

A Rhodium Peroxido Complex in Mono-, Di-, and Peroxygenation Reactions**

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Dedicated to Professor Dieter Lentz on the occasion of his 60th birthday

One of the main challenges in oxygenation chemistry is transition-metal-mediated oxygenation using molecular oxygen as the primary oxidant.^[1] Peroxido transition metal compounds have been suggested to play a significant role as intermediates in oxygenation reactions with dioxygen.^[1,2] In most instances only one oxygen atom of the peroxido unit is transferred to the organic substrate to yield mono-oxygenated products.^[2,3] Several of these mono-oxygenation reactions therefore require additional oxophilic substrates such as phosphines or sulfoxides as sacrificial agents.^[3]

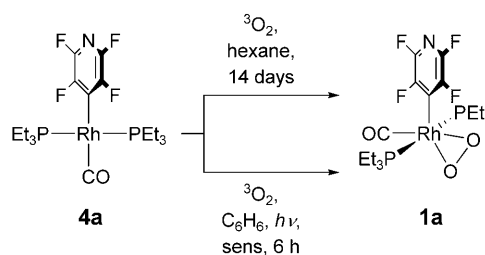
However, peroxido ligands can also react with various substrates to give new peroxido entities, which remain bound to a late transition metal center.^[4,5] For instance, *trans*-[Ir(O₂)(CH₃)(CO){P(*p*-tolyl)₃}₂] transforms CO, CO₂, and SO₂ into the corresponding carbonato, peroxidocarbonato, and sulfato ligands.^[6] The rhodium peroxido complex *trans*-[Rh(O₂)(4-C₅F₄N)(CN*t*Bu)(PEt₃)₂] reacts with boronic acids RB(OH)₂ (R = C₆H₅, C₆F₅) to give heterocyclic compounds with five-membered RhOOBO rings.^[7]

Examples of transfer of both oxygen atoms from a transition metal peroxido complex to a substrate are sparse,^[8] and formation of peroxides is relatively seldom. The complexes [M(O)(O₂)₂(py)] (M = Cr, Mo; py = pyridine) react with electron-rich enol ethers to yield the corresponding dioxetanes,^[8a] but the products are formed by two consecutive mono-oxygenation reactions and involve intermediate formation of the corresponding epoxides. Apart from mono-oxygenation of 1,5-cyclooctadiene,^[2c] oxygenation of 1,5-cyclooctadiene with [Rh(O₂)(Cl)(PPh₃)₃], which can be prepared from dioxygen, produces 1,4-cyclooctanediol.^[8b,c] However, this rare case of transition metal mediated alkene dioxygenation with O₂ is rather slow and is accompanied by competitive monooxygenation of the phosphine ligand.

Here we report the synthesis of the rhodium(III) peroxido complex *trans*-[Rh(O₂)(4-C₅F₄N)(CO)(PEt₃)₂] (**1a**) using triplet or singlet dioxygen. Under irradiation **1a** exhibits a variety of selective oxygenation reactions. It mono-oxygen-

ates phosphines, dioxygenates tetrakis(dimethylamino)ethylene (**2**), and peroxygenates 9,10-dimethylantracene (**3**). The last-named transformation can be regarded as a model reaction for direct transfer of a dioxygen unit from a peroxido complex to an organic substrate. According to our knowledge, such a reaction is unprecedented. Moreover, in a photocatalytic experiment an anthracene endoperoxide can be generated in stoichiometric excess.

Treatment of a solution of *trans*-[Rh(4-C₅F₄N)(CO)(PEt₃)₂] (**4a**)^[9] in hexane with dioxygen gave the peroxido compound *trans*-[Rh(O₂)(4-C₅F₄N)(CO)(PEt₃)₂] (**1a**) over two weeks (Scheme 1). *trans*-[Rh(¹⁸O₂)(4-C₅F₄N)(CO)-



Scheme 1. Syntheses of **1a** (sens = methylene blue).

(PEt₃)₂] (**1b**) is available in a similar fashion by using ¹⁸O₂. Reaction of the ¹³C-labeled isotopomer *trans*-[Rh(4-C₅F₄N)-(¹³CO)(PEt₃)₂] (**4b**)^[9] with dioxygen yielded *trans*-[Rh(O₂)(4-C₅F₄N)(¹³CO)(PEt₃)₂] (**1c**). Formation of **1a**, **1b**, and **1c** is spin-forbidden and requires crossing between the singlet and triplet surfaces on the reaction coordinate.^[10] Consequently, **1a** can be synthesized within six hours on using singlet dioxygen, generated in situ by irradiation of triplet dioxygen with a tungsten halogen lamp in the presence of methylene blue as sensitizer (Scheme 1). Alternatively, the photochemical reaction conditions may provide a reaction pathway which involves initial electron transfer from **4a** to dioxygen.^[10a] A similar method was used to synthesize *trans*-[Rh(O₂)(SC₆F₅)(CO)(PPh₃)₂], *trans*-[Rh(O₂)(Cl)(CO)(PPh₃)₂], and *trans*-[Rh(O₂)(CO)(PPh₃)₂(NCCH₃)]ClO₄, which are unstable at room temperature.^[11] Without sensitizer only tiny amounts of **1a** were generated. When **4a** was photolyzed in the presence of triplet dioxygen with an Xe UV lamp, phosphine oxide was produced.^[12]

The peroxido compound **1a** is soluble in aromatic hydrocarbons (benzene, toluene) and polar solvents like THF, Et₂O, and CH₂Cl₂, and is inert to air and water. In contrast to some other rhodium peroxido species^[11c,13] dioxygen is not released

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[**] We would like to acknowledge the Deutsche Forschungsgemeinschaft for financial support. We are grateful to P. Kläring and A. Penner for the crystallography. We also would like to acknowledge Prof. C. Limberg for valuable discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201007315>.

by bubbling argon through a solution of **1a** in benzene, or under high vacuum in the solid state.^[11,13–15] In addition, irradiation of **1a** in the presence of $^{18}\text{O}_2$ did not lead to formation of **1b**. The stabilizing properties of the perfluorinated pyridyl ligand may play a certain role in this context.^[7,9,16]

The ^{19}F NMR spectrum of **1a** consists of three signals (ratio: 2:1:1) for the tetrafluoropyridyl ligand, which indicate hindered rotation about the rhodium–carbon bond. Formation of a rhodium(III) complex is evidenced by a rhodium–phosphorus coupling constant of 82 Hz for the signal at $\delta = 28.8$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and by an absorption band at 2026 cm^{-1} in the IR spectrum, which can be assigned to the CO stretching vibration.^[7,9,16a,b] Note that the (*N*-heterocyclic carbene)rhodium(I) species *cis*-[RhCl(IMes)-(PPh₃)₂] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and the phosphine pincer rhodium(I) compound [(Me₂C₆H(CH₂PtBu₂)₂)Rh(η^1 -N₂)] both react with dioxygen to give dioxygenated rhodium derivatives, but with no concomitant change in the oxidation state of the transition metal.^[17] The IR spectrum of **1a** shows an absorption band at 866 cm^{-1} (Figure 1). This band shifts to 820 cm^{-1} for the ^{18}O -labeled isotopologue **1b** and can therefore be assigned

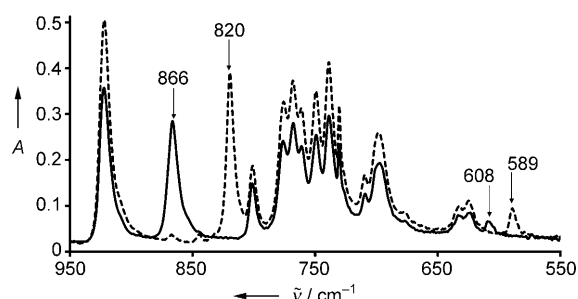


Figure 1. Part of the IR spectra of **1a** (—) and **1b** (----) (ATR, diamond).

unambiguously to the O–O stretching vibration of the η^2 -peroxido unit.^[18] An absorption band at 608 cm^{-1} (for **1a**) shifts to 589 cm^{-1} (for **1b**) and can tentatively be assigned to the RhO moiety. The peroxido complex **1a** exhibits a band at 387 nm and a shoulder at 311 nm in the UV/Vis spectrum.

The molecular structure of **1a** in the solid state was determined by X-ray crystallography (Figure 2).^[19] If the peroxido unit is treated as a bidentate ligand, the molecule exhibits a distorted octahedral structure. Alternatively if the dioxygen unit is treated as occupying a single coordination site, the structure is approximately trigonal-bipyramidal with the two phosphine ligands at the axial positions.

The O–O distance in **1a** of $1.4477(15)\text{ Å}$ is similar to those found in other rhodium η^2 -peroxido complexes,^[15] for example, in *trans*-[Rh(O₂)(4-C₅F₄N)(CNiBu)(PEt₃)₂] ($1.452(3)\text{ Å}$)^[16b] and in *cis*-[Rh(O₂)(CF₃)(CNXy)₂(PPh₃)] ($1.438(3)\text{ Å}$, Xy = 2,6-Me₂C₆H₃).^[15c] The rhodium carbonyl unit is not perfectly linear (Rh1–C1–O3 $174.80(14)^\circ$). A comparable situation was found for several other rhodium(III) carbonyl compounds.^[20] The fluorine atom F1 is directed to C1 of the carbonyl group, and the F1...C1 distance of 2.86 Å

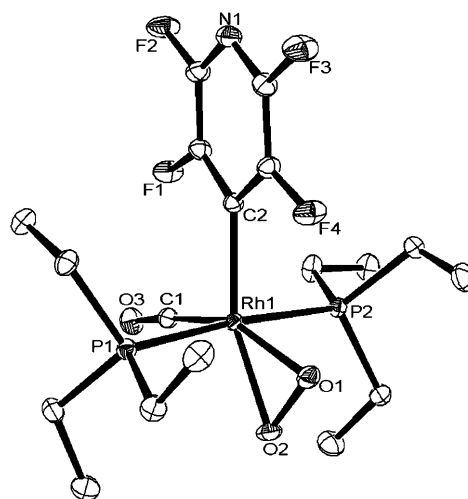
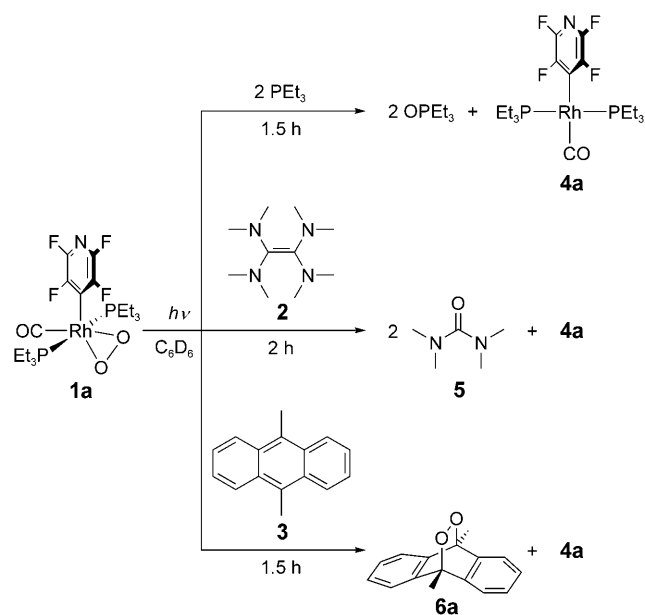


Figure 2. Molecular structure of **1a** in the crystal (ORTEP, ellipsoids at 50% probability). Selected distances [Å] and angles [°]: O1–O2 $1.4477(15)$, Rh1–O1 $2.0298(11)$, Rh1–O2 $2.0372(11)$, Rh1–C1 $1.8935(15)$, Rh1–C2 $2.0943(14)$; Rh1–C1–O3 $174.80(14)$, C1–Rh1–C2 $96.28(6)$.

is shorter than the sum of the van der Waals radii.^[9] There is no significant lengthening of the carbon–fluorine distance to F1. Evidence for a similar interaction in solution is given by the ^{19}F NMR spectrum of the ^{13}C isotopologue **1c**. The spectrum reveals a fluorine–carbon coupling constant to the $^{13}\text{C}=\text{O}$ carbon atom of 11.9 Hz for the resonance of the *ortho* fluorine atom at $\delta = -114.7\text{ ppm}$. The signal for the CO ligand at $\delta = 192.3\text{ ppm}$ in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1c** exhibits the same coupling. Presumably the coupling occurs “through space” via the lone pairs at the fluorine atom.^[9]

Irradiation of **1a** with an Xe UV lamp in benzene without an organic substrate led to a monooxygenation of the triethylphosphine ligands to form OPET₃.^[21] We were not able to identify any rhodium compound. In the presence of PET₃ the phosphine oxide and *trans*-[Rh(4-C₅F₄N)(CO)-(PET₃)₂] (**4a**) were generated (Scheme 2).

When **1a** was irradiated in the presence of three equivalents of tetrakis(dimethylamino)ethylene (**2**), both oxygen atoms were transferred to the substrate. This led to the formation of *trans*-[Rh(4-C₅F₄N)(CO)(PET₃)₂] (**4a**) and *N,N,N',N'*-tetramethylurea (**5**; Scheme 2). After 2 h the reaction was complete and complex **4a** was the sole rhodium species. Note that free phosphine oxide was not generated. The yield of **5** with respect to **1a** is 40% (based on the formation of 2 equiv of **5** = 100%). Without irradiation oxygenation of **2** is slow. After 14 d in benzene 20% yield of **4a** and 10% yield of **5** could be detected. In the presence of protic solvents, **2** also reacts with dioxygen to form **5** as the main component,^[22] but in the absence of protic solvents no significant reaction of **2** with dioxygen occurs.^[22d] Mechanistically, the latter generates a 1,2-dioxetane species (Me₂N)₂-(COOC)(NMe₂)₂, which can undergo cycloreversion to yield **2** and dioxygen or dissociate into two equivalents of **5**.^[22] We suggest a comparable reaction pathway, initiated by attack of the olefin at the rhodium peroxido entity. As indicated above, late transition metal peroxido complexes react with ketones,

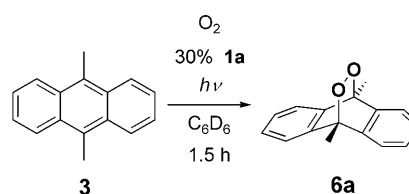


Scheme 2. Mono-oxygenation of triethylphosphine, dioxygenation of tetrakis(dimethylamino)ethylene (**2**), and peroxyoxygenation of 9,10-dimethylantracene (**3**).

olefins, or activated electron-poor acetylenes to form five-membered rings containing a peroxido linkage.^[3a,5] In most instances these metallacyclic peroxido compounds are stable. $[\text{Rh}(\text{O}_2)(\text{AsPh}_3)_4]^+ \text{A}^-$ ($\text{A}^- = \text{ClO}_4^-, \text{PF}_6^-$) reacts with electron-deficient olefins to yield metalladioxolanes, which decompose to the corresponding ketone and triphenylarsine oxide.^[3a]

Remarkably, irradiation of peroxido complex **1a** in the presence of 3.5 equiv of 9,10-dimethylantracene (**3**) led to transfer of the dioxygen unit to the substrate to yield 9,10-dimethylantracene-9,10-endoperoxide (**6a**) and $\text{trans}[\text{Rh}(\text{C}_5\text{F}_4\text{N})(\text{CO})(\text{PEt}_3)_2]$ (**4a**; Scheme 2). The rhodium(I) complex **4a** can be recovered in 94% yield; 75% of **6a** (with respect to the amount **1a**) can be isolated.^[23] Irradiation of a solution of 2,3-dimethylbut-2-ene and **1a** in benzene afforded neither the allylic hydroperoxide 3-hydroperoxy-2,3-dimethylbut-1-ene derived by a singlet-oxygen ene reaction nor acetone by [2+2] cycloaddition.^[24] Therefore, we exclude release of singlet dioxygen from **1a** under the reaction conditions, which could also react with **3** to give **6a**.^[23d,25] Instead, we presume direct oxygenation of the anthracene derivative by attack at the peroxido complex **1a**. This proposal finds further support in an experiment in which a mixture of **1a** and **1b** was used for peroxyoxygenation of **3**. Endoperoxides **6a** and $^{18}\text{O}/^{16}\text{O}$ -labeled isotopologue **6b** were generated, but the $^{18}\text{O}/^{16}\text{O}$ cross product was not formed.

We then tested peroxyoxygenation of 9,10-dimethylantracene (**3**) in the presence of substoichiometric amounts of the peroxido complex **1a**. Indeed, when **3** was irradiated with 30 mol% of **1a** under dioxygen atmosphere, 2.5 equiv of **6a** were formed with respect to **1a** (Scheme 3). Thus, the oxygenated product **6a** was formed in stoichiometric excess with respect to transition metal peroxide **1a**. Note that phosphine oxide was not generated, whereas irradiation of



Scheme 3. Peroxyoxygenation of 9,10-dimethylantracene (**3**) with dioxygen and substoichiometric amounts of **1a**.

$\text{trans}[\text{Rh}(\text{C}_5\text{F}_4\text{N})(\text{CO})(\text{PEt}_3)_2]$ (**4a**) in the presence of triplet dioxygen gave OPEt_3 .

In conclusion, we have synthesized the rhodium(III) peroxido complex $\text{trans}[\text{Rh}(\text{O}_2)(\text{C}_5\text{F}_4\text{N})(\text{CO})(\text{PEt}_3)_2]$ (**1a**) using singlet or triplet dioxygen. Participation of **1a** in mono-, di-, and peroxyoxygenation reactions is a unique property of this complex. Complex **1a** mono-oxygenates phosphines and dioxygenates tetrakis(dimethylamino)ethylene (**2**) to give the phosphine oxide and the urea derivative **5**, respectively. It also transfers the dioxygen unit photochemically to 9,10-dimethylantracene (**3**) to yield the endoperoxide **6a**. Possibly, one of the rhodium–oxygen bonds is cleaved in an initial photochemical step, which is followed by reaction of a resulting superoxo complex with the organic substrate. To the best of our knowledge, transfer of an entire O_2 entity from a transition metal peroxido complex to an organic substrate is unprecedented. An additional ligand or a second molecule need not be sacrificed. Neither are the phosphine ligands oxygenated nor does an oxygen atom insert into the rhodium–carbon bond of the tetrafluoropyridyl ligand. Furthermore, CO_2 formation by oxygenation of the CO ligand was also not observed.^[4,5] The peroxyoxygenation reaction is photocatalytic and can be mediated in the presence of dioxygen and substoichiometric amounts of **1a**.

Received: November 21, 2010

Published online: March 2, 2011

Keywords: fluorinated ligands · oxygen · oxygenation · peroxido ligands · rhodium

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