Peroxo Complexes

DOI: 10.1002/anie.200705715

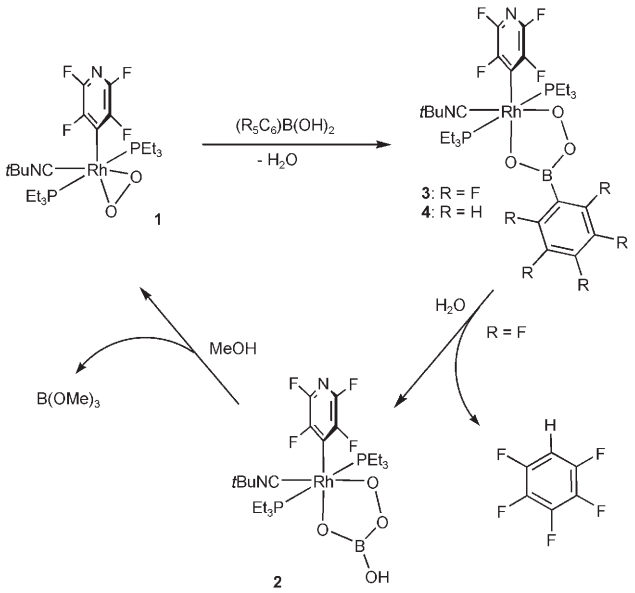
Rhodium Derivatives of Peroxoboronic Acids and Peroxoboric Acid: Formation of Metallatrioxaborolanes from an η^2-Peroxo Complex**

*Marcel Ahijado and Thomas Braun**

Transition-metal peroxo complexes play an important role in oxidation and oxygenation reactions including the generation of epoxides and peroxides.[1] The oxygen atoms of η^2-bound peroxo ligands at electron-rich transition metals are often nucleophilic. Thus, it has been reported that protonation of a palladium(II) η^2-peroxo species with acetic acid leads to the formation of hydrogen peroxide and a Pd^0 complex via a hydroperoxo species.[2] Comparable transformations are discussed as being involved in palladium-catalyzed aerobic oxidation reactions.[3] η^2-Peroxo palladium species might also play a key role in the catalytic homocoupling of aryl boronic acids or aryl boronic esters in the presence of air.[4] It has been proposed that a reaction of $[Pd(\eta^2\text{-}O_2)(dppp)]$ with $ArB(OR)_2$ [$(OR)_2 = (OH)_2$, $O_2C_3H_6$; dppp = 1,3-bis(diphenylphosphino)propane; e.g., Ar = Ph, 4-MeC_6H_4, 4-FC_6H_4] would give $[PdAr\{\eta^1\text{-}OOB(OR)_2\}(dppp)]$ as intermediate.[5] The palladium complex reacts with another equivalent of $ArB(OR)_2$ to furnish ArAr and $(RO)_2BOOB(OR)_2$, but the latter could not be identified. Amatore, Jutand et al. found indications for adduct formation in reactions of $[Pd(\eta^2\text{-}O_2)(PPh_3)_2]$ with aryl boronic acids $ArB(OH)_2$ (Ar = 4-Z-C_6H_4, where Z = MeO, H, CN).[6] The adducts $[Pd\{\eta^2\text{-}OOB(Ar)(OH)_2\}(PPh_3)_2]$ exhibit the interaction of an oxygen atom of the η^2-bound peroxo unit to the oxophilic boron atom of the aryl boronic acid. It has been suggested that $[Pd\{\eta^2\text{-}OOB(Ar)(OH)_2\}(PPh_3)_2]$ transforms into $[PdAr\{\eta^1\text{-}OOB(OH)_2\}(PPh_3)_2]$, which reacts with water to give $[PdAr(OH)(PPh_3)_2]$ and the peroxo compound $HOOB(OH)_2$. It has been proposed that the latter is hydrolyzed subsequently to H_2O_2. A transmetalation reaction yields ArAr from $[PdAr(OH)(PPh_3)_2]$ and $ArB(OH)_2$.

We found recently that the rhodium peroxo complex *trans*-$[Rh(\eta^2\text{-}O_2)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ (**1**), which is prepared from *trans*-$[Rh(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ and oxygen, reacts with HCl, Me_3SiCl, or MeOTf as sources of electrophiles to give η^1-hydroperoxo, η^1-silylperoxo, and η^1-methylperoxo complexes.[7] We now report studies on the reactivity of **1** towards the Lewis acids $(R_5C_6)B(OH)_2$ (R = H, F), which led to isolation of unique heterocyclic peroxides with a five-membered {RhOOBO} ring. These rhodatrioxaborolanes can be regarded as rhodium derivatives of perboric acid and phenylperboronic acids.

Treatment of a solution of **1** in $[D_8]$THF with pentafluorophenylboronic acid afforded heterocycle **2** and pentafluorobenzene (Scheme 1). Compound **2** is insoluble in organic solvents such as benzene, THF, CH_2Cl_2, acetone, and acetonitrile. Experiments at −40 °C revealed the formation of an initial product, which we assign as heterocyclic complex **3**. Treatment of **1** with phenylboronic acid gave rhodium perboronate **4**, which is comparable to **3** but does not react further.



Scheme 1. Formation of **2**–**4**.

We believe that the conversion of **3** to **2** is initiated by the presence of water, which is a product when **3** is formed, or it may even be generated by boroxine formation from the aryl boronic acid.[8] Cleavage of the carbon–boron bond in **3** to give **2** resembles a "hydrolytic deboronation" of aryl boronic acids.[9] The different reactivity of compound **3** towards water in comparison to **4** is notable. A stable water adduct of $B(C_6F_5)_3$ has been reported recently, but it has also been suggested that boronic acids which carry electron-withdrawing substituents are more susceptible to carbon–boron bond cleavage.[10]

Evidence for the presence of a peroxo unit in **2** is given by the IR (ATR, diamond) and Raman (Figure 1) spectra together with isotopic-labeling experiments. The spectra show an absorption band at 3051 cm^{-1} for the OH group.

[*] M. Ahijado, Prof. Dr. T. Braun
Institut für Chemie
Humboldt-Universität zu Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-6939
E-mail: thomas.braun@chemie.hu-berlin.de

[**] We acknowledge the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

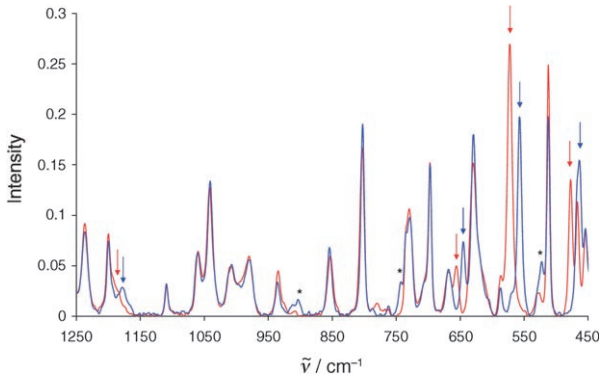


Figure 1. Part of the Raman spectra of **2** (red line) and **2′** (blue line); absorption bands which exhibit an isotopic shift (see text) are labeled with arrows; asterisks indicate a small amount of **1′** in the spectrum of **2′**.

The presence of an isonitrile ligand at a rhodium(III) center is revealed by an absorption at 2193 cm^{-1}.[7] A band at 1189 cm^{-1} can tentatively be assigned to in-plane B–O ring stretching.[11] The signal shifts to 1176 cm^{-1} for the isotopologue *trans*-[Rh{κ^2-$^{18}O^{18}$OB(OH)*O*}(4-C_5F_4N)(CN*t*Bu)-(PEt_3)$_2$] (**2′**). The absorption at 654 cm^{-1} (644 cm^{-1} for **2′**) and the isotopic shift are also indicative of the presence of the peroxo unit.[7,12] Two other bands at 572 cm^{-1} (556 cm^{-1} for **2′**) and 477 cm^{-1} (463 cm^{-1} for **2′**) may be assigned to relatively pure Rh–O antisymmetric and symmetric vibrations.[13] The latter can be seen only in the Raman spectrum.

The molecular structure of **2** was also determined by X-ray crystallography (Figure 2).[14] The molecule exhibits a distorted octahedral geometry with the two phosphines in mutually *trans* positions. The O1-Rh1-O3 angle of 82.80(4)° is comparable to the corresponding angle in the peroxocarbonato complex [Rh{κ^2-*O*OC(O)*O*}(4-MeC_6H_4)-{*t*BuP($CH_2CH_2CH_2PPh_2$)$_2$}].[15] The O–O distance of 1.49(2) Å in the latter is similar to the O1–O2 bond length of 1.4974(14) Å in **2**. The O–O distances in other cyclic transition metal percarbonate complexes are also in the same range.[16] The boron–oxygen distance to the peroxo unit in **2** (B1–O2 1.4001(18) Å) is slightly longer than the other boron–oxygen bond lengths (B1–O3 1.3449(18) Å, B1–O4 1.3719(19) Å), but the data are in accordance with the literature.[17] The rhodium–oxygen bond lengths of 2.0366(10) and 2.0585(10) Å are shorter than in the rhodium(I) boronate [Rh{OB(OH)(*p*-Tol}(PEt_3)$_3$] (2.102(2) Å),[17] but are close to the corresponding distances in *trans*-[RhCl(η^1-OOH)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] and *trans*-[Rh(η^1-OOMe)(4-C_5F_4N)(NC_5H_5)(CN*t*Bu)-(PEt_3)$_2$]OTf.[7] Intermolecular hydrogen bonding provides strong evidence for the presence of the OH group. These interactions result in the formation of dimers with an intermolecular oxygen–oxygen distance of 2.690 Å (Figure 3). The structure of phenylboronic acid in the solid state exhibits a similar arrangement of two distinct molecules bound through a pair of hydrogen bonds.[18]

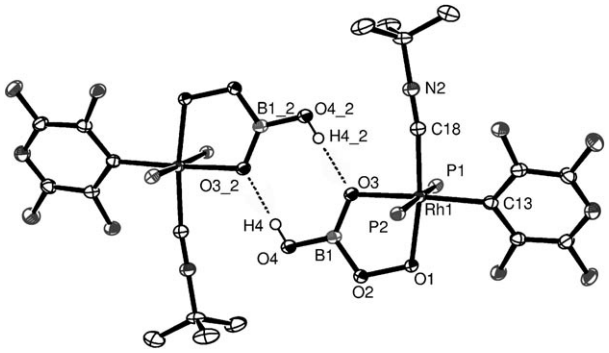


Figure 3. Arrangement of **2** in the crystal showing the hydrogen bonds between two molecules; ethyl groups have been omitted for clarity (ORTEP diagram, thermal ellipsoids at 50% probability).

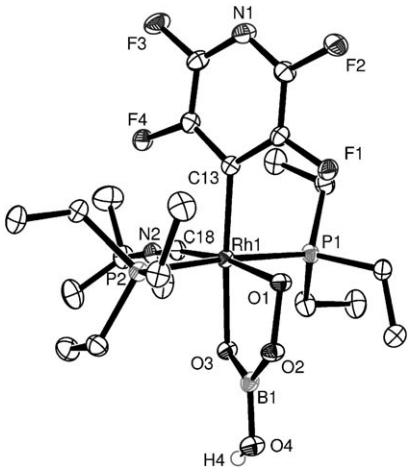


Figure 2. Molecular structure of **2** in the crystal (ORTEP diagram, thermal ellipsoids set at 50% probability). Selected distances [Å] and angles [°]: Rh1–O1 2.0366(10), Rh1–O3 2.0585(10), O1–O2 1.4974(14), B1–O2 1.4001(18), B1–O3 1.3449(18), B1–O4 1.3719(19), O4–H4 0.77(2); O1-Rh1-O3 82.80(4), O2-B1-O3 121.73(13), O2-O1-Rh1 108.29(7), B1-O2-O1 112.58(10), B1-O3-Rh1 109.92(9).

The IR (ATR, diamond) and Raman spectra of **4** show characteristic absorption bands at energies comparable to those of **2**. Distinctive features appear at 2189, 1057 (1051 for **4′**), 660 (652 for **4′**) and 552 cm^{-1} (542 cm^{-1} for **4′**). Mass spectra of **4** and of the isotopologue *trans*-[Rh{κ^2-$^{18}O^{18}$OB(Ph)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**4′**) exhibit peaks which reflect the correct isotopic distributions. High-resolution accurate ESI mass spectra of **4** and **4′** (principal ion of $[M+H]^+$ peaks in acetonitrile) also substantiate the presence of the peroxo unit. A broad signal at $\delta = 29.0$ ppm in the ^{11}B NMR spectrum of **4** is indicative of the trioxaborolane moiety. For comparison, the resonance for pentafluorophenylboronic acid appears at $\delta = 28.7$ ppm, whereas the rhodium boronate [Rh{OB(OH)(Ph}(PEt_3)$_3$] exhibits a signal at $\delta = 25.6$ ppm.[17]

The structure of intermediate **3**, which was identified during formation of **2**, presumably resembles that of **4**. Although **3** is formed quantitatively according to the NMR data, we were not able to isolate it at low temperature. High-resolution accurate ESI mass spectra of **3** and of the isotopologue *trans*-[Rh{κ^2-$^{18}O^{18}$OB(C_6F_5)*O*}(4-C_5F_4N)-

$(CNtBu)(PEt_3)_2]$ (**3′**) suggest the presence of the peroxo unit. The $[M+H]^+$ peaks also display the correct isotopic distribution. The ^{11}B NMR spectrum exhibits a signal at $\delta =$ 24.8 ppm. The absorption bands in the IR (ATR, ZnSe) and Raman (Figure 4) spectra at 2189, 1182 (weak in the Raman

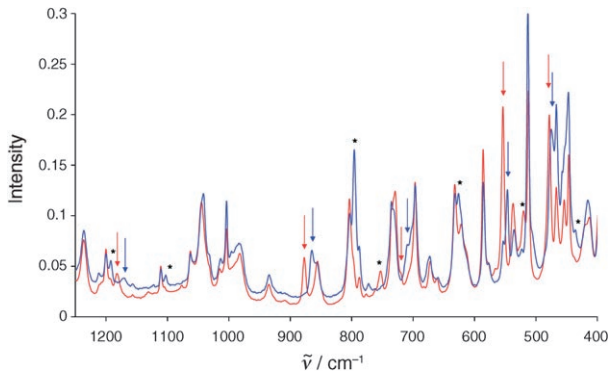


Figure 4. Part of the Raman spectra of **3** (red line) and **3′** (blue line); absorption bands which exhibit an isotopic shift (see text) are labeled with arrows; asterisks indicate the presence of **1** and **1′**.

spectrum; 1172 for **3′**), and 552 cm^{-1} (545 cm^{-1} for **3′**), as well as a band at 478 cm^{-1} (only in the Raman spectrum; 474 cm^{-1} for **3′**) resemble these found for **2** and **4**. Again, the last two can tentatively be assigned to Rh–O antisymmetric and symmetric vibrations.[13] However, distinctive bands at 878 (866 for **3′**) and 718 cm^{-1} (very weak in the Raman spectrum; 709 cm^{-1} for **3′**) are found at different energies. Note that an absorption band for $[Pt\{\kappa^2\text{-}^{16}O^{16}OC(CH_3)_2O\}(PPh_3)_2]$ appears in the IR spectrum at 811 cm^{-1} and shifts to 786 cm^{-1} for the $^{18}O^{18}O$ isotopologue, whereas for the silylperoxo complex *trans*-$[RhCl(\eta^1\text{-}OOSiMe_3)(4\text{-}C_5F_4N)(CNtBu)(PEt_3)_2]$ absorption bands at 901 and 884 cm^{-1} were found for the two corresponding isotopologues.[7,12a,b] A band at 840 cm^{-1} has been assigned to the O–O vibration in $(nPrO)_2BOOB(OnPr)_2$.[12c]

Although **2** is insoluble in most organic solvents, treatment with methanol resulted in alcoholysis, and peroxo complex **1** and $B(OMe)_3$ were generated (Scheme 1). If the reaction is performed with the isotopologue **2′**, the corresponding $^{18}O_2$ isotopologue *trans*-$[Rh(\eta^2\text{-}^{18}O_2)(4\text{-}C_5F_4N)(CNtBu)(PEt_3)_2]$ (**1′**) is formed as the sole organometallic product.[7] Thus, cleavage of the boron–oxygen bond in **2′** along with regeneration of **1′** suggests that the peroxo unit in **2′** retains its identity. The perboronato complexes **3** and **4** do not react with MeOH. In these cases the B–O bond to the peroxo unit seems to be less labile.

Compounds **2**–**4** are unique and the structural motif {MOOB} (M = metal) involving trivalent boron is without precedent in main group or transition metal coordination chemistry, although 1,3,4-trioxadiborolanes and alkylperoxyboron entities have been described.[11,19] Note that *cis*-$[MoO(O_2)\{\kappa^2\text{-}PhN(O)C(O)Ph\}_2]$ reacts with $B(C_6F_5)_3$ to give $[MoO(O_2)\{B(C_6F_5)_3\}\{\kappa^2\text{-}PhN(O)C(O)Ph\}_2]$, but it is not clear whether the Lewis acid is bound to the oxo or to the peroxo ligand.[20] Moreover, only a limited number of transition metal derivatives of boric acid, boronic acid or borinic acid is known.[17,21–23] Complexes **3** and **4** are somewhat related to the palladium compounds $[Pd\{\eta^2\text{-}OOB(Ar)(OH)_2\}(PPh_3)_2]$, which were identified as intermediates in the homocoupling of aryl boronic acids.[6] We have no indication for the formation of a similar Lewis acid/Lewis base adduct, although species such as *trans*-$[Rh\{\eta^2\text{-}OOB(C_6R_5)(OH)_2\}(4\text{-}C_5F_4N)(CNtBu)(PEt_3)_2]$ (R = H, F) may play a certain role in the formation of **3** and **4**. Also, it was recently reported that $[MO_2(PPh_3)_2]$ reacts with LCu^I precursors (L = β-diketiminate, di- and triamine ligands) to give heterobimetallic CuPd and CuPt bis(μ-oxo) complexes.[24] Compounds **2**–**4** are surprisingly stable. So far, we did not observe any oxygenation of the metal-bound phosphines, free PEt_3, or the tetrafluoropyridyl ligand.[1,13b,20,25] The stabilizing influence of a fluorinated pyridyl ligand may be a crucial factor in this context.[7,26]

In conclusion, two metallacycles have been isolated which may formally be regarded as rhodium derivatives of a perboronic acid and perboric acid. To the best of our knowledge, these acids do not exist in pure form and have not been identified spectroscopically, and metal derivatives thereof are also without precedent. Peroxoborates $[B(OH)_3(OOH)]^-$ and $[B(OH)_2(OOH)_2]^-$ are formed in aqueous solutions of hydrogen peroxide and $B(OH)_3$, but the generation of peroxoboronic acid $B(OH)_2(OOH)$ in low concentration has also been deduced by evaluation of equilibrium constants.[27] Considering the capability of, for instance, sodium perborate $Na_2[B_2(OH)_4(\mu\text{-}OO)_2]$ as oxidizing agent as well as rhodadioxolanes as oxygenating agents,[1e,28,29] our results should stimulate further studies on the properties of neutral metallaperborates and -perboronates to elucidate their stability and their potential in oxidation and oxygenation reactions.

Experimental Section

A solution of **1**[7] (30 mg, 0.05 mmol) in $[D_8]$THF (0.5 mL) was treated with a solution of $(F_5C_6)B(OH)_2$ (11 mg, 0.05 mmol) in $[D_8]$THF (0.1 mL) at 233 K. After warming the solution to 273 K formation of **3** was observed by NMR spectroscopy over 1 h. The reaction solution was then warmed to room temperature. After 4 h the generation of pentafluorobenzene was observed and colorless needles of complex **2** precipitated. Yield: 24 mg (73 %). Analytical data for **3**: ^1H NMR (600 MHz, $[D_8]$THF, 273 K): δ = 1.97 (m, 6H; PCH_aH_b), 1.67 (m, 6H; PCH_aH_b), 0.93 (s; $NC(CH_3)_3$), 0.82 ppm (m; PCH_2CH_3); ^{19}F NMR (564.7 MHz, $[D_8]$THF, 273 K): δ = −101.0 (m, 1F), −101.2 (m, 1F), −118.5 (m, 1F), −123.5 ppm (m, 1F); $^{31}P\{^1H\}$ NMR (242.9 MHz, $[D_8]$THF, 273 K): δ = 22.7 ppm (d, $^1J_{P,Rh}$ = 86 Hz); ^{11}B NMR (192.6 MHz, $[D_8]$THF, 273 K): δ = 24.8 ppm (s, br, $\Delta\nu_{1/2}$ = 710 Hz; accurate HR-ESI-MS calcd for $C_{28}H_{39}BF_9N_2O_3P_2Rh^+$: *m/z* 799.1513; found: 799.1517; accurate ESI-MS **3′** calcd for $C_{28}H_{39}BF_9N_2O^{18}O_2P_2Rh^+$: *m/z* 803.1598; found: 803.1608. Analytical data for **2**: C,H,N analysis (%) calcd for $C_{22}H_{40}BF_4N_2O_4P_2Rh$: C 40.76, H 6.22, N 4.32; found: C 40.86, H 6.25, N 4.46.

A solution of **1**[7] (30 mg, 0.05 mmol) in THF (0.5 mL) was treated with a solution of $(H_5C_6)B(OH)_2$ (6 mg, 0.05 mmol) in THF (0.1 mL) at 233 K. After warming the solution to 273 K the volatile substances were removed in vacuo. The residue was extracted with benzene (3 × 0.5 mL), and the extract dried to obtain a colorless powder. Yield: 31 mg (87 %). Analytical data for **4**: ^1H NMR (600.1 MHz, C_6D_6): δ = 8.36 (d, $J_{H,H}$ = 7.1 Hz, 2H; Ph), 7.34 (t, $J_{H,H}$ = 7.3 Hz, 2H; Ph), 7.25 (t, $J_{H,H}$ = 7.2 Hz, 1H; Ph), 1.86 (m, q in $^1H\{^{31}P\}$ NMR, $^3J_{H,H}$ = 7.3 Hz,

6H; PCH_aH$_b$), 1.59 (m, q in ^{1}H{^{31}P} NMR $^3J_{H,H}$ = 7.3 Hz, 6H; PCH$_a$$H_b$), 0.98 (s, 9H; NC(C$H_3$)$_3$), 0.76 ppm (m, t in ^{1}H{^{31}P} NMR, $^3J_{H,H}$ = 7.3 Hz, 18H; PCH$_2$CH_3); ^{19}F NMR (564.7 MHz, C_6D_6): δ = −97.3 (m, 1F), −98.3 (m, 1F), −114.9 (m, 1F), −118.9 ppm (m, 1F); ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 20.4 ppm (d, $^1J_{P,Rh}$ = 89 Hz); ^{11}B NMR (192.6 MHz, C_6D_6): δ = 29.0 ppm (s, br, $\Delta\nu_{1/2}$ = 922 Hz); accurate HR-ESI-MS (*m*/*z*) calcd for $C_{28}H_{45}BF_4N_2O_3P_2Rh^+$: 709.1984; found: 709.1985; accurate HR-ESI-MS (*m*/*z*) of **4′** calcd for $C_{28}H_{45}BF_4N_2O^{18}O_2P_2Rh^+$: 713.2069; found: 713.2069.

Received: December 13, 2007
Revised: January 15, 2008
Published online: March 7, 2008

Keywords: boron · fluorinated ligands · heterocycles · peroxo ligands · rhodium

[1] See, for example: a) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**; b) C. Limberg, *Angew. Chem.* **2003**, *115*, 6112 – 6136; *Angew. Chem. Int. Ed.* **2003**, *42*, 5932 – 5954; c) *Topics in Organometallic Chemistry* (Eds.: C. Limberg, F. Meyer), Springer, Heidelberg, **2007**; d) J.-M. Brégeault, *Dalton Trans.* **2003**, 3289 – 3302; e) M. Krom, T. P. J. Peters, R. G. E. Coumans, T. J. J. Sciarone, T. V. J. Hoogboom, S. I. ter Beek, P. J. P. Schlebos, J. M. M. Smits, R. de Gelder, A. W. Gal, *Eur. J. Inorg. Chem.* **2003**, 1072 – 1087; f) H Mimoun in *The Chemistry of Peroxides* (Ed.: S. Patai), Wiley, Chichester, **1985**, pp. 463 – 482; g) C. W. Dudley, G. Read, P. J. C. Walker, *J. Chem. Soc. Dalton Trans.* **1974**, 1926 – 1931; h) T. Nishimura, N. Kakiuchi, T. Onoue, K. Ohe, S. Uemura, *J. Chem. Soc. Perkin Trans. 1* **2000**, 1915 – 1918; i) F. Igersheim, H. Mimoun, *Nouv. J. Chim.* **1980**, *4*, 711 – 713; j) G. Read, *J. Mol. Cat.* **1988**, *44*, 15 – 33; k) *Modern Oxidation Methods* (Ed.: J.-E. Bäckvall), Wiley-VCH, Weinheim, **2004**.

[2] a) M. M. Konnick, I. A. Guzei, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 10212 – 10213; b) S. S. Stahl, J. L. Thorman, R. C. Nelson, M. A. Kozee, *J. Am. Chem. Soc.* **2001**, *123*, 7188 – 7189; c) T. Privalov, C. Linde, K. Zetterberg, C. Moberg, *Organometallics* **2005**, *127*, 885 – 893.

[3] Inter alia*:* a) N. R. Conley, L. A. Labios, D. M. Pearson, C. C. L. McCroy, R. M. Waymouth, *Organometallics* **2007**, *26*, 5447 – 5453; b) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480 – 3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400 – 3420; c) B. A. Steinhoff, I. A. Guzei, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 11268 – 11278; d) D. R. Jensen, M. J. Schultz, J. A. Mueller, M. S. Sigman, *Angew. Chem.* **2003**, *115*, 3940 – 3943; *Angew. Chem. Int. Ed.* **2003**, *42*, 3810 – 3813; e) M. M. Konnick, B. A. Gandhi, I. A. Guzei, S. S. Stahl, *Angew. Chem.* **2006**, *118*, 2970 – 2973; *Angew. Chem. Int. Ed.* **2006**, *45*, 2904 – 2907; f) B. A. Steinhoff, S. R. Fix, S. S. Stahl, *J. Am. Chem. Soc.* **2002**, *124*, 766 – 767; g) G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* **2002**, *344*, 355 – 369; h) G.-J. ten Brink, I. W. C. E. Arends, M. Hoogenraad, G. Verspui, R. A. Sheldon, *Adv. Synth. Catal.* **2003**, *345*, 497 – 505; i) J. A. Mueller, C. P. Goller, M. S. Sigman, *J. Am. Chem. Soc.* **2004**, *126*, 9724 – 9734; j) W. Zierkiewicz, T. Pivalov, *Organometallics* **2005**, *24*, 6019 – 6028; k) J. M. Keith, R. J. Nielsen, J. Oxgaard, W. A. Goddard III, *J. Am. Chem. Soc.* **2005**, *127*, 13172 – 13179; l) M. S. Sigman, *Acc. Chem. Res.* **2006**, *39*, 221 – 229.

[4] a) M. Moreno-Mañas, M. Pérez, R. Pleixats, *J. Org. Chem.* **1996**, *61*, 2346 – 2351; b) M. A. Aramendia, M. Lafont, M. Moreno-Mañas, M. Pérez, R. Pleixats, *J. Org. Chem.* **1999**, *64*, 3592 – 3594; c) K. A. Smith, E. M. Campi, R. Jackson, S. Marcuccio, C. G. M. Naeslund, G. B. Deacon, *Synlett* **1997**, 131 – 132; d) J. P. Parrish, Y. C. Jung, R. J. Floyd, K. W. Jung, *Tetrahedron Lett.* **2002**, *43*, 7899 – 7902.

[5] H. Yoshida, Y. Yamaryo, J. Ohshita, A. Kunai, *Tetrahedron Lett.* **2003**, *44*, 1541 – 1544.

[6] C. Adamo, C. Amatore, I. Ciofini, A. Jutand, H. Lamini, *J. Am. Chem. Soc.* **2006**, *128*, 6829 – 6836.

[7] M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammler, *Angew. Chem.* **2005**, *117*, 7107 – 7111; *Angew. Chem. Int. Ed.* **2005**, *44*, 6947 – 6951.

[8] a) M. F. Lappert, *Chem. Rev.* **1956**, *56*, 959 – 1064; b) *Boronic Acids. Preparation and Applications in Organic Synthesis and Medicine* (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2005**.

[9] a) T. Watanabe, N. Miyaura, A. Suzuki, *Synlett* **1992**, 207 – 210; b) H. Zhang, K. Y. Kwong, Y. Tian, K. S. Chan, *J. Org. Chem.* **1998**, *63*, 6886 – 6890; c) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457 – 2483.

[10] a) T. Baringhelli, D. Maggioni, G. D'Alfonso, *Organometallics* **2007**, *26*, 4927 – 4938; b) A. Suzuki in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2004**, pp. 53 – 106; c) see also: M. H. Abraham, P. L. Grellier in *The Chemistry of the Metal-Carbon Bond*, *Vol. 2* (Eds.: F. R. Hartley, S. Patai), Wiley, New York, **1985**, p. 115.

[11] a) L. Barton, J. M. Crump, *Inorg. Chem.* **1973**, *12*, 2252 – 2256; b) for vibrational assignments of $H_2B_2O_3$ see: F. A. Grimm, R. F. Porter, *Inorg. Chem.* **1969**, *8*, 731 – 737.

[12] a) T. Tatsuno, S. Otsuka, *J. Am. Chem. Soc.* **1981**, *103*, 5832 – 5839; b) P. J. Hayward, D. M. Blake, G. Wilkinson, C. J. Nyman, *J. Am. Chem. Soc.* **1970**, *92*, 5873 – 5878; c) V. P. Maslennikov, G. I. Makin, V. N. Alyaov, Y. A. Aleksandrov, *Zh. Obshch. Khim.* **1973**, *43*, 1972 – 1973.

[13] a) A. Nakamura, Y. Tatsuno, M. Yamamoto, S. Ostuka, *J. Am. Chem. Soc.* **1971**, *93*, 6052 – 6057; b) M. Aresta, I. Tommasi, E. Quaranta, C. Fragale, J. Mascetti, M. Tranquille, F. Galan, M. Fouassier, *Inorg. Chem.* **1996**, *35*, 4254 – 4260.

[14] Data for the X-ray structure analysis of **2**·THF $C_{26}H_{48}BF_4N_2O_5P_2Rh$: M = 720.32, crystal dimensions 0.31 × 0.27 × 0.16 mm^3; triclinic; $P\bar{1}$; a = 10.58400(10), b = 13.4080(2), c = 13.4920(2) Å, α = 108.0410(7), β = 111.7220(8), γ = 96.5580(9)°, Z = 2, V = 1633.51(4) Å^3, ρ_{calcd} = 1.464 g cm^{-3}; $2\theta_{max}$ = 60°, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), T = 100(2) K, 63994 reflections collected, of which 9480 were unique (R_{int} = 0.039); Nonius KappaCCD diffractometer; multiscan absorption correction (min./max. transmission 0.8169/0.8990), μ = 0.680 mm^{-1}. The structure was solved by direct methods and refined with full-matrix least-square methods on F^2 (SHELX-97).[30] Final R_1, wR_2 values on all data: 0.0312, 0.0670; R_1, wR_2 values for 8402 reflections with $I_0 > 2\sigma(I_0)$: 0.0254, 0.0630; residual electron density +0.700/−0.710 e Å^{-3}; the disordered THF molecule was refined on two positions (73:27); hydrogen atoms were placed at calculated positions and refined with a riding model except for H4, which was refined isotropically. CCDC-668560 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.

[15] L. Dahlenburg, C. Prengel, *J. Organomet. Chem.* **1986**, *308*, 63 – 71.

[16] a) A. Wada, S. Yamaguchi, K. Jitsukawa, H. Masuda, *Angew. Chem.* **2005**, *117*, 5844 – 5847; *Angew. Chem. Int. Ed.* **2005**, *44*, 5698 – 5701; b) K. Hashimoto, S. Nagatomo, S. Fucinami, H. Furutachi, S. Ogo, M. Suzuki, A. Uehara, Y. Maeda, Y. Watanabe, K. Kitagawa, *Angew. Chem.* **2002**, *114*, 1250 – 1253; *Angew. Chem. Int. Ed.* **2002**, *41*, 1202 – 1205.

[17] P. Zhao, C. D. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 1876 – 1877.

[18] S. J. Rettig, J. Trotter, *Can. J. Chem.* **1977**, *55*, 3071 – 3075.

[19] a) L. Barton, D. Brinza, R. A. Frease, F. L. Longcor, *J. Inorg. Nucl. Chem.* **1977**, *39*, 1845 – 1847; b) R. Goetze, H. Nöth, H. Pommerening, D. Sedlak, B. Wrackmeyer, *Chem. Ber.* **1981**, *114*, 1884 – 1893; c) H. C. Brown, M. M. Midland, *Tetrahedron* **1987**, *43*, 4059 – 4070; d) R. Köster, G. Seidel, *Angew. Chem.* **1984**, *96*, 145 – 146; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 155 – 156; e) R. W. Hoffmann, K. Ditrich, *Synthesis* **1983**, 107 – 109.

[20] L. H. Doerrer, J. R. Galsworthy, M. L. H. Green, M. A. Leech, M. Müller, *J. Chem. Soc. Dalton Trans.* **1998**, 3191 – 3194.

[21] a) D. S. Laitar, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* **2005**, *127*, 17196 – 17197; b) S. Hawkeswood, D. W. Stephan, *Dalton Trans.* **2005**, 2182 – 2187; c) K. L. Fujdala, A. G. Oliver, F. J. Hollander, T. Don Tilley, *Inorg. Chem.* **2003**, *42*, 1140 – 1150; d) A. Dibas, J. Howard, S. Anwar, D. Stewart, A. Khan, *Biochem. Biophys. Res. Commun.* **2000**, *270*, 383 – 386.

[22] a) J. E. Balkwill, S. E. Cole, M. P. Coles, P. B. Hitchcock, *Inorg. Chem.* **2002**, *41*, 3548 – 3552; b) D. S. Marlin, E. Bill, T. Weyhermüller, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **2005**, *127*, 6095 – 6108; c) I. Pantcheva, Y. Nishihara, K. Osakada, *Organometallics* **2005**, *24*, 3815 – 3817; d) B. Crociani, S. Antonaroli, A. Marini, U. Matteoli, A. Scrivanti, *Dalton Trans.* **2006**, 2698 – 2705; e) R. Anulewicz-Ostrowska, S. Luliński, E. Pindelska, J. Serwatowski, *Inorg. Chem.* **2002**, *41*, 2525 – 2528.

[23] a) S. C. Cole, M. P. Coles, P. B. Hitchcock, *Organometallics* **2005**, *24*, 3279 – 3289; b) S. J. Birch, S. R. Boss, S. C. Cole, M. P. Coles, R. Haigh, P. B. Hitchcock, A. E. H. Wheatley, *Dalton Trans.* **2004**, 3568 – 3574; c) S. C. Cole, M. P. Coles, P. B. Hitchcock, *Dalton Trans.* **2004**, 3428 – 3430.

[24] J. T. York, A. Llobet, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2007**, *129*, 7990 – 7999.

[25] a) M. Aresta, A. Dibenedetto, I. Tommasi, *Eur. J. Inorg. Chem.* **2001**, 1801 – 1806; b) T. Braun, A. Steffen, V. Schorlemer, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2005**, 3331 – 3336; c) T. Braun, V. Schorlemer, B. Neumann, H.-G. Stammler, *J. Fluorine Chem.* **2006**, *127*, 367 – 372; d) T. Braun, S. Rothfeld, A. Stammler, H.-G. Stammler, *Inorg. Chem. Commun.* **2003**, *6*, 752 – 755.

[26] a) D. Noveski, T. Braun, B. Neumann, A. Stammler, H.-G. Stammler, *Dalton Trans.* **2004**, 4106 – 4119; b) T. Braun, D. Noveski, M. Ahijado, F. Wehmeier, *Dalton Trans.* **2007**, 3820 – 3825; c) T. Braun, J. Izundu, A. Steffen, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2006**, 5118 – 5123; d) A. Steffen, T. Braun, B. Neumann, H.-G. Stammler, *Angew. Chem.* **2007**, *119*, 8828 – 8832; *Angew. Chem. Int. Ed.* **2007**, *46*, 8674 – 8678; e) T. Braun, B. Blöcker, V. Schorlemer, B. Neumann, A. Stammler, H.-G. Stammler, *J. Chem. Soc. Dalton Trans.* **2002**, 2213 – 2218; f) T. Braun, M. I. Sladek, B. Neumann, H.-G. Stammler, *New J. Chem.* **2003**, *27*, 313 – 318.

[27] a) R. Pizer, C. Tihal, *Inorg. Chem.* **1987**, *26*, 3639 – 3642; b) D. M. Davies, M. E. Deary, K. Quill, R. A. Smith, *Chem. Eur. J.* **2005**, *11*, 3552 – 3558; c) G. Hausdorf, K. Krüger, G. Küttner, H.-G. Holzhütter, C. Frömmel, W. E. Höhne, *Biochim. Biophys. Acta Protein Struct. Mol. Enzymol.* **1987**, *952*, 20 – 26.

[28] a) G. W. Kabalka, T. M. Shoup, N. M. Goudgaon, *J. Org. Chem.* **1989**, *54*, 5930 – 5933; b) A. McKillop, J. A. Tarbin, *Tetrahedron* **1987**, *43*, 1753 – 1758.

[29] a) M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2002**, *114*, 595 – 599; *Angew. Chem. Int. Ed.* **2002**, *41*, 575 – 579; b) M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2001**, *113*, 2164 – 2166; *Angew. Chem. Int. Ed.* **2001**, *40*, 2106 – 2108; c) B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236 – 4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142 – 4157.

[30] a) SHELXTL-PLUS, Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA, **1990**; b) G. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Sigli, M. C. Burla, G. Polidori, M. Camalli, *Acta Crystallogr. Sect. A* **1996**, *52*, C-79.

