A Transition Metal-Hydroperoxo Complex Stabilized by Hydrogen-Bonding Interaction: The First Example of a Hydroperoxopalladium Species Characterized by X-Ray Crystallography, (κ^2-Tp^{iPr})Pd(PPh$_3$)(OOH) [Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borato]

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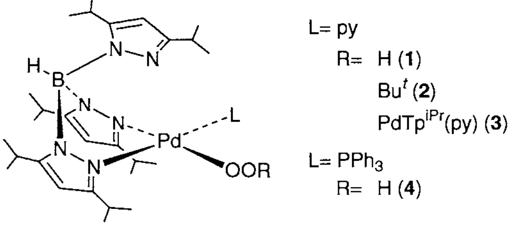
(Received May 20, 1999; CL-990410)

(κ^2-Tp^{iPr})Pd(PPh$_3$)-OOH, the first example of a structurally characterized hydroperoxopalladium species, contains hydrogen-bonding interaction between the OOH moiety and the non-coordinated pyrazolyl ring.

Transition metal-hydroperoxo species have been postulated as key intermediates of catalytic oxygenation of organic compounds [1] as well as biological transformations (e.g. P-450).[2] Little knowledge about their structure and reactivity, however, has been accumulated so far, mainly because they are too thermally unstable to be isolated and characterized.[3] In recent years, we have been carrying out systematic studies on synthesis and reactivity of transition metal-dioxygen species with Tp^R ligand [5] in order to get information on the properties of possible intermediates of oxygenation [4] and, in a previous paper, we reported synthesis of a series of peroxopalladium complexes, Tp^{iPr}Pd(py)-OOR [R= H (**1**), Bu^t (**2**), PdTp^{iPr}(py) (**3**)],[5] *via* dehydrative condensation of a hydroxopalladium complex, Tp^{iPr}Pd(py)-OH (Chart 1).[4a] In particular, a rare example of the hydroperoxo complex (**1**) was obtained by condensation with H_2O_2. Although complex **1** was characterized by comparison of its spectral data with those of the structurally characterized Bu^t derivative **2**, a couple of ambiguous points concerning the OOH moiety in **1** remained to be clarified; no absorption assignable to ν_{OH} vibration was detected and the ^{1}H-NMR signal of the OOH part appeared in considerably low field [δ_H(in C_6D_6) 6.86; cf. Tp^{iPr}Pd(py)-OH: -1.79]. During the course of our study we succeeded in structure determination of a derivative of **1**.

Chart 1.



The hydroperoxo complex **1** showed activity for oxidation of organic compounds. For example, reaction of **1** with an excess amount of PPh$_3$ produced O=PPh$_3$ in 71% yield.[4a] When an ethereal solution of **1** was treated with an equimolar amount of PPh$_3$ in order to detect a reaction intermediate, orange crystals **4** were isolated from a reaction mixture after crystallization from CH_2Cl_2-hexane. Spectroscopic features of **4** [6] were very similar to those of **1** mentioned above, and X-ray crystallographic analysis [7] revealed that **4** was the substitution product formulated as (κ^2-Tp^{iPr})Pd(PPh$_3$)-OOH as shown in Figure 1. The hydroperoxo complex **4** turned out to be stable at ambient temperature both in a solution and as a solid.

The square planar coordination geometry around the Pd center is essentially the same as that of the Bu^t derivative (**2**) and the μ-peroxo complex (**3**), and the N31 atom [5] was not coordinated to Pd as judged by the separation [3.069(8) Å] and the ν_{BH} value.[6,4b] The O-O length [1.457(8) Å] is comparable to those in the previously reported hydroperoxo complexes, (η^5-C_5Me_5)Ir(μ-pz)$_3$Rh(dppe)(OOH) [1.432(8) Å] [3b] and (pyH)$_2$[MoO(O$_2$)$_2$(OOH)]$_2$ [1.458(10) Å],[3c] and the related t-butylperoxo **2** [1.440(5) Å] and μ-peroxo Pd complexes **3** [1.445(5) Å].[4a] The Pd-O distance and the Pd-O-O angle [1.971(6) Å; 109.6(4)°] are also similar to those of **2** [1.981(4) Å; 114.2(3)°] and **3** [1.971(3) Å; 111.8(2)°].[4a]

The most striking structural feature of **4** is the hydrogen-bonding interaction evidenced by the following observations. When the core structure is closed up (Figure 1b), the lone pair electrons of the O2 and N31 atoms separated by 2.86(1) Å are projected toward the OOH hydrogen atom (H0). In general, the non-coordinated pz ring in square-planar (κ^2-Tp^R)ML$_2$-type complexes is projected away from the metal center to minimize the steric repulsion due to the 3- and 5-substituents of the pz ring.[4b,d] The extent of flipping of the non-coordinated pz ring can be

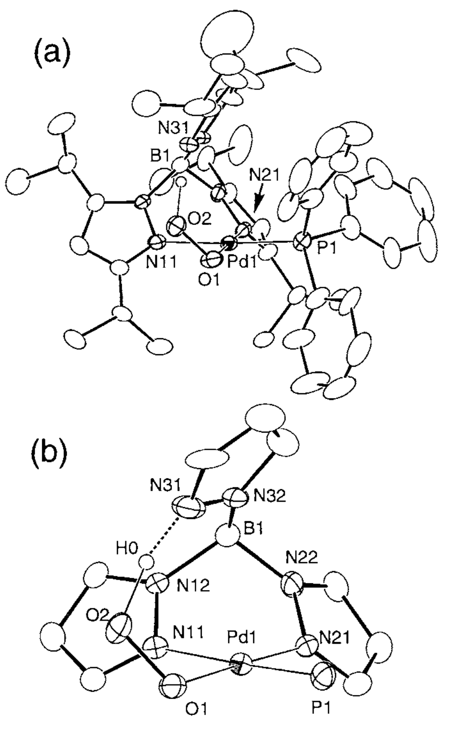


Figure 1. Molecular structure of **4** drawn at the 30% probability level. (a) An overview. (b) An expanded view of the core part illustrating the hydrogen-bonding interaction.

evaluated by (i) the N31···Pd1 and N32···Pd1 distances and (ii) the N-B1-N32-N31 dihedral angles. In the case of **2** and **3**, the N32 atom is located closer to Pd1 than the N31 atom [**2**: N31···Pd1: 3.582 (5) Å > N32···Pd1: 3.248(4) Å; **3**: N31···Pd1: 3.74(2) Å > N32···Pd1: 3.54(2) Å] and thus N31 is projected away from Pd1. On the contrary, the N31 atom in **4** is closer to Pd1 than the N32 atom [N31···Pd1: 3.069(8) Å < N32···Pd1: 3.143(6) Å] and the Pd···N distances in **4** are shorter than those in **2** and **3** by 0.2 - 0.5 Å as well, suggesting occurrence of an attractive interaction at N31. As for the second aspect, the two dihedral angles, N12-B1-N32-N31 and N22-B1-N32-N31, for **2** and **3** are similar [**2**: 24.4(6) ° and 37.3(5)°; **3**: 33(2)° and 41(2)°] illustrating cofacial arrangement of the non-coordinated pz ring with respect to the Pd coordination square, whereas the large difference observed for **4** [1.3(9)° and 118.8(8)°] suggests a twisted conformation of the pz ring. The unusual orientation of the non-coordinated pz ring in **4** should be interpreted in terms of the hydrogen-bonding interaction between O2 and N31 (Chart 2), and a similar interaction was proposed for H_2O_2-amine adducts.[8]

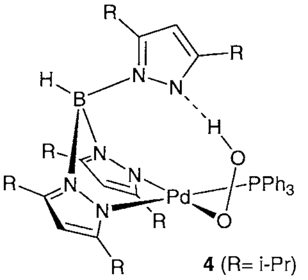


Chart 2.

4 (R= i-Pr)

In accord with this description, the hydrogen-bonding interaction should obscure the ν_{OH} vibration and cause the shift of the δ_H(OOH) signal to the region as low as δ_H 8.93 [6] due to an increase of the acidity of the OOH proton [cf. δ_H(OOH) for (η^5-C_5Me_5)Ir(μ-pz)$_3$Rh(dppe)(OOH): 4.55].[3b] The ^{1}H-NMR data points out that the hydrogen-bonding interaction is retained in a solution. In addition, the similar spectroscopic properties of **1** [δ_H(OOH) 6.86] and **4** suggest that the py-derivative **1** also contains the OOH···N(pz) hydrogen bond. Their stability could be partly ascribed to the hydrogen-bonding interaction causing the increase of electron density at the OO moiety and, therefore, they don't show remarkable reactivity toward a nucleophilic substrate such as PPh_3. Finally, the formation of **4** from **1** reveals that the pyridine ligand in **1** is dissociated from the Pd center in a solution, and the olefin oxygenation reported previously [4a] should involve a ligand exchange process with the substrate.

In summary, we have disclosed synthesis and structural characterization of $Tp^{iPr}Pd(PPh_3)(OOH)$ **4**, an example of very few structurally characterized transition metal-hydroperoxo species (the first example of a Pd-OOH species characterized by X-ray crystallography). The systematic comparison of the structural features of the related peroxopalladium species **2** - **4** reveals the hydrogen-bonding interaction in **4**. Hydrogen-bonding interaction is not always a crucial factor for stabilization of M-OOH species, because stable hydroperoxo species of the redox-inactive second row metals (e.g. Rh, Pd, Pt) [3,9] without hydrogen-bond are known. But the hydrogen bonding interaction would contribute to stabilization of a hydroperoxometal species as mentioned above, and similar interaction has been found for a Tp^{iPr}Rh-OOH complex.[10] In addition, the present study suggests that, when a functional group with lone-pair electrons is located close to a M-OOH species (e.g. in metalloproteins containing various amino acid residues), they would form a hydrogen-bond. Further studies on the reactivity of **1** - **4** are now under way and the results will be reported in due course.

We are grateful to the Ministry of Education, Science, Sports, and Culture of the Japanese Government for financial support of this research (Grant-in-Aid for Scientific Research).

References and Notes

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5 Abbreviations used in this paper: Tp^{iPr}= hydrotris(3,5-diisopropylpyrazolyl)borate; pz= pyrazolyl group.

6 Selected spectroscopic data for **4**: ν(B-H) 2483 cm^{-1}; δ_H($CDCl_3$; at -60°C) 5.48, 5.64, 5.89 (1H x 3, s x 3, pz-H), 8.93 (1H, s, OOH); δ_P($CDCl_3$; -60 °C) 20.6. Broad spectra were obtained at room temperature due to a ligand exchange process.

7 X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo Kα radiation (λ= 0.71069 Å). Crystal data for $4{\cdot}2CH_2Cl_2$: $C_{47}H_{66}BN_6O_2PCl_4PdNi$, fw= 1037.1, temp. -60 °C, orthorhombic, space group $Pna2_1$, a= 21.120(2) Å, b= 16.888(3) Å, c= 14.678(3) Å, V= 5235(1) Å^3, Z= 4, d_{calcd}= 1.31 g·cm^{-3}, μ= 6.30 cm^{-1}, R= 0.0671 for 5636 data with $F_o > 4\sigma(F_o)$ and 600 parameters.

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