Peroxido Complexes

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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

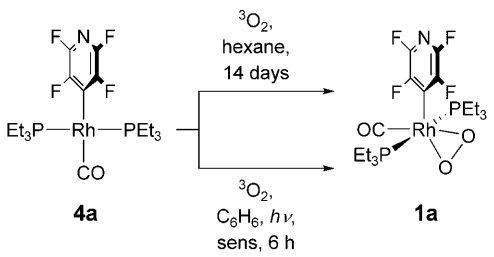
One of the main challenges in oxygenation chemistry is transition-metal-mediated oxygenation using molecular oxygen as the primary oxidant.[1] Peroxido transition metal compounds have been suggested to play a significant role as intermediates in oxygenation reactions with dioxygen.[1,2] In most instances 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*-$[Ir(O_2)(CH_3)(CO)\{P(p\text{-tolyl})_3\}_2]$ transforms CO, CO_2, and SO_2 into the corresponding carbonato, peroxidocarbonato, and sulfato ligands.[6] The rhodium peroxido complex *trans*-$[Rh(O_2)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ reacts with boronic acids $RB(OH)_2$ ($R = C_6H_5$, C_6F_5) 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 $[M(O)(O_2)_2(py)]$ (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 $[Rh(O_2)(Cl)(PPh_3)_3]$, which can be prepared from dioxygen, produces 1,4-cyclooctanedione.[8b,c] However, this rare case of transition metal mediated alkene dioxygenation with O_2 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*-$[Rh(O_2)(4\text{-}C_5F_4N)(CO)(PEt_3)_2]$ (**1a**) using triplet or singlet dioxygen. Under irradiation **1a** exhibits a variety of selective oxygenation reactions. It mono-oxygenates phosphines, dioxygenates tetrakis(dimethylamino)ethylene (**2**), and peroxygenates 9,10-dimethylanthracene (**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*-$[Rh(4\text{-}C_5F_4N)(CO)(PEt_3)_2]$ (**4a**)[9] in hexane with dioxygen gave the peroxido compound *trans*-$[Rh(O_2)(4\text{-}C_5F_4N)(CO)(PEt_3)_2]$ (**1a**) over two weeks (Scheme 1). *trans*-$[Rh(^{18}O_2)(4\text{-}C_5F_4N)(CO)(PEt_3)_2]$ (**1b**) is available in a similar fashion by using $^{18}O_2$. Reaction of the ^{13}C-labeled isotopomer *trans*-$[Rh(4\text{-}C_5F_4N)(^{13}CO)(PEt_3)_2]$ (**4b**)[9] with dioxygen yielded *trans*-$[Rh(O_2)(4\text{-}C_5F_4N)(^{13}CO)(PEt_3)_2]$ (**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*-$[Rh(O_2)(SC_6F_5)(CO)(PPh_3)_2]$, *trans*-$[Rh(O_2)(Cl)(CO)(PPh_3)_2]$, and *trans*-$[Rh(O_2)(CO)(PPh_3)_2(NCCH_3)]ClO_4$, 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]



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

The peroxido compound **1a** is soluble in aromatic hydrocarbons (benzene, toluene) and polar solvents like THF, Et_2O, and CH_2Cl_2, 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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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 $^{18}O_2$ 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}P{^{1}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)-$(PPh_3)_2$] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and the phosphine pincer rhodium(I) compound [{$Me_2C_6H(CH_2PtBu_2)_2$}Rh(η^1-N_2)] 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

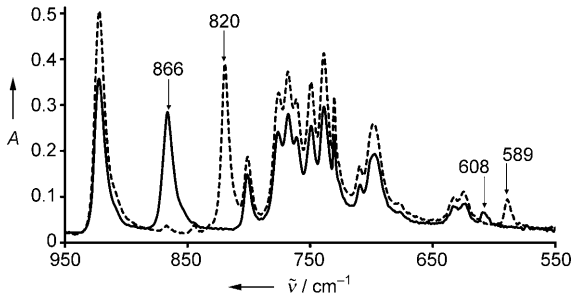


Figure 1. Part of the IR spectra of **1a** (——) and **1b** (-----) (ATR, diamond).

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) Å is similar to those found in other rhodium η^2-peroxido complexes,[15] for example, in *trans*-[Rh(O_2)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (1.452(3) Å)[16b] and in *cis*-[Rh(O_2)(CF_3)($CNXy$)$_2$(PPh_3)] (1.438(3) Å, Xy = 2,6-$Me_2C_6H_3$).[15e] The rhodium carbonyl unit is not perfectly linear (Rh1-C1-O3 174.80(14)°). 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

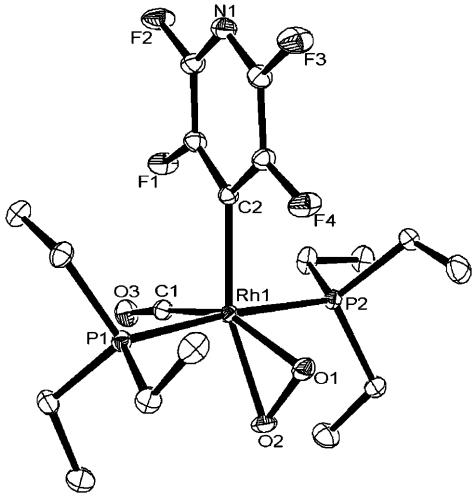
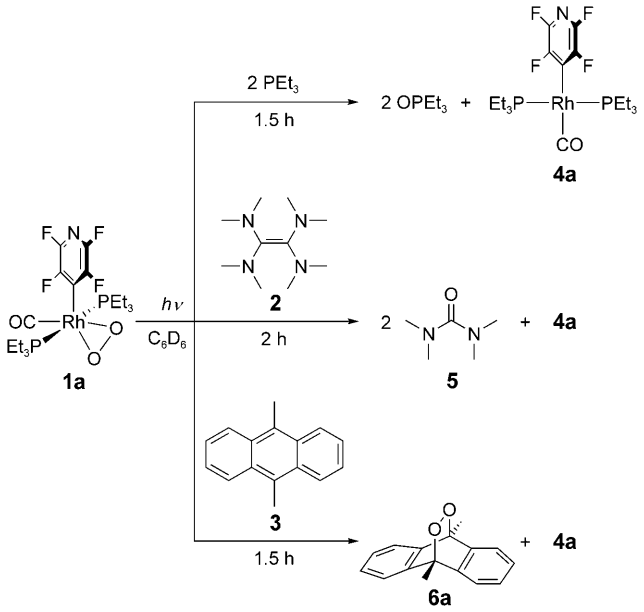


Figure 2. Molecular structure of **1a** in the crystal (ORTEP, ellipsoids at 50% probability). Selected distances [Å] and angles [°]: O1–O2 1.4477(15), Rh1–O1 2.0298(11), Rh1–O2 2.0372(11), Rh1–C1 1.8935(15), Rh1–C2 2.0943(14); Rh1-C1-O3 174.80(14), C1-Rh1-C2 96.28(6).

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}C=O carbon atom of 11.9 Hz for the resonance of the *ortho* fluorine atom at $\delta = -114.7$ ppm. The signal for the CO ligand at $\delta = 192.3$ ppm in the ^{13}C{^{1}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 $OPEt_3$.[21] We were not able to identify any rhodium compound. In the presence of PEt_3 the phosphine oxide and *trans*-[Rh(4-C_5F_4N)(CO)-$(PEt_3)_2$] (**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-C_5F_4N)(CO)(PEt_3)$_2$] (**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 $(Me_2N)_2$-$(COOC)(NMe_2)_2$, 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,

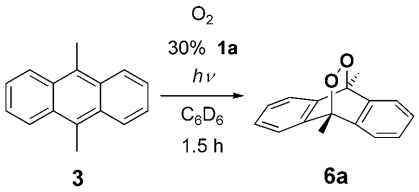


Scheme 2. Mono-oxygenation of triethylphosphine, dioxygenation of tetrakis(dimethylamino)ethylene (**2**), and peroxygenation of 9,10-dimethylanthracene (**3**).

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. $[Rh(O_2)(AsPh_3)_4]^+A^-$ ($A^- = ClO_4^-$, 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-dimethylanthracene (**3**) led to transfer of the dioxygen unit to the substrate to yield 9,10-dimethylanthracene-9,10-endoperoxide (**6a**) and *trans*-[Rh(4-C_5F_4N)(CO)(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 peroxygenation of **3**. Endoperoxides **6a** and ^{18}O-labeled isotopologue **6b** were generated, but the $^{18}O/^{16}O$ cross product was not formed.

We then tested peroxygenation of 9,10-dimethylanthracene (**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. Peroxygenation of 9,10-dimethylanthracene (**3**) with dioxygen and substoichiometric amounts of **1a**.

trans-[Rh(4-C_5F_4N)(CO)(PEt_3)$_2$] (**4a**) in the presence of triplet dioxygen gave $OPEt_3$.

In conclusion, we have synthesized the rhodium(III) peroxido complex *trans*-[Rh(O_2)(4-C_5F_4N)(CO)(PEt_3)$_2$] (**1a**) using singlet or triplet dioxygen. Participation of **1a** in mono-, di-, and peroxygenation 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-dimethylanthracene (**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 peroxygenation reaction is photocatalytic and can be mediated in the presence of dioxygen and substoichiometric amounts of **1a**.

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[19] X-ray structure analysis of **2a**: $C_{18}H_{30}F_4NO_3P_2Rh$, $M = 549.28$, crystal dimensions $0.30 \times 0.14 \times 0.14$ mm; monoclinic; $P2_1/n$; $a = 8.4473(8)$, $b = 27.665(4)$, $c = 10.4228(11)$ Å, $\beta = 107.078(11)°$, $Z = 4$, $V = 2328.4(4)$ Å^3, $\rho_{calcd} = 1.567$ g cm^{-3}; $2\theta_{max} = 56.74°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, 51271 reflections collected, of which 5799 were unique ($R_{int} = 0.0459$); STOE IPDS 2T diffractometer; multiscan absorption correction (min./max. transmission 0.7697/0.8819), $\mu = 0.921$ mm^{-1}. The structure was solved by direct methods and refined with full-matrix least-squares methods on F^2 (SHELX-97).[26] Final R_1, wR_2 values on all data: 0.0255, 0.0571; R_1, wR_2 values for 5799 reflections with $I_o > 2\sigma(I_o)$: 0.0232, 0.0559; residual electron density $+0.499/-0.654$ e Å^{-3}. CCDC 801333 contains 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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