7), b = 14.580(7), c = 11.29(1) Å, α = 109.69(6), β = 92.41(7), γ = 88.66(5)°, U = 2014(3) Å^3, Z = 2, D_c = 1.22 g cm^{-3}, μ = 5.0 cm^{-1}, $R(R_w)$ = 0.079 (0.089) for the 7254 independent reflections (of 7854 measured reflections) and 424 parameters. **4**·$2C_5H_{12}$: $C_{74}H_{126}B_2N_{14}O_2Pd_2$, M_w = 1478.3, orthorhombic, space group *Pbca*, a = 18.791(3), b = 22.280(3), c = 19.158(4) Å, U = 8020(2) Å^3, Z = 4, D_c = 1.22 g cm^{-3}, μ = 5.0 cm^{-1}, $R(R_w)$ = 0.051 (0.056) for the 7015 independent reflections (of 8202 measured reflections) and 424 parameters. CCDC 182/805.

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