Oxygenation Chemistry

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Hydrogenation of a Rhodium Peroxido Complex by Formate Derivatives: Mechanistic Studies and the Catalytic Formation of H_2O_2 from O_2**

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An interesting task in oxygenation chemistry is the transition-metal-mediated hydrogenation of dioxygen.[1] One desired product is hydrogen peroxide,[2] which is an economically important industrial product for the manufacture of a wide range of everyday items.[2a] At present, H_2O_2 is predominantly produced by the anthraquinone process, which involves a catalytic hydrogenation of 2-alkylanthraquinone derivatives and a subsequent oxidation of the resulting 2-alkylanthrahydroquinones with O_2.[2a] However, the development of an alternative homogeneously catalyzed process to access H_2O_2 from O_2 can be considered as a demanding challenge.[2]

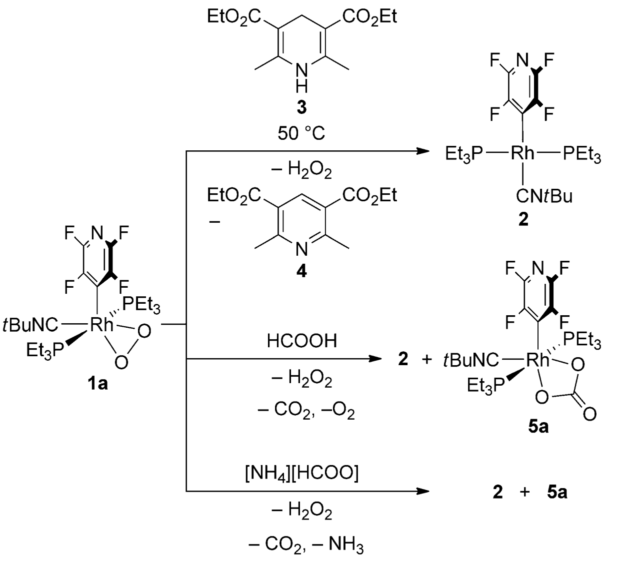
Hence, a variety of catalytic investigations have been carried out to develop new reaction routes to access H_2O_2 from dioxygen with appropriate reducing agents.[2–6] For example, it was reported that the hydrogenation of dioxygen gives hydrogen peroxide when using palladium complexes and alcohols as reductants.[4] Note that copper complexes as functional models for galactose oxidase were also applied to catalyze the oxidation of alcohols with O_2, yielding the corresponding aldehydes or ketones, as well as H_2O_2.[7] Moreover, palladium-catalyzed transformations of mixtures of CO, O_2, and H_2O provide CO_2 and H_2O_2 in the presence of an excess of a Brønsted acid.[2b,5,6] A combination of $[Pd(OAc)_2]$ and triphenylphosphine or triarylarsine was originally employed.[5] The conversions are hampered by the vulnerability of the ligands towards oxygenation. However, ligand oxidation is avoided by the application of palladium complexes which bear phenanthroline ligands, and H_2O_2 is catalytically accessible under comparatively harsh reaction conditions (70 atm, O_2/CO 64:6, 70 °C).[6] Mechanistic steps might include dioxygen activation to yield a transition metal–peroxido complex,[8] followed by protonation of the peroxido ligand to generate H_2O_2.[2,9,10] However, a second possibility consists of the insertion of O_2 into a palladium–hydrogen bond.[2b,9,11] Both reaction pathways involve the formation of hydroperoxido complexes as intermediates.[10–12]

In the case of rhodium, we found in model reactions that the protonation of the peroxido complex *trans*-$[Rh(O_2)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ (**1a**) with HCl initially led to the formation of *trans*-$[Rh(OOH)(Cl)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ and subsequently to H_2O_2 and the rhodium(III) complex *cis-trans*-$[Rh(Cl)_2(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$.[10] Complex **1a** was prepared from dioxygen and *trans*-$[Rh(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ (**2**).

Herein, we report on the unique reactivity of **1a** towards dihydrogen sources to yield hydrogen peroxide and **2**. The metal-bound oxygen can be reduced either by the Hantzsch ethyl ester diethyl-1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (**3**), formic acid or ammonium formate. In a catalytic experiment, H_2O_2 was generated at ambient temperature and atmospheric pressure from dioxygen and ammonium formate.

Reaction of the peroxido complex *trans*-$[Rh(O_2)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ (**1a**) with the Hantzsch ethyl ester **3** at 50 °C led to the formation of the rhodium(I) compound *trans*-$[Rh(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ (**2**),[13] diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (**4**) and H_2O_2 within eight hours (Scheme 1). Considerable amounts (10 %) of $OPEt_3$ could be detected, because of the slow degradation of rhodium(I) species **2** by reaction with H_2O_2. However, in the presence of one equivalent of PPh_3, no $OPEt_3$ was formed and PPh_3 was instead monooxygenated to give $OPPh_3$.[14]

Alternatively, the treatment of **1a** with a solution of HCOOH in THF at −70 °C afforded H_2O_2, CO_2, and



Scheme 1. Formation of H_2O_2 by hydrogenation of **1a**.

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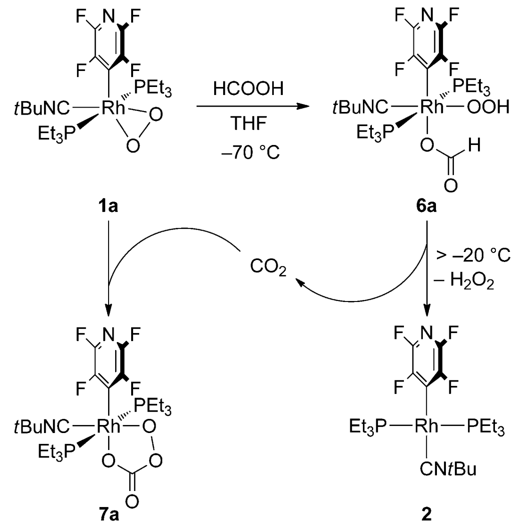
rhodium(I) complex **2**, as well as the rhodium(III) carbonato complex *trans*-[Rh{κ^2-*O*C(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**5a**; Scheme 1). The H_2O_2 can be separated as an aqueous solution by trap to trap vacuum distillation of the volatiles followed by treatment of the distillate with water. Note that in an experiment at room temperature small amounts of 2,3,5,6-tetrafluoropyridine were produced, owing to the protonation of the tetrafluoropyridyl ligand instead of the peroxido entity.[13,15] However, at low-temperature 2,3,5,6-tetrafluoropyridine was not formed.

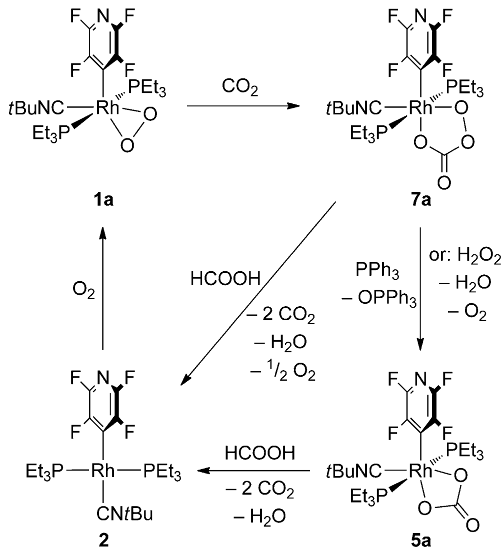
Low-temperature NMR and Raman experiments at −70 °C revealed the formation of the hydroperoxido formato complex *trans*-[Rh(OOH){OC(O)H}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**6a**) as the initial product (Scheme 2). The ^{18}O isotopologue *trans*-[Rh(^{18}O^{18}OH){OC(O)H}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**6b**) is available in a similar fashion, starting from *trans*-[Rh($^{18}O_2$)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**1b**).[10] In addition to the signals for **6a**, small amounts of **1a** were still detectable in the ^{31}P{^{1}H} NMR spectrum. Further monitoring of the reaction by NMR spectroscopy at low temperature revealed that **1a** was converted into an additional intermediate species, which was identified as the peroxycarbonato compound *trans*-[Rh{κ^2-*O*OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**7a**; Scheme 2). We presume that initially CO_2 is generated, which reacts with **1a** to give **7a**. However, with increasing temperature, complexes **2** and **5a** were the sole rhodium species that could be identified.



Scheme 2. Reactivity of **1a** towards formic acid.

The presence of the rhodium(III) complex **6a** is evidenced by a rhodium–phosphorus coupling constant of 86.3 Hz for the signal at $\delta = 22.0$ ppm in the ^{31}P{^{1}H} NMR spectrum, and by an absorption band at 2210 cm^{-1} in the Raman spectrum, which can be assigned to the stretching vibration of the CN*t*Bu ligand.[10,13,16] The ^{19}F NMR spectrum of **6a** displays four signals for the tetrafluoropyridyl ligand, which indicates a hindered rotation about the rhodium–carbon bond.[10,13,16] A broad signal in the ^{1}H NMR spectrum at $\delta = 8.38$ ppm can be attributed to the hydroperoxido ligand,[10,12,17] and a resonance at $\delta = 8.15$ ppm is assigned to the formato ligand.[18] The latter signal correlates with a signal for the {OC(O)H} ligand at $\delta = 167.5$ ppm in the ^{13}C domain of a ^{1}H,^{13}C-HMQC NMR spectrum.[18] Furthermore, the Raman spectrum of **6a** shows an absorption band at 1624 cm^{-1} for the formato ligand. Another band at 859 cm^{-1} shifts to 815 cm^{-1} for the ^{18}O-labeled isotopologue **6b** ($\Delta\tilde{\nu} = 44$ cm^{-1}) and can be assigned to the OOH stretching vibration.[12a,19]

There is some precedence for late transition metal compounds reacting with O_2 and subsequently CO_2 to yield peroxycarbonato complexes.[20–22] To get a deeper understanding of the formation and reactivity of complexes **5a** and **7a**, the latter was synthesized in an independent synthesis. Thus, a solution of *trans*-[Rh(O_2)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**1a**) in benzene was treated with CO_2 to give the peroxycarbonato compound *trans*-[Rh{κ^2-*O*OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**7a**; Scheme 3). The compounds *trans*-[Rh{κ^2-*^{18}O*^{18}OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**7b**) and *trans*-[Rh{κ^2-*^{17}O*^{17}OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**7c**) were available in a similar fashion from the ^{18}O- and ^{17}O-labeled isotopomers **1b** and **1c**, respectively. Treatment of the ^{17}O-labeled peroxido complex **1c** with $^{13}CO_2$ afforded the ^{13}C-enriched isotoplogue *trans*-[Rh{κ^2-*^{17}O*^{17}O^{13}C(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**7d**).



Scheme 3. Formation and reactivity of the peroxycarbonato complex **7a** and carbonato complex **5a**.

The carbonato complex *trans*-[Rh{κ^2-*O*C(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**5a**) and its ^{18}O isotopologue *trans*-[Rh{κ^2-*^{18}O*C(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**5b**) were also synthesized by an independent reaction pathway. The treatment of **7a** or **7b** with PPh_3 led to a monooxygenation of the phosphine to form $OPPh_3$ and the carbonato complexes *trans*-[Rh{κ^2-*O*C(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**5a**) and *trans*-[Rh{κ^2-*^{18}O*C(O)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**5b**), respectively (Scheme 3). Remarkably, complex **7a** also reacts in an unprecedented reaction with aqueous H_2O_2 to yield **5a**, water, and O_2 (Scheme 3). Thus overall, the reaction of **1a** with formic acid initially gives H_2O_2 and CO_2, as well as **2** (Scheme 2). Carbon dioxide reacts subsequently with **1a** to generate the peroxycarbonato compound **7a**, which yielded the carbonate **5a**, H_2O, and O_2 by reaction with H_2O_2 (Scheme 3). Above all, it is intriguing that the rhodium(III) compounds **5a** and **7a** also both react with HCOOH to give the rhodium(I) complex **2** (Scheme 3).

A signal in the ${}^{31}P\{{}^{1}H\}$ NMR spectrum for **5a** at $\delta =$ 23.0 ppm exhibits a rhodium–phosphorus coupling constant of 83.4 Hz. An absorption band at 2194 cm^{-1} in the IR spectrum (ATR) corresponds to the stretching vibration of the CN*t*Bu ligand at a rhodium(III) complex.[10,13,16] The absorption bands at 673 cm^{-1} for **5a**, as well as 674 cm^{-1}, 662 cm^{-1}, and 649 cm^{-1} for **5b** can tentatively be assigned to in-plane deformation vibrations of the Rh{κ^2-*O*C(O)*O*} moiety.[23] The structure of **5a** in the solid state was determined by X-ray crystallography (Figure 1).[24] The Rh1–O1 and Rh1–O2 distances (2.0625(17) Å and 2.0856(17) Å) are equivalent to those found in *trans*-[Rh{κ^2-*O*C(O)*O*}(S_2CNMe_2)($(PPh_3)_2$)][20a] (2.071(8) Å and 2.083(8) Å); the O-Rh-O angle of 63.3(3)° in the latter is similar to the O1-Rh1-O2 angle of 63.75(7)° in **5a**.

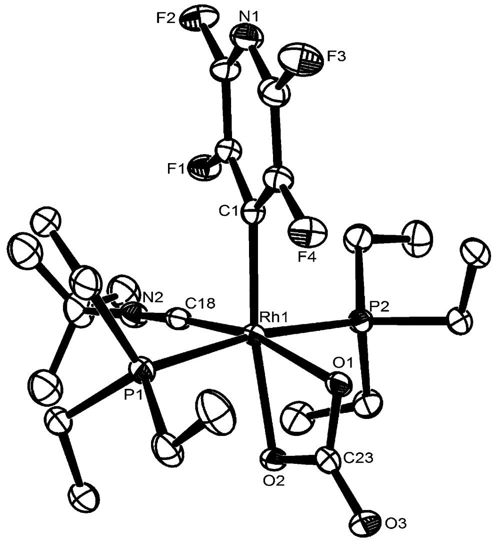


Figure 1. Crystal structure of **5a** (ORTEP, ellipsoids set at 50% probability). Selected distances [Å] and angles [°]:C1–Rh1 2.060(3), C18–Rh1 1.926(3), O1–Rh1 2.0625(17), O2–Rh1 2.0856(17), C23–O1 1.322(3), C23–O2 1.320(3),C23–O3 1.222(3); N2-C18-Rh1 175.3(2), C18-Rh1-C1 91.72(10), C18-Rh1-O1 165.70(9), C1-Rh1-O1 102.54(9), O1-Rh1-O2 63.75(7), O2-C23-O1 112.0(2).

The presence of rhodium(III) complex **7a** is again evidenced by a rhodium–phosphorus coupling constant of 85.5 Hz for the signal at $\delta = 22.9$ ppm in the ${}^{31}P\{{}^{1}H\}$ NMR spectrum and by an absorption band at 2191 cm^{-1} in the IR spectrum (ATR), which can be assigned to the stretching vibration of the CN*t*Bu ligand.[10,13,16] The ${}^{17}O$ NMR spectrum of **7c** displays two signals (Figure 2a). A signal at $\delta =$ 38.7 ppm with a rhodium-oxygen coupling constant of 150.0 Hz can be attributed to the metal bound oxygen atom of the ${}^{17}O$–${}^{17}O$ moiety in the peroxycarbonato ligand. A resonance at $\delta = 76.2$ ppm is assigned to the carbon-bound oxygen atom of the ${}^{17}O$–${}^{17}O$ moiety. The ${}^{17}O$ NMR spectrum of the ${}^{13}C$ isotopologue **7d** reveals a carbon-oxygen coupling constant of 15.3 Hz for the latter resonance (Figure 2b). The IR spectrum of **7a** shows an absorption band at 969 cm^{-1} for the Rh{κ^2-*O*OC(O)*O*} moiety.[20b] This band shifts to 959 cm^{-1} for the ${}^{17}O$-labeled isotopologue **7c** ($\Delta\tilde{\nu} = 10\ cm^{-1}$) and to 948 cm^{-1} for the ${}^{18}O$-labeled isotopologue **7b** ($\Delta\tilde{\nu} = 21\ cm^{-1}$), respectively (Table 1).

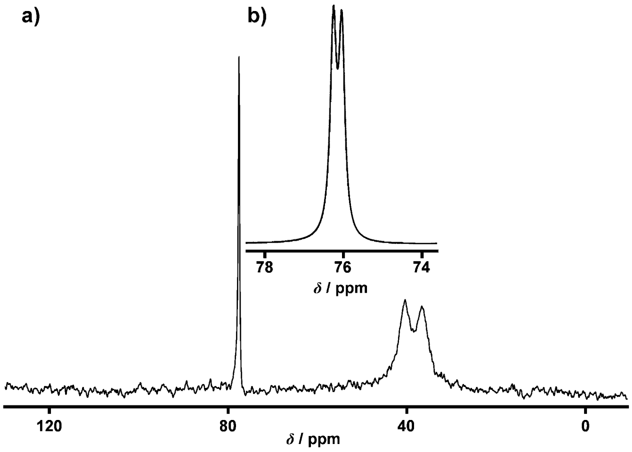


Figure 2. a) ${}^{17}O$ NMR spectrum of *trans*-[Rh{κ^2-${}^{17}O^{17}$OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)($(PEt_3)_2$)] (**7c**); b) Part of the ${}^{17}O$ NMR spectrum of *trans*-[Rh{κ^2-${}^{17}O^{17}O^{13}$C(O)*O*}(4-C_5F_4N)(CN*t*Bu)($(PEt_3)_2$)] (**7d**).

Table 1: Selected IR spectroscopic data (ATR) for the peroxycarbonato complexes **7a**–**7d**.

Entry	Complex	$\tilde{\nu}$ [cm^{-1}][a]	$\Delta\tilde{\nu}$ [cm^{-1}]	$\tilde{\nu}$ [cm^{-1}][b]	$\Delta\tilde{\nu}$ [cm^{-1}]
1	**7a**	969	–	585; 543	–
2	**7b**	948	21[c]	566; 519	19; 24[c]
3	**7c**	959	10[c]	575; 531	10; 12[c]
4	**7d**	952	7[d]	575; 531	0; 0[d]

[a] Vibrational frequencies of the Rh{κ^2-*O*OC(O)*O*} moiety. [b] Vibrational frequencies of the RhO moiety. [c] Isotopic shifts compared to **7a**. [d] Isotopic shifts compared to **7c**. **7a**: *trans*-[Rh{κ^2-*O*OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)($(PEt_3)_2$)], **7b**: *trans*-[Rh{κ^2-${}^{18}O^{18}$OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)($(PEt_3)_2$)], **7c**: *trans*-[Rh{κ^2-${}^{17}O^{17}$OC(O)*O*}(4-C_5F_4N)(CN*t*Bu)($(PEt_3)_2$)], **7d**: *trans*-[Rh{κ^2-${}^{17}O^{17}O^{13}$C(O)*O*}(4-C_5F_4N)(CN*t*Bu)($(PEt_3)_2$)].

These frequency shifts are too small to be associated with isolated ν(O–O) modes in the peroxycarbonato ligands of **7a**, **7b**, and **7c**, respectively.[20b] Moreover, the IR spectrum of **7d** shows an absorption band at 952 cm^{-1}. Thus, the absorption band at 959 cm^{-1} for the ${}^{17}O$-labeled isotopologue **7c** displays an isotopic shift of $\Delta\tilde{\nu} = 7\ cm^{-1}$ upon ${}^{13}C$ labeling. Absorption bands at 585 cm^{-1} and 543 cm^{-1} for **7a** shift to 575 cm^{-1} ($\Delta\tilde{\nu} =$ 10 cm^{-1}) and 531 cm^{-1} ($\Delta\tilde{\nu} = 12\ cm^{-1}$) for **7c** and to 566 cm^{-1} ($\Delta\tilde{\nu} = 19\ cm^{-1}$) and 519 cm^{-1} ($\Delta\tilde{\nu} = 24\ cm^{-1}$) for **7b**. These bands do not show any isotopic shift upon ${}^{13}C$ labeling and can tentatively be associated with vibrations which include the RhO moiety.[20b] Based on the ${}^{17}O$ NMR and IR data, we suggest that CO_2 reacts with rhodium peroxido complexes by insertion into a metal–oxygen[22] bond rather than by insertion into the O–O bond, as was previously suggested.[20b,c] A comparable reactivity was found in the reaction of boronic acids with **1a**, in which *trans*-[Rh{κ^2-*O*OB(C_6R_5)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (R = H, F) are formed by cleavage of the Rh–O bond of the peroxido moiety in **1a**.[16a]

The molecular structure of **7a**·H_2O in the solid state was determined by X-ray crystallography (Figure 3).[24] The molecule exhibits a distorted octahedral geometry with the two phosphines in a mutually *trans* orientation. The O1-Rh1-O3 angle of 78.65(12)° is comparable to the corresponding angle in the peroxycarbonatocomplex [Rh{κ^2-*O*OC(O)*O*}(4-MeC_6H_4){*t*BuP($CH_2CH_2CH_2$-PPh_2)$_2$}].[21a] The O–O distance of 1.49(2) Å in the latter,[21a] as well as the O–O distance of 1.4974(14) Å in *trans*-[Rh{κ^2-*O*OB(OH)*O*}(4-C_5F_4N)-(CN*t*Bu)(PEt_3)$_2$],[16a] are comparable to the O1–O2 bond length of 1.469(4) Å in **7a**. The O–O distances in other cyclic peroxycarbonatocomplexes are also in a similar range, as found for **7a**.[21]

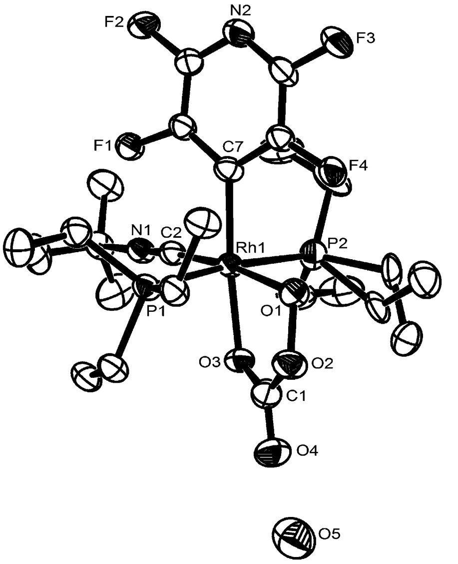
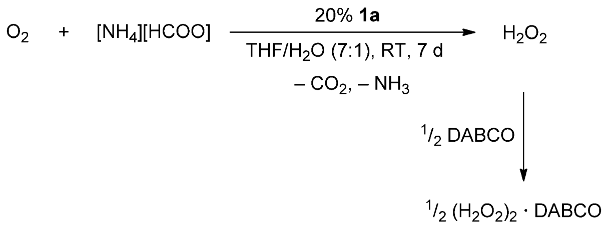


Figure 3. Crystal structure of **7a**·H_2O (ORTEP, ellipsoids set at 50% probability). Complex **7a** crystallizes with an additional water molecule, which is hydrogen bonded to the peroxycarbonato ligand. Selected distances [Å] and angles [°]: Rh1–C2 1.943(4), Rh1–C7 2.085(4), Rh1–O1 2.040(3), Rh1–O3 2.081(3), O1–O2 1.469(4), C1–O2 1.354(6), C1–O3 1.255(5), C1–O4 1.238(5); N1-C2-Rh1 175.1(4), C2-Rh1-C7 90.80(16), C2-Rh1-O1 171.48(14), O1-Rh1-C7 97.72(14), C2-Rh1-O3 92.85(14), O1-Rh1-O3 78.65(12).

In the next step we applied ammonium formate as dihydrogen source and as a mild alternative to formic acid.[25,26] Notably, reaction with **1a** afforded H_2O_2, CO_2, NH_3, and the rhodium complexes **2** and **5a** at ambient temperature (Scheme 1). We then tested the reactivity of dioxygen towards ammonium formate in the presence of substoichiometric amounts of the peroxido complex **1a** (Scheme 4). Indeed, dioxygen and ammonium formate can be transformed into H_2O_2, NH_3, and CO_2 in the presence of **1a** (20%) at ambient temperature and atmospheric pressure. The generated hydrogen peroxide can be utilized in oxygenation reactions, such as the in situ oxygenation of PPh_3.[14]



Scheme 4. Formation of H_2O_2 with substoichiometric amounts of **1a**. DABCO = 1,4-diazabicyclo[2.2.2]octane.

Furthermore, H_2O_2 was trapped as the adduct $(H_2O_2)_2$·DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; Scheme 4). Based on **1a**, 3.6 equiv of H_2O_2 were formed.[27]

In conclusion, we have demonstrated a variety of hydrogenation reactions of the peroxido ligand in *trans*-[Rh(O_2)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**1a**), which can be prepared from dioxygen and **2**, to yield H_2O_2 and the rhodium(I) compound **2**. To the best of our knowledge, the hydrogenation of dioxygen with formic acid or ammonium formate in the homogeneous phase mediated by a transition metal complex is unprecedented.[28] The reduction of dioxygen at ambient temperature and atmospheric pressure with ammonium formate yielding H_2O_2 can be mediated by substoichiometric amounts of **1a**.

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Keywords: hydrogenation · hydrogen peroxide · oxidation · peroxido ligands · rhodium

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[24] Data for X-ray structure analysis: All structures were solved by direct methods and refined with the full matrix least square methods on F^2(SHELX-97).[29] **5a**: $C_{23}H_{39}F_4N_2O_3P_2Rh$, $M = 632.41$, crystal dimensions $0.42 \times 0.35 \times 0.23$ mm^3; monoclinic; $P2_1/c$; $a = 9.9319(3)$, $b = 32.7822(8)$, $c = 9.5360(3)$ Å, $\beta = 113.617(2)^\circ$, $Z = 4$, $V = 2844.77(14)$ Å^3, $\rho_{\text{calcd.}} = 1.477$ g cm^{-3}; $2\theta_{\text{max}} = 54.46^\circ$, $\text{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, 39170 reflections collected, 6305 were unique ($R_{\text{int.}} = 0.0707$); STOE IPDS 2T diffractometer; multiscan absorption correction (min./max. transmission 0.8728/0.7162), $\mu = 0.765$ mm^{-1}. Final R_1, wR_2 values on all data: 0.0408, 0.0656; R_1, wR_2 values for 6305 reflections with $I_o > 2\sigma(I_o)$: 0.0287, 0.0644; residual electron density $+0.583/-0.874$ e Å^{-3}. **7a**·H_2O: $C_{23}H_{41}F_4N_2O_5P_2Rh$, $M = 666.43$, crystal dimensions $0.13 \times 0.09 \times 0.02$ mm^3; triclinic; $P\bar{1}$; $a = 9.5236(5)$, $b = 9.9425(5)$, $c = 17.3346(10)$ Å, $\alpha = 78.518(4)$, $\beta = 82.396(4)$, $\gamma = 65.179(4)^\circ$, $Z = 2$, $V = 1457.75(13)$ Å^3, $\rho_{\text{calcd.}} = 1.518$ g cm^{-3}; $2\theta_{\text{max}} = 58.00^\circ$, $\text{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, 15384 reflections collected, 6572 were unique ($R_{\text{int.}} = 0.0475$); STOE IPDS 2T diffractometer; multiscan absorption correction (min./max. transmission 0.9749/0.8534), $\mu = 0.756$ mm^{-1}. Final R_1, wR_2 values on all data: 0.0662, 0.1236; R_1, wR_2 values for 6572 reflections with $I_o > 2\sigma(I_o)$: 0.0446, 0.1118; residual electron density $+0.756/-0.998$ e Å^{-3}. CCDC 899217 (**5a**) and 899218 (**7a**) 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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