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Stable Hydroperoxido Complex

Stabilization of the Hydroperoxido Ligand: A $1\kappa O,2\kappa O'$ Dimetallic Coordination Mode**

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Recent advances in homogeneous catalytic oxidation of organic compounds have focused on the use of environmentally benign oxidants, ideally oxygen.[1] Nevertheless, the ways in which transition-metal complexes activate oxygen and the mechanisms by which the oxidation reactions occurs remain a complicated puzzle. Typically, low-valent metal centers oxidatively add oxygen to give peroxido (or superoxido) complexes, but this essentially nucleophilic peroxido ligand requires further activation to form a more electrophilic species for effective oxygenation of organic substrates, as pointed out by Akita, Moro-oka et al.[2] Possibilities for such further activation could be weakening of the O–O bond by its bridging two metal centers[3] and protonation of the peroxido ligand. Thus, metal hydroperoxido complexes have been proposed as intermediates in both transition-metal-catalyzed and enzymatic oxidations with molecular oxygen, for example, in Pd-catalyzed aerobic oxidation of alcohols[4] and biological oxidation achieved by copper enzymes such as galactose oxidase[5] and superoxide dismutase.[6] Hydroperoxido iron species play an important role in oxidations catalyzed by cytochrome P450.[7] In spite of this interest, such complexes appear in the literature as very elusive species with low thermal stability and short lifetimes, and very few transition-metal hydroperoxido complexes have been structurally characterized so far.[8,9] As part of our ongoing efforts to understand oxygenation reactions,[10] we investigated the reactivity of rhodium complexes with oxygen. Herein we describe the isolation and full characterization of a thermally stable dinuclear complex of rhodium containing the first bridging hydrogen(peroxido) (hydroperoxido) ligand coordinated in a μ-$1\kappa O,2\kappa O'$-OOH mode and a bridging peroxido (peroxo) ligand, as well as related compounds.

Peroxido-bridged dirhodium complex $[\{Rh(PhBP_3)\}_2(\mu\text{-}\kappa^1{:}\eta^2\text{-}O_2)_2]$ (**1**; $[PhBP_3]^- =$ tris(methylenediphenylphosphane)phenylborate) was obtained as an orange crystalline solid by placing a solution of $[Rh(PhBP_3)(cod)]$ (**2**; cod = 1,5-cyclooctadiene) in dichloromethane under an oxygen atmosphere at 35 °C for 10 h. The oxygenation reaction occurs cleanly at the metal centers without oxidation of the phosphane arms of the ligand. Figure 1 shows the X-ray structure of **1**,[11] in which two rhodium atoms are κ^3-coordinated to a *fac*-$[PhBP_3]^-$ ligand and are joined together by two peroxido ligands that bridge the metal centers through a single oxygen atom. In the $Rh(\eta^2\text{-}O_2)$ moiety, the peroxido ligand is noticeably nonsymmetric (Rh(1)–O(2) 2.013(2), Rh(1)–O(1) 2.151(2) Å), whereby the longer distance corresponds to the bridging oxygen atom, which in turn is closer to the other rhodium atom (Rh(1′)–O(1) 2.105(2) Å). The O(1)–O(2) bond length of 1.463(3) Å is in the range of O–O single bonds. Two precedents of this unusual bridging mode of a peroxido ligand have been reported to date for late transition metals: the related complex $[\{Rh(Cl)(PPh_3)_2\}_2(\mu\text{-}\kappa^1{:}\eta^2\text{-}O_2)_2]$,[12] and the recently described $[\{Pd(\kappa^2\text{-}Tp^{iPr})\}_2(\mu\text{-}\kappa^1{:}\eta^2\text{-}O_2)(py)]$ ($Tp^{iPr} =$ hydridotris(3,5-diisopropylpyrazolyl)borato).[8d] The dinuclear nature of **1** is maintained in solution according to NMR diffusion (DOSY) experiments.[13] For selected NMR spectroscopic data of the new complexes, see the Supporting Information.

The nucleophilic character of the peroxido ligands in **1** was further confirmed by reaction with one molar equivalent of HBF_4. Protonation of one of the peroxido ligands of **1** leads to formation of peroxido/hydroperoxido complex $[\{Rh(PhBP_3)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)(\mu\text{-}1,2\text{-}OOH)]BF_4$ ($[\mathbf{3}]BF_4$). In the structure of the cation $[\mathbf{3}]^+$ in the solid state (Figure 2),[11] two $Rh(PhBP_3)$ moieties are bridged by one hydroperoxido ligand in a μ-$1\kappa O,2\kappa O'$-OOH coordination mode and a peroxido ligand bonded in a μ-$1\eta^2{:}2\eta^2$-O_2 fashion. The location of the hydroperoxido proton on the O(1)/O(2) atoms was established from NMR spectroscopy measurements (see below). The hydroperoxido ligand is quite symmetrically situated between the rhodium atoms, with Rh(1)–O(1) and Rh(2)–O(2) distances of 2.135(3) and 2.046(3) Å, respectively. The O–OH distance of 1.450(4), Å and the Rh-O-O-Rh angles centered on the oxygen atoms of 108.2(2) and 106.3(2)° indicate an end-on coordination mode to each metal center. Furthermore, the coordination of the peroxido ligand O(3)O(4) in **3** is also remarkable.

Crystallographically characterized precedents of this unusual μ-$\eta^2{:}\eta^2$-O_2 coordination mode of the peroxido ligand to transition metals have only been reported for copper complexes that are models of oxyhemocyanin.[14] However, the related CuO_2Cu moieties are systematically planar,[14] while the RhO_2Rh framework has a butterfly conformation with a folding angle of 120.6(2)°. Moreover,

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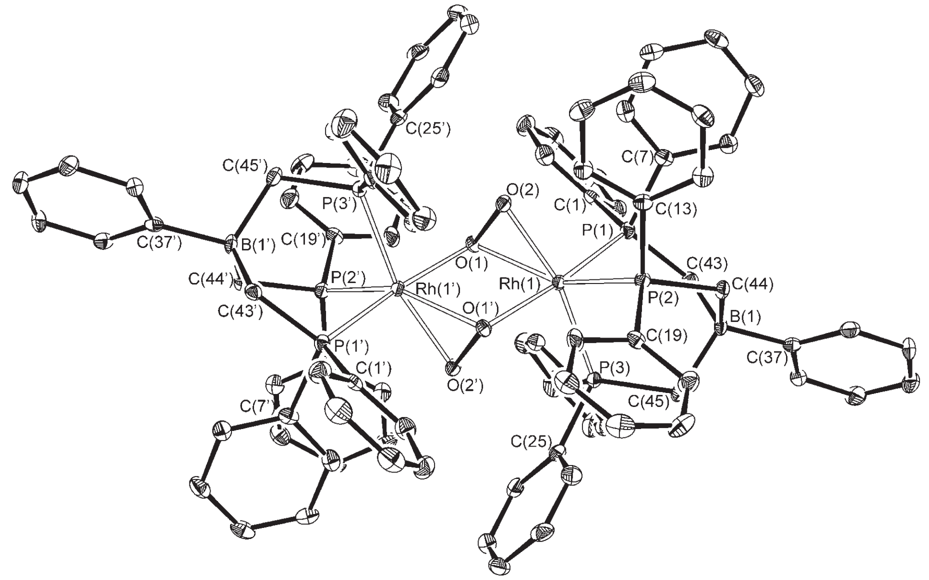


Figure 1. ORTEP drawing of **1** (primed atoms are related to unprimed atoms by an inversion center).

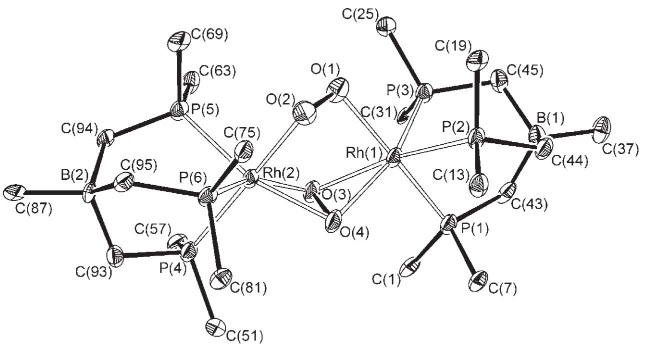


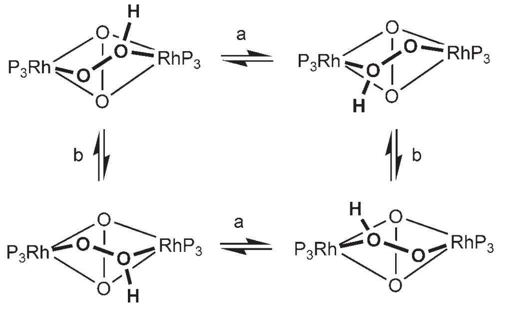
Figure 2. ORTEP drawing of **3**. For phenyl substituents, only *ipso* carbon atoms are depicted. Selected bond lengths [Å]: Rh(1)–O(3) 2.125(3), Rh(1)–O(4) 2.144(3), Rh(2)–O(3) 2.151(3), Rh(2)–O(4) 2.132(3).

the O–O distance in the peroxido ligand (1.504(4) Å) is longer than that of the hydroperoxido ligand in **3** (1.450(4) Å) and that of **1** (1.463(3) Å) but similar to those of related μ-η^2:η^2-O_2 Cu complexes with hexapyridine dinucleating ligands (1.491(5), 1.485(8) Å).[14] These elongated peroxido ligands are on the way to cleavage of the O–O bond leading to a bis(μ-oxo) complex.[15]

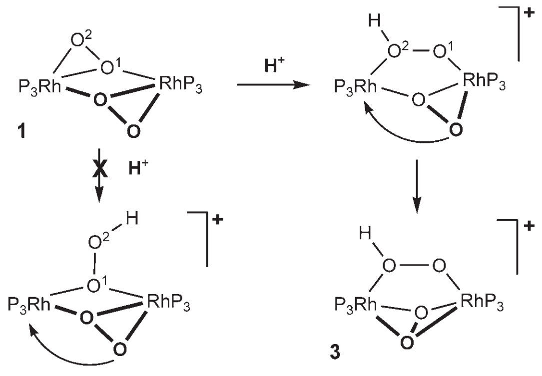
Complex **3**, like **1**, was found to be dinuclear in solution by DOSY experiments,[13] while the NMR spectra (see the Supporting Information) are consistent with averaged C_{2h} fluxional species. Indeed, variable-temperature ^{31}P{^{1}H} NMR spectra in dichloromethane show that the process is frozen below −75 °C. At this temperature the spectrum consists of six broad signals which indicate that all phosphorus nuclei are inequivalent. This rules out a static structure with a μ-1,1-hydroperoxo ligand, which would also give a symmetric spectrum. Rationalization of the observed spectra entails simultaneous occurrence of the two processes indicated in Scheme 1: tautomerism arising from a 1,2-hydrogen shift from one oxygen atom to the other in the hydroperoxido ligand (Scheme 1, a), and twisting of this ligand (Scheme 1, b) to generate a symmetry plane bisecting both rhodium atoms. Accordingly, the ^{31}P{^{1}H} NMR spectrum shows two signals (in 1:2 intensity ratio). This motion is expected to have a low energy barrier, as can be inferred from the experimental facts. Another plausible mechanism producing the observed spectra is interconversion of the μ-1,1-OOH and μ-1,2-OOH coordination modes on the rhodium atoms. However, this should be a higher-energy process since it involves cleavage and formation of Rh–O bonds. The OOH proton, which gives a sharp signal at $\delta = 4.44$ ppm in the ^{1}H NMR spectrum, is located on the O(1)/O(2) atoms (Figure 2), because it is coupled to the *trans* P(1)/P(4) atoms and reveals a NOE signal enhancement of the *ortho* protons of the phenyl groups bonded to P(2),P(3)/P(5),P(6) on saturation of the hydroperoxido signal (see the Supporting Information).

Hydroperoxido ligands acting as bridges are quite rare, with only one example in the chemistry of Co, Cu and Mo crystallographically characterized up to date.[9] Moreover, in these three compounds the OOH moiety was found to be coordinated in a μ-1,1-OOH fashion, while complex **3** represents the first example of a μ-1,2-OOH hydroperoxido ligand, that is, each oxygen atom is bonded to only one metal center.

The structural changes in the core of the complex after protonation of one of the peroxido ligands on route from **1** to **3** are shown in Scheme 2. The interaction of the proton with one oxygen atom, probably O(2), leads to opening of the RhO_2 metallacycle by selectively breaking the Rh–O(1) bond. This generates a coordination vacancy on this rhodium atom that is immediately occupied by the neighboring oxygen atom to produce a μ-η^2:η^2-peroxido ligand with a longer O–O bond than in the starting complex. The alternative pathway to



Scheme 1.



Scheme 2.

the μ-1,1-OOH moiety by breaking of the Rh–O(2) bond does not occur.

Another interesting feature of the hydroperoxido complex **3** is its remarkable stability in the absence of coordinating anions. Indeed, [**3**]BF_4 remains unaltered in solution at room temperature for days, which is quite surprising, since hydroperoxido complexes have been evoked as quite unstable species requiring isolation at low temperature or additional modes of stabilization such as hydrogen bonds. However, addition of chloride ions, in the form of bis(triphenylphosphine)iminium chloride (PPNCl), to a solution of [**3**]BF_4 in dichloromethane triggers the release of the hydroperoxido ligand with formation of $[\{Rh(PhBP_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(\mu\text{-}Cl)]BF_4$ ([**4**]BF_4) along with the bis-peroxido complex **2** and mononuclear bis-chlorido Rh^{III} complex $[Rh(PhBP_3)Cl_2]$ (**5**). Moreover, complex **5** results from the reaction of **2** with four molar equivalents of dry HCl, since protonation of the peroxido ligand to H_2O_2 is combined with ligand replacement by chloride. However, if only two molar equivalents of HCl(aq) are used, complex [**4**]Cl is the major product of the reaction, with **5** and unconsumed **2** as minor components of the reaction mixture. Figure 3 shows the structure of the cation $[\mathbf{4}]^+$,[11] in which the peroxido ligand bridges the metal atoms in a butterfly conformation. Again, the O–O distance is long (1.482(5) Å) but in the range of O–O bonds. Moreover, the Rh–Rh distance of 3.425 Å is too large to propose the bis-oxido isomer with an Rh–Rh bond. The cation $[\mathbf{4}]^+$ provides a second example of a rhodium complex with a peroxido ligand in $\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2$ coordination mode.

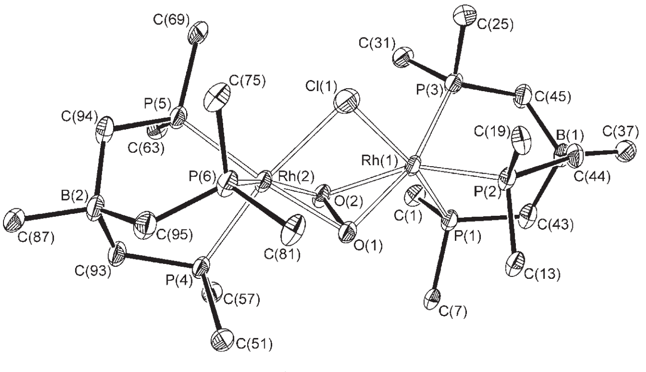


Figure 3. ORTEP drawing of $[\mathbf{4}]^+$. For phenyl substituents, only *ipso* carbon atoms are depicted. Selected bond lengths [Å]: Rh(1)–Cl(1) 2.4332(16), Rh(1)–O(1) 2.104(4), Rh(1)–O(2) 2.165(4), Rh(2)–Cl(1) 2.4215(17), Rh(2)–O(1) 2.158(4), Rh(2)–O(2) 2.141(4).

Resonance Raman spectra of complexes **1**, **3**, and **4** obtained with laser excitation at 785 nm showed bands at 810, 802, and 801 cm^{-1}, respectively, which shift to 764, 757, and 755 cm^{-1}, respectively, for the ^{18}O-labeled compounds. These bands were assigned to the O–O stretch in the three complexes on the basis of frequency and isotopic shift (46 cm^{-1}). Complex **3**, which contains both peroxido and hydroperoxido ligands in different coordination modes, should give two distinct ν(O–O) bands in this region, but only one broad band was observed under these conditions.

Irradiation of the solid with polarized laser light at 488 nm and observation of the crossed component revealed two bands at 790 and 806 cm^{-1} (see the Supporting Information). Although lower frequencies could be expected for the complexes **3**–**4** with the $\mu\text{-}\eta^2\text{:}\eta^2$-coordinated peroxide ligand, bending of the $\mu\text{-}\eta^2\text{:}\eta^2\text{-}Rh_2O_2$ core could be responsible for the O–O stretch moving to higher energies.[16]

In summary, we have isolated and fully characterized the first complex with a bridging hydroperoxido ligand in a μ-1,2-OOH coordination mode, which is remarkably stable at room temperature. This hydroperoxido ligand coexists with a bridging peroxido ligand in the same compound. Moreover, two examples of a novel $\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2$ coordination mode of the peroxido ligand in rhodium chemistry are reported. They provide a new insight into the modes of activation of dioxygen by two metal centers.

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[11] CCDC 649525 (**1**), 649526 (**3**), and 649527 (**4**) contain 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.

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[13] The dinuclear complexes **1** and **3** show diffusion coefficients of $D = 5.76 \times 10^{-10}$ and $5.82 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$, respectively, while D for the mononuclear complex **2** is $7.21 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ (measured under similar conditions: $8.5 \times 10^{-3}\,\mathrm{M}$, $CDCl_3$, 28 °C) by the pulsed gradient spin-echo (PGSE) NMR diffusion method (DOSY). Since the D value is inversely proportional to the hydrodynamic radius of the molecule or ion, it allows estimation of the molecular volume. Accordingly, the ratio of the D values for molecules related by a twofold volume is $2^{1/3} = 1.26$. The ratio of the D values for **1** and **3** relative to **2**, $D(\mathbf{2})/D(\mathbf{1}) = 1.25$ and $D(\mathbf{2})/D(\mathbf{3}) = 1.24$, are in excellent agreement with structures which have about twice the molecular volume of **2**, that is, **1** and **3** exist as dinuclear species in solution. For a review on the DOSY method, see P. S. Pregosin, P. G. A. Kumar, I. Fernández, *Chem. Rev.* **2005**, *105*, 2977 – 2998.

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