

Oxygenation

Rhodium-Mediated Oxygenation of Nitriles with Dioxygen:
Isolation of Rhodium Derivatives of Peroxyimidic AcidsAnnemarie Bittner, Thomas Braun,* Roy Herrmann, and Stefan Mebs^[a]

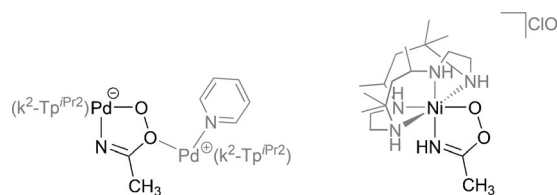
Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: Dioxygen is used as the oxygenation agent in the rhodium-mediated conversion of nitriles into amides. The characterization of intermediate species and model compounds as well as isotope-labeling studies provided an insight into the reaction mechanism. The conversions of rhodium hydroperoxido or methylperoxido complexes with nitriles into metallacyclic rhodium- κ^2 -(N,O)-peroxyimide compounds represent essential key steps. The former are accessible from a rhodium(III) peroxido complex and the latter represent rhodium derivatives of Payne's reagent (peroxyimidic acids).

The use of dioxygen as oxygenation agent in transition-metal-mediated C–O bond formation reactions is of high interest due to its availability and environmental sustainability.^[1] Treatment of late transition-metal complexes with dioxygen often give peroxido complexes, which can act as key intermediates in the conversion of organic compounds.^[1k,2] At rhodium, the oxygen atoms of the peroxido ligand are often nucleophilic.^[2a,c,3] Thus, a reaction of *trans*-[Rh(O₂)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**1a**) with formic acid yields initially the rhodium hydroperoxido complex *trans*-[Rh(OOH){OC(O)H}(4-C₅NF₄)(CNtBu)(PEt₃)₂] at low temperatures.^[2c] Subsequently, hydrogen peroxide and the rhodium(I) complex *trans*-[Rh(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**2**) are furnished.

The reaction of hydrogen peroxide with nitriles yields the peroxyimidic acids (RC(NH)OOH, R = alkyl- or aryl group), which decompose immediately to give the corresponding amides and dioxygen.^[4] Peroxyimidic acids can be used in situ as oxygenation agents for different substrates like alkenes or tertiary amines (Payne's reagent).^[5] The instability of the peroxyimidic acids hampers their identification and, so far, peroxybenzimidic acid was in situ characterized by FT-Raman and FT-IR spectroscopy.^[6] However, there are two transition-metal-stabilized derivatives of peroxyimidic acids reported in the literature. The palladium complex [Pd(Tp^{IPr2}){ κ^2 -OO{Pd(Tp^{IPr2})(1-C₅NH₅)}C(CH₃)N}] (Tp^{IPr2} = hydrotris(3,5-diisopropylpyrazolyl)bor-

ato) exhibits a five-membered peroxyimide ring structure (Pd{ κ^2 -OOC(CH₃)N}) and is furnished by reacting the hydroperoxido complex [Pd(OOH)(Tp^{IPr2})(py)] with acetonitrile (Scheme 1).^[7] It has a zwitterionic 2,3-dioxo-5-azapallada-cyclopenten-4-ene structure and it is additionally stabilized by cationic Pd(Tp^{IPr2})(1-C₅NH₅) fragment bound the β -oxygen atom. In addition, based on microanalysis and IR spectroscopy the formation of the nickel complex [Ni{ κ^2 -OOC(CH₃)NH}{Dl-Me₆-14-aneN₄}(ClO₄) (Dl-Me₆-14-aneN₄ = Dl-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was postulated after a reaction of [Ni(Dl-Me₆-14-aneN₄)](ClO₄)₂ in acetonitrile with hydrogen peroxide (Scheme 1).^[8]



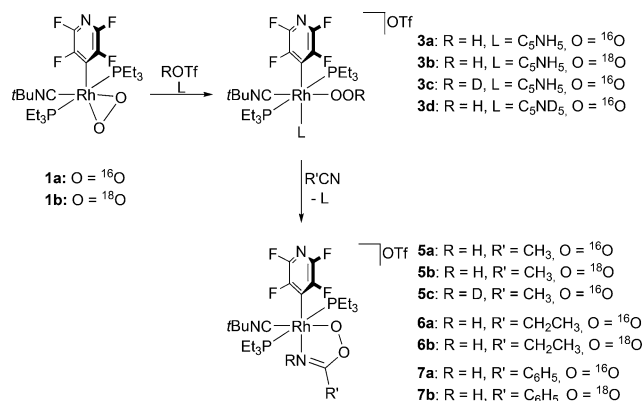
Scheme 1. The palladium complex [Pd(Tp^{IPr2}){ κ^2 -OO{Pd(Tp^{IPr2})(1-C₅NH₅)}C(CH₃)N}] and the nickel complex [Ni{ κ^2 -OOC(CH₃)NH}{Dl-Me₆-14-aneN₄}(ClO₄)] exhibit the structural motif [M{ κ^2 -OOC(CH₃)N}], which represents a transition-metal-stabilized version of a peroxyimidic acid.

Herein we report on the oxygenation of nitriles with dioxygen mediated by the rhodium hydroperoxido complex *trans*-[Rh(OOH)(4-C₅NF₄)(CNtBu)(PEt₃)₂](1-C₅NH₅)]OTf (**3a**) to give initially metallacyclic rhodium- κ^2 -(N,O)-peroxyimides. Treatment of the latter with NaBH₄ led to the formation of the corresponding amides and *trans*-[Rh(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**2**). An additional insight into the mechanism is provided by reactivity studies at *trans*-[Rh(OOCH₃)(4-C₅NF₄)(CNtBu)(PEt₃)₂](1-C₅NH₅)]OTf (**4**).

Treatment of *trans*-[Rh(O₂)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**1a**) with trifluoromethanesulfonic acid (HOTf) in the presence of pyridine gave *trans*-[Rh(OOH)(4-C₅NF₄)(CNtBu)(PEt₃)₂](1-C₅NH₅)]OTf (**3a**) (Scheme 2). Compound **1a** is accessible from *trans*-[Rh(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**2**) and dioxygen.^[2a] **3a** is stable in solution at room temperature, but decomposes under vacuum immediately due to the loss of the pyridine ligand. Note that *trans*-[Rh(O₂)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**1a**) reacts with HCl or HCOOH in a comparable manner to give the hydroperoxido complexes *trans*-[Rh(OOH){X}(4-C₅NF₄)(CNtBu)(PEt₃)₂] (X = Cl, OC(O)H), but the complexes are only stable at temperatures below –50 °C.^[2a,c]

[a] A. Bittner, Prof. Dr. T. Braun, R. Herrmann, Dr. S. Mebs
Department of Chemistry, Humboldt-Universität zu Berlin
Brook-Taylor-Straße 2, 12489 Berlin (Germany)
E-mail: thomas.braun@chemie.hu-berlin.de

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Scheme 2. Synthesis of the rhodium hydroperoxido complex **3a** and its isotopologues **3b**, **3c**, and **3d**. Reactivity of the latter towards nitriles.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3a** shows a doublet at $\delta = 15.8$ ppm with a rhodium–phosphorus coupling constant of 85 Hz, which indicates the presence of a rhodium complex in the oxidation state +3.^[2a] The IR spectrum shows a characteristic absorption band at 2199 cm^{-1} for the isonitrile ligand bound to the rhodium(III) center.^[9] The ^{19}F NMR spectrum displays four multiplets for the tetrafluoropyridyl ligand, which indicates a hindered rotation about the rhodium–carbon bond.^[10] Five multiplet signals are found for **3a** in the ^1H NMR spectrum in the range from $\delta = 9.5$ to 7.5 ppm, each with a similar intensity. They can be assigned to the coordinated pyridine. A broad singlet signal at $\delta = 8.29$ ppm is assigned to the hydroperoxido ligand.^[2a,c] Treatment of rhodium peroxido complex **1a** with DOTf in the presence of pyridine led to the formation of $[\text{Rh}(\text{OOD})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2(1\text{-C}_5\text{NH}_5)]\text{OTf}$ (**3c**). On using $[\text{D}_5]$ pyridine instead of the non-deuterated pyridine, the isotopologue $[\text{Rh}(\text{OOH})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2(1\text{-C}_5\text{ND}_5)]\text{OTf}$ (**3d**) was obtained. The complexes **3c** and **3d** show resonances in the ^2H NMR spectra for the OOD ($\delta = 8.43$ ppm) or for the deuterated pyridine ligand ($\delta = 9.53, 9.04, 8.52, 8.29, 8.03$ ppm), respectively. Synthesis of the complex $\text{trans-}[\text{Rh}(^{18}\text{O}^{18}\text{OH})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2(1\text{-C}_5\text{NH}_5)]\text{OTf}$ (**3b**) was achieved by conversion of $\text{trans-}[\text{Rh}(^{18}\text{O}_2)(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]$ (**1b**) with HOTf in the presence of pyridine. The HR-ESI-MS data of both hydroperoxido complexes **3a** and **3b** reveal peaks at m/z ratios for $[\text{M-pyridine}]^+$ at 605.1556 ($[\text{Rh}(\text{OOH})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]^+$) or 609.1626 ($[\text{Rh}(^{18}\text{O}^{18}\text{OH})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]^+$), respectively. Although the rhodium hydroperoxido complexes **3a–d** were stable at room temperature in solution, isolation of the complexes was not possible.

In situ treatment of $\text{trans-}[\text{Rh}(\text{OOH})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2(1\text{-C}_5\text{NH}_5)]\text{OTf}$ (**3a**) with acetonitrile in a THF solution yielded the complex $\text{trans-}[\text{Rh}\{\kappa^2\text{-OOC}(\text{CH}_3)\text{NH}\}(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]\text{OTf}$ (**5a**) by carbon–oxygen bond formation. In a similar manner, the complexes $\text{trans-}[\text{Rh}\{\kappa^2\text{-OOC}(\text{R})\text{NH}\}(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]\text{OTf}$ (**6a**: R = CH₂CH₃; **7a**: R = C₆H₅) were synthesized using propionitrile or benzonitrile (Scheme 1). In the ^1H NMR spectra of **5a–7a** the protons at the nitrogen atom of the peroxyimides give rise to broad singlets (**5a**: $\delta =$

9.54 ppm; **6a**: $\delta = 9.46$ ppm; **7a**: $\delta = 9.85$ ppm). The conversion of $\text{trans-}[\text{Rh}(\text{OOD})(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2(1\text{-C}_5\text{NH}_5)]\text{OTf}$ (**3c**) with acetonitrile led to the formation of both isotopologues **5a** and **5c**. This is presumably due to a H/D exchange between **3c** and adventitious water in the acetonitrile. The absorption bands in the IR spectra for the isonitrile ligands in **5a**, **6a**, and **7a** appear between 2205 and 2211 cm^{-1} which is consistent with the presence of a rhodium(III) center.^[9] Comparison of the IR- and Raman spectra of complexes **5a**, **6a**, and **7a** with those of their isotopologues **5b**, **6b**, and **7b** (Scheme 2) allows an assignment of the absorption bands for the oxygen–oxygen and metal–oxygen vibrations. Thus, the IR spectrum of $\text{trans-}[\text{Rh}\{\kappa^2\text{-OOC}(\text{CH}_3)\text{NH}\}(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]\text{OTf}$ (**5a**) displays absorption bands for the O–O and for the RhO₂ moiety at 975 and 583 cm^{-1} . The bands shift to lower energy at 948 and 562 cm^{-1} for the isotopologue **5b** (Figure 1). The shifts are rather small to be associated with isolated O–O modes.^[2c] The data are in accordance with the absorption bands for the rhodium peroxycarbonato complex $\text{trans-}[\text{Rh}\{\kappa^2\text{-OOC}(\text{O})\text{O}\}(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]$ ($\text{Rh}\{\kappa^2\text{-OOC}(\text{O})\text{O}\}$: 969 cm^{-1} ; $\text{Rh}\{\kappa^2\text{-}^{18}\text{O}^{18}\text{OC}(\text{O})\text{O}\}$: 948 cm^{-1}),^[2c] they differ from the data for the rhodium metallacycle $\text{trans-}[\text{Rh}\{\kappa^2\text{-OOB}(\text{OH})\text{O}\}(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]$ (O–O: 654 cm^{-1} ; $^{18}\text{O}\text{--}^{18}\text{O}$: 644 cm^{-1}).^[9c]

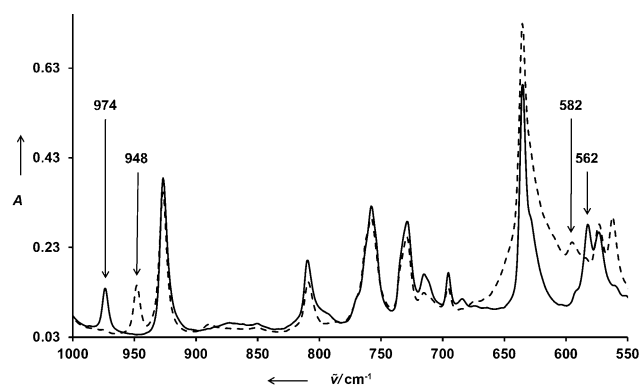


Figure 1. Part of the IR spectra of **5a** (solid line) and **5b** (dashed line) (attenuated total reflection (ATR), diamond).

The Raman spectrum of **6a** (Nd-YAG 1064 nm) shows absorption bands at 852 cm^{-1} for the O–O vibration and at 584 cm^{-1} for the RhO₂ unit. For the ^{18}O -isotopologue **6b**, the bands shift to 815 and 561 cm^{-1} . In the same manner, the absorption bands for the O–O vibration of complexes **7a** and **7b** (**7a**: $^{16}\text{O}\text{--}^{16}\text{O}$ 899 cm^{-1} , Rh^{16}O_2 594 cm^{-1} ; **7b**: $^{18}\text{O}\text{--}^{18}\text{O}$ 879 cm^{-1} , Rh^{18}O_2 549 cm^{-1}) can be assigned (see the Supporting Information). The structures of **5a** and **7a** in the solid state were determined by X-ray crystallography (Figure 2 and the Supporting Information).^[11] Both complexes **5a** and **7a** exhibit an octahedral geometry. The oxygen atom of the peroxyimide ligand binds at the *trans* position to the isonitrile ligand, whereas the nitrogen atom coordinates in the *trans* position to the tetrafluoropyridyl ligand. The O–O ($1.4914(17)\text{ Å}$) and Rh–O ($2.0473(13)\text{ Å}$) bond lengths of **5a** are comparable to the corresponding distances found for other rhodium dioxametal-

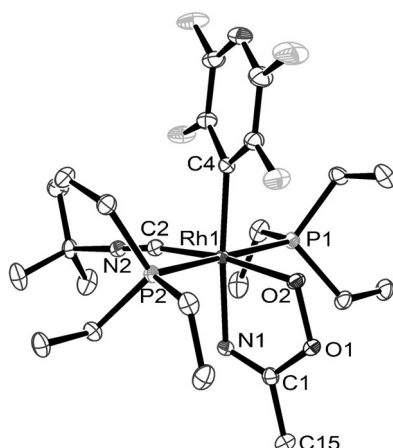
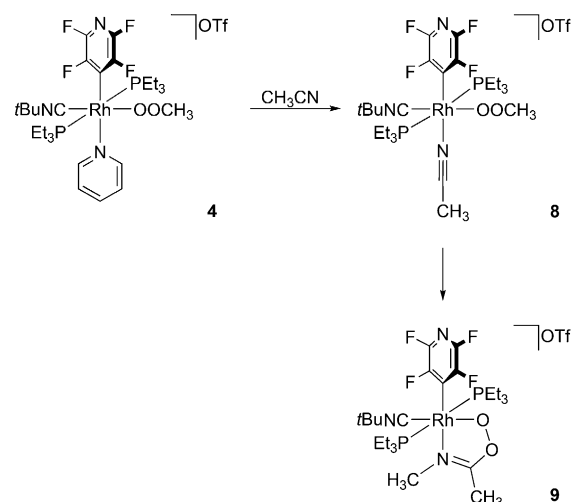


Figure 2. Structure of the cation in **5a** in the crystal (ORTEP plot, ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C2–Rh1 1.9355(18), C4–Rh1 2.0616(18), O2–Rh1 2.0473(13), N1–Rh1 2.0479(16), O1–O2 1.4914(17), C1–O1 1.323(2), C1–N1 1.275(2), C1–C15 1.494(3), N1–C1–O1 120.97 (17), N2–C2–Rh1 172.36(16), C2–Rh1–C4 93.58(7), C2–Rh1–O2 171.72(6), O2–Rh1–C4 94.70(6), C2–Rh1–N1 92.41(7), O2–Rh1–N1 79.31(6), O1–O2–Rh1 109.61(9).

lacycles such as *trans*-[Rh(κ^2 -OOB(OH)O)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (O–O: 1.4974(14) Å; Rh–O 2.0366(10) Å)^[9c] or *trans*-[Rh(κ^2 -OOC(O)O)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (O–O: 1.469(4) Å; Rh–O 2.040(3) Å).^[2c] The O–O–Rh angle of *trans*-[Rh(κ^2 -OOB(OH)O)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (108.29(7)°) and *trans*-[Rh(κ^2 -OOC(O)O)(4-C₅NF₄)(CNtBu)(PEt₃)₂] (107.7(2)°) are slightly smaller than that in **5a** (109.61(9)°). The bond lengths and angles of **7a** are comparable to the data discussed for **5a**.

Mechanistically, it can be assumed that a nucleophilic attack of the β -oxygen atom of the hydroperoxido ligand at the carbon atom of a metal-coordinated nitrile moiety occurs to furnish the five-membered ring. A proton shift from the oxygen atom to the nitrogen atom finally yields **5a–7a**. Remarkably, a metallaperoxyimide can also be generated from a methylperoxido complex. Thus, *trans*-[Rh(OOCH₃)(4-C₅NF₄)(CNtBu)(PEt₃)₂](1-C₅NH₃)]OTf^[2a] (**4**) reacted in acetonitrile to afford the complex *trans*-[Rh(κ^2 -OOC(CH₃)NCH₃)(4-C₅NF₄)(CNtBu)(PEt₃)₂)]OTf (**9**) (Scheme 3). The ³¹P{¹H} NMR and ¹⁹F NMR data of **9** are comparable to those of **5a**. Two singlet signals in the ¹H NMR spectrum are attributed to the two methyl groups at the peroxyimide entity.

The reaction of the methylperoxido complex **4** with acetonitrile was monitored by NMR spectroscopy at room temperature. The ¹⁹F and ³¹P{¹H} NMR spectra reveal the formation of the intermediate complex *trans*-[Rh(OOCH₃)(4-C₅NF₄)(CNtBu)(PEt₃)₂](CH₃CN)]OTf (**8**). After five minutes an additional doublet at δ = 19.7 ppm was detected in the ³¹P{¹H} NMR spectrum with a rhodium–phosphorus coupling constant of 81.4 Hz. The ¹⁹F NMR spectrum showed four additional multiplets for the metal-bound tetrafluoropyridyl ligand. In the ¹H NMR spectra the formation of free pyridine was observed. Furthermore a singlet signal at 3.53 was assigned to the methylperoxido ligand in **8**. After an additional 5 min the resonances for the rhodium complex **9** are also detectable in the NMR spectra. The conversion into **9** is completed within 30 min. Al-

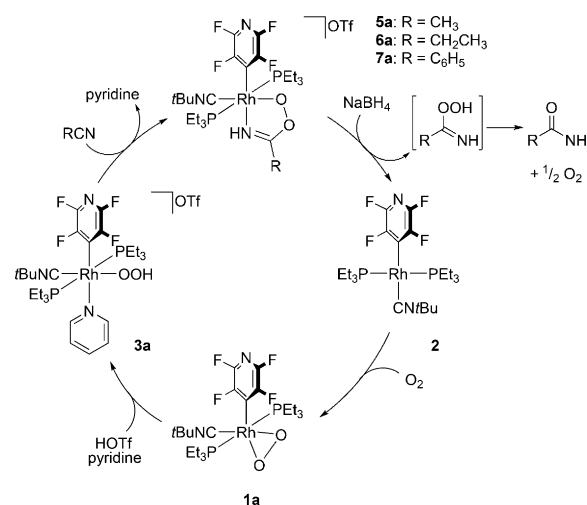


Scheme 3. Reaction of *trans*-[Rh(OOCH₃)(4-C₅NF₄)(CNtBu)(PEt₃)₂](1-C₅NH₃)]OTf (**4**) with acetonitrile.

though we were not able to detect an intermediate comparable to **8** in the conversion of the hydroperoxido complex **3a** into **5a**, the presence of such a species is very likely.

The compounds **5a**, **6a**, and **7a** can be regarded as rhodium derivatives of the peroxyimides. As mentioned above, peroxyimides decompose immediately at room temperature to give the corresponding amides and dioxygen.^[4] However, treatment of **5a**, **6a**, or **7a** with an excess NaBH₄ in a THF solution led to the formation of the amides and *trans*-[Rh(4-C₅NF₄)(CNtBu)(PEt₃)₂] (**2**) (Scheme 4).^[12] We presume that an attack of the hydride with a concomitant cleavage of the Rh–N bond leads to complexes *trans*-[Rh(H){OOC(R)NH}(4-C₅NF₄)(CNtBu)(PEt₃)₂] bearing a κ^1 -OOC(N)HR unit. A reductive elimination of the latter and the metal-bound hydrogen might give the free peroxyimides, which convert into the amides and oxygen.^[4]

The amides and the literature-known rhodium(I) complex **2** were characterized by NMR spectroscopy.^[10,13] The former were



Scheme 4. Cyclic process for the oxygenation of nitriles with dioxygen.

additionally identified by GC mass spectrometry. Considerable amounts of OPeT_3 were also detected by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and GC mass spectrometry. No subsequent formation of *trans*- $[\text{Rh}(\text{O}_2)(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]$ (**1a**) as oxygenation product occurred due to a different time scale for the reactions. However, treatment of the isolated rhodium complex **2** with dioxygen leads to formation of rhodium peroxido complex **1a** within 24 h,^[2a] which completes a cyclic process (Scheme 4).

In conclusion, we have demonstrated the generation of peroxyimide rhodium(III) complexes from oxygen, HOTf, and nitriles via hydroperoxido rhodium intermediates. Rhodium-stabilized peroxyimides can be regarded as metal salts of Payne's reagent, which is not stable and generated in situ from H_2O_2 and acetonitrile.^[5b,c] A reduction of the rhodium center with a hydride source presumably leads to a release of the peroxyimide acid, which converts into the amide and oxygen.^[4] The characterization of the rhodium- κ^2 -(*N,O*)-peroxyimides **5a**, **6a**, and **7a** give a mechanistic insight in the oxygenations of nitriles to yield amides on using O_2 and not H_2O_2 as oxygen source.

Acknowledgement

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Keywords: metallacycle • oxygenation • peroxyimide acid • reaction mechanism • rhodium

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- [11] CCDC 1059912 (**5a**) and 1059911 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [12] Conversion of *trans*- $[\text{Rh}(\kappa^2\text{-OOC}(\text{CH}_3)\text{NCH}_3)(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]\text{OTf}$ (**9**) with NaBH_4 led also to formation of *trans*- $[\text{Rh}(4\text{-C}_5\text{NF}_4)(\text{CNtBu})(\text{PEt}_3)_2]$ (**2**) as characterized by NMR spectroscopy. However, an organic product of the reaction could not be identified by NMR spectroscopy or GC mass spectrometry.
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