Peroxo Complexes

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Stepwise Oxygenation of Pinacolborane by a Rhodiumperoxo Complex: Detection of an Intermediate Metal Borate and Perborate**

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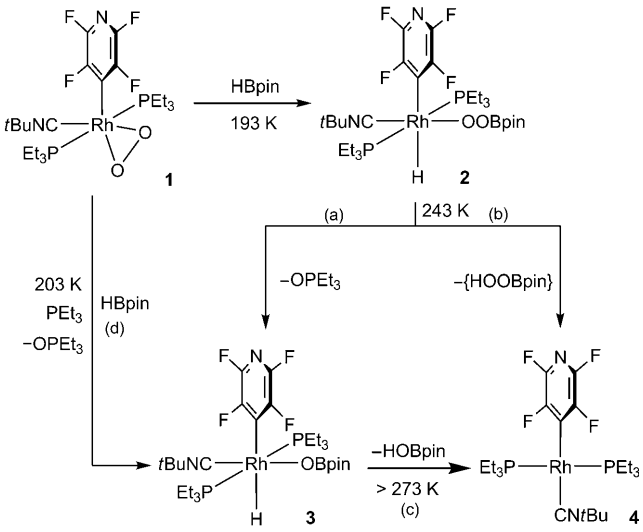
A current challenge in transition-metal-mediated oxidation and oxygenation chemistry is to use oxygen itself as an environmentally friendly reagent.[1] One of the essential objectives for understanding the mechanistic details is to study the properties of peroxo compounds, which often play a key role in these processes.[1–3] η^2-Peroxo complexes are crucial intermediates in the palladium-catalyzed homocoupling of aryl boronic acids or aryl boronic esters in the presence of O_2.[4,5] Thus, the palladium(II)–η^2-peroxo complex $[Pd(\eta^2\text{-}O_2)(PPh_3)_2]$ is transformed in the presence of $ArB(OH)_2$ (Ar = 4-*Z*-C_6H_4, where *Z* = MeO, H, CN) into peroxoborates such as $[PdAr\{\eta^1\text{-}OOB(OH)_2\}(PPh_3)_2]$, but the latter species have not been identified.[4] It has been suggested that the hydroxo complex $[PdAr(OH)(PPh_3)_2]$ as well as the putative $HOOB(OH)_2$ species are generated in the presence of water. Furthermore, it is presumed that the perboronic acid immediately hydrolyzes to H_2O_2 and $B(OH)_3$. The addition of another equivalent of $ArB(OH)_2$ gives Ar–Ar, and the Pd center is reduced to Pd^0 which can again react with O_2. Overall, this homocoupling reaction involves, as a key step, the oxidation of a transition metal by reduction of O_2 to afford H_2O_2 or $HOOB(OH)_2$. Comparable reoxidations of a metal center by O_2 can also be crucial for such catalytic cycles as the aerobic oxidation of alcohols or for Wacker-type oxidations of olefins without applying any redox mediator, such as $CuCl_2$.[3,6] However, from a different point of view, the deoxygenation of metal–peroxo intermediates is also of interest to gain mechanistic insights into reaction pathways, so as to enable the prevention of catalyst decomposition by O_2 in various catalytic borylation processes.[7–10] Burgess, Marder et al. have shown that rhodium–peroxo complexes can even be applied as catalyst precursors for the hydroboration of styrene.[9a]

Herein we report on the rhodium-mediated oxygenation of HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane) with O_2. The transfer of an oxygen atom from a rhodium(III)–peroxo complex to HBpin to yield a rhodium(I) complex occurs via key species which are assigned as a rhodium borate and perborate. The reaction sequence is of interest because: 1) metal perborates might play a crucial role in the homocoupling of boronic acid esters, and 2) the model reactions open up new opportunities for the deoxygenation of catalytically inactive metal–peroxo species to enable their transformation into catalytically active compounds.

Treatment of peroxo compound **1**, which was prepared from *trans*-$[Rh(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)_2]$ (**4**) and dioxygen,[11] with substoichiometric amounts of HBpin (0.7 equiv) in $[D_8]$toluene at 193 K afforded a rhodium(III) compound, which we assign as the rhodium peroxoborate species **2** (Scheme 1). Complex **2** is only stable at low temperature.



Scheme 1. Reactivity of **1** towards substoichiometric amounts of HBpin.

Warming the reaction mixture to 243 K results in the formation of the rhodium borate **3** and the phosphine oxide, as evident by NMR spectroscopy (Scheme 1, pathway a). Figure 1 shows the $^{31}P\{^1H\}$ NMR spectra of the reaction sequence. Complex **3** and $OPEt_3$ are generated in a ratio of roughly 1:2. This finding is an indication of an intramolecular oxygenation reaction of the phosphine ligand in **2**.[12] We believe that decomposition of the conceivable, five-coordinate intermediate $[RhH(OBpin)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)]$ furnishes free phosphine, which is trapped by another equivalent of $[RhH(OBpin)(4\text{-}C_5F_4N)(CN\mathit{t}Bu)(PEt_3)]$ to yield **3**. The concomitant formation of the rhodium(I) complex **4** has also been observed (pathway b).[13] Although **4** can be generated directly from **3** (see below), it was formed in a much greater amount than the phosphine oxide. We suggest that **4** is formed by a different reaction pathway (b), in which **2** converts directly into **4** by reductive elimination of HOOBpin. The latter species could not be identified, and is

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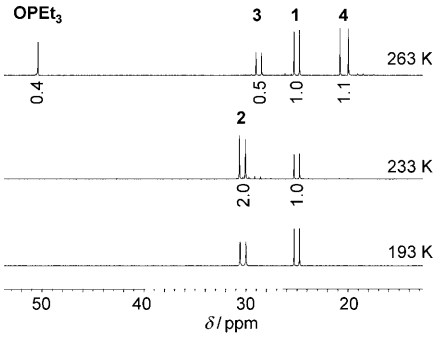


Figure 1. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **1** with substoichiometric amounts of HBpin at different temperatures; the numbers below the signals represent the integration of the signals.

considered not to be stable.[4,14] The analytical data do, however, reveal the formation of HOBpin (^{11}B NMR: $\delta =$ 21.6 ppm, $\Delta\nu_{1/2} = 160$ Hz), which was identified by comparison with an authentic sample.[15] Above 273 K, the amount of **4** and HOBpin increased further at the cost of **3**, but on a slower time scale. This finding suggests that another reaction pathway is operative, in which **3** acts as the starting compound for the generation of **4** (pathway c). We were also able to prepare complex **3** by an alternative method. Treatment of **1** with HBpin in the presence of free phosphine at approximately 203 K afforded the rhodium borate **3** and phosphine oxide (pathway d). No formation of intermediate **2** was observed in this case, but the generation of **4** from **3** could be confirmed.

A signal at $\delta = -8.72$ ppm in the ^{1}H NMR spectrum of **2** proves the presence of the hydrido ligand.[16] Fluorine decoupling the spectrum resulted in the resonance resolving into a quartet with identical rhodium and phosphorus coupling constants of 11.5 Hz. The rhodium–phosphorus coupling constant of 92 Hz for the signal at $\delta = 30.4$ ppm in the ^{31}P NMR spectrum reveals the presence of a rhodium(III) complex.[13,16] An absorption band at 1934 cm^{-1} in the low-temperature Raman spectrum recorded in THF is also indicative of a rhodium hydride. Features at 1067, 802, and 610 cm^{-1} can tentatively be assigned to the peroxo moiety. These features shift by 10–20 cm^{-1} in the case of the ^{18}O-labeled isotopomer *trans*-[RhH($^{18}O^{18}O$Bpin)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**2a**). It is noteworthy that absorption bands at 901/884 cm^{-1} and 852/805 cm^{-1} have been found for the two corresponding $^{16}O_2/^{18}O_2$ isotopologues of the peroxo complexes *trans*-[RhCl(η^1-OOSiMe_3)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] and *trans*-[Rh(η^2-O_2)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$].[11a] A band at 840 cm^{-1} has been assigned to the O–O unit in (nPrO)$_2$BOOB(OnPr)$_2$.[17] We were not able to detect any resonance in the ^{11}B NMR spectrum of **2**. Therefore, we can not entirely exclude any additional interaction of the boron atom with the oxygen atom in the α position to the metal center.

The Raman spectra of **3** and of the isotopologue *trans*-[RhH(^{18}OBpin)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] (**3a**) resemble the spectra of **2** and **2a** except for the absorption band for the metal hydride, which now appears at 1967 cm^{-1}. Furthermore, there is no band corresponding to a peroxo unit upon ^{18}O substitution.[16] A band at 632 cm^{-1} (612 cm^{-1} for **3a**) may possibly be assigned to a RhO vibration.[11b] The ^{1}H NMR spectrum of **3** shows a signal at $\delta = -8.62$ ppm for the hydrido ligand. A broad signal at $\delta = 22.8$ ppm ($\Delta\nu_{1/2} \approx 1200$ Hz) in the ^{11}B NMR spectrum of **3** is indicative of the borato ligand.[18–20] For comparison, the rhodium boronate [Rh{OB(OH)(Ph)}(PEt_3)$_3$] exhibits a signal at $\delta = 25.6$ ppm, whereas the resonance for [Cp_2Zr(OBpin)$_2$] (Cp = C_5H_5) appears at $\delta =$ 19.2 ppm.[18,20] The X-ray structure of **3** supports the suggested structure, although the refinement suffers from disorder of two of the ethyl groups and of the pinacole unit. The configuration around the rhodium center is such that the borate moiety is in the *trans* position relative to the isonitrile ligand (Figure 2).[21]

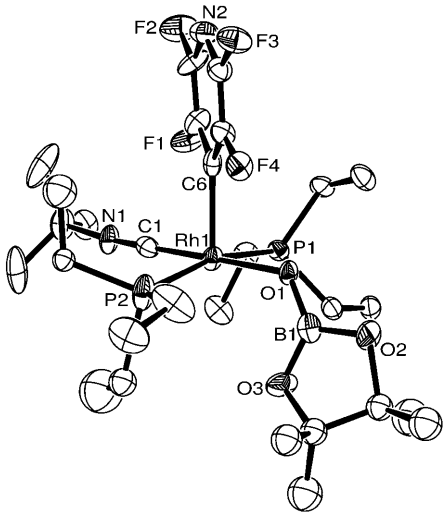
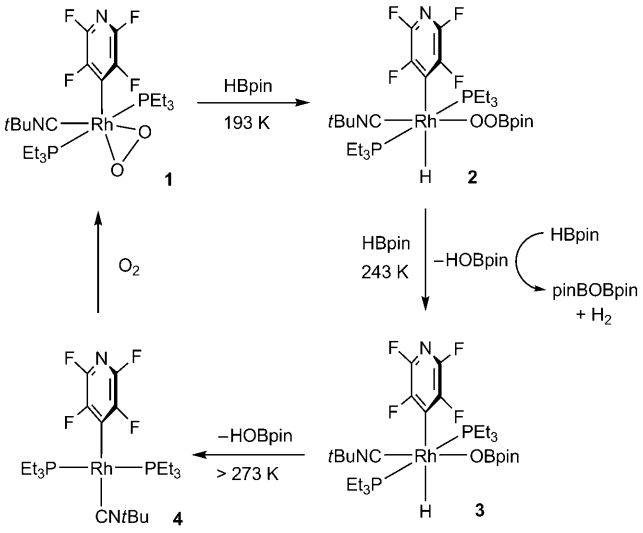


Figure 2. Molecular structure of **3** in the crystal (ORTEP diagram, thermal ellipsoids are set at the 50% probability level).

We presume that the formation of **2** is initiated by an interaction of the Lewis acidic HBpin with one of the oxygen atoms in the peroxo ligand in **1**. In a subsequent step, the hydrogen atom shifts from the four-coordinated boron to the rhodium center, thereby leading to **2**. A comparable reaction sequence has been proposed for the reaction of palladium–peroxo complexes with aryl boronic acids to yield, through cleavage of the carbon–boron bond, palladium perborates, which could not be identified.[4,5] It is generally known that the oxygen atoms of η^2-bound peroxo ligands at electron-rich transition metals often exhibit nucleophilic properties and can interact with Lewis acids.[3,11,22,23]

To get further insight into the reactivity of **2** we treated a solution of the peroxo complex **1** in [D_8]toluene with an excess (three equivalents) of HBpin at 193 K. This reaction also afforded the rhodium(III) compound **2** (Scheme 2). However, as HBpin is still present in this case, **2** reacts at 243 K with two more equivalents HBpin to yield the rhodium borate **3** and pinBOBpin. The resonance for **3** in the ^{11}B NMR spectrum is obscured by a signal at $\delta = 21.8$ ppm ($\Delta\nu_{1/2} \approx 400$ Hz), which can be assigned to the pinBOBpin species.[20] We assume that the original product of the reaction is HOBpin, produced by oxygenation of HBpin at **2**. It has



Scheme 2. Oxygenation of HBpin coordinated at a rhodium center.

previously been suggested that HBpin can react with HOBpin to yield pinBOBpin and H_2.[20] Indeed, we did observe the generation of H_2 in the ^{1}H NMR spectrum. The H_2 does not react with **1** or **4**. Complex **3** is not stable above 273 K and reacts slowly in [D_8]toluene to give **4** and once more HOBpin, which has been detected by ^{11}B NMR spectroscopy. The reaction sequence is illustrated by the ^{31}P{^{1}H} NMR spectra shown in Figure 3. Complex **4** is the starting compound for the rhodium(III)–peroxo species **1**. This completes a cyclic process for the oxygenation of HBpin with O_2.

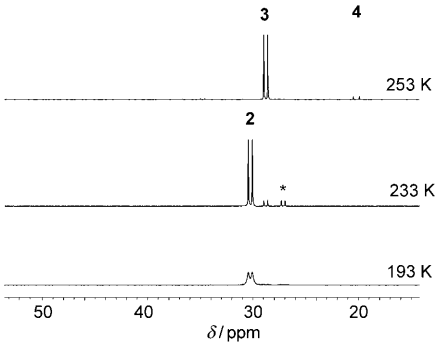


Figure 3. ^{31}P{^{1}H} NMR spectra of the reaction of **1** with an excess of HBpin at different temperatures; * depicts an unknown compound.

It is intriguing that no oxygenation of a metal-bound phosphine or at the tetrafluoropyridyl ligand occurs in the presence of an excess of HBpin.[1,11,22,24,25] Both oxygen atoms of the peroxo unit in **1** can be employed for the oxygenation of Hbpin, which proceeds via the borylperoxo species **2**. Note that CO_2 has recently been applied for the oxygenation of B_2pin_2 to give CO and pinBOBpin by a copper-mediated process.[19] The reductive elimination of HOBpin or HOOBpin (Schemes 1 and 2) seems to be unique, but conceivable. O–H reductive elimination reactions of alkoxo ligands have been described, for example, by Milstein et al., as well as other research groups.[26] The generation of 2,3,5,6-tetrafluoropyridine was not observed, possibly because the hydride and pyridyl ligands are situated in a mutual *trans* arrangement.[16] The stabilizing properties of a fluorinated pyridyl ligand might also be a crucial factor in that context.[11,13,27]

The rhodium borate **3** and, even more so, the perborate **2** are unique, and the structural motif {MOOB} involving a three-valent boron center (M = metal) has only rarely been identified in transition-metal coordination chemistry. The only example consists of metallacycles such as *trans*-[Rh{κ^2-OOB(OH)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] or *trans*-[Rh{κ^2-OOB(C_6F_5)*O*}(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$].[11b] There are also only a very limited number of transition-metal derivatives of boric acid.[19,20,28]

In conclusion, the rhodium(III)–peroxo complex **1** reacts with the Lewis acidic boron compound HBpin by oxygen transfer from the rhodium center to HBpin to give a rhodium(I) species. The detection of intermediate rhodium perborates and borates has given some mechanistic insight. The model reactions are of importance in catalytic applications and they deepen the understanding of oxygenation and oxidation reactions on a molecular level. Complex **2** resembles a key intermediate in the homocoupling of aryl boronic acids in the presence of oxygen.[4,5] Peroxo compounds might also play a crucial role in catalyst decomposition reactions in the presence of oxygen. Mechanistic studies on a controlled deoxygenation process of peroxo species with a concomitant reduction of the metal center are, therefore, of considerable interest for catalytic applications to regain a catalytically active species.[9a,29] Rhodium and iridium boronates are known to play a crucial role in the borylation of arenes to give, for example, Bpin derivatives.[8,9] Rhodium complexes can be applied in rhodium-mediated hydroboration or dehydrogenative boration reactions of olefins or even in the borylation of alkanes.[9,10]

Experimental Section

Treatment of **1** with substoichiometric amounts of HBpin: HBpin (5 μL, 0.03 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) in [D_8]toluene (0.6 mL) in an NMR tube at 193 K. The NMR spectroscopic data revealed the formation of **2**. Above 243 K the generation of **3**, **4**, $OPEt_3$, and HOBpin was evident. Storing the solution at 253 K led to the precipitation of light-yellow crystals of **3**. Warming the solution up to 273 K led to the generation of **4** and HOBpin.

In a comparable experiment, HBpin (5 μL, 0.03 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) and PEt_3 (10 μL, 0.1 mmol) in [D_8]toluene (0.6 mL) at 203 K. The NMR data revealed the formation of **3** and $OPEt_3$ only.

Treatment of **1** with an excess of HBpin: HBpin (30 μL, 0.18 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) in [D_8]toluene (0.6 mL) in an NMR tube at 193 K. The NMR spectroscopic data revealed the formation of **2**. Above 243 K the generation of **3**, $O(Bpin)_2$, and H_2 was evident. Warming the solution to 273 K led to the formation of **4** and HOBpin.

Analytical data for **2**: ^{1}H NMR (600 MHz, [D_8]toluene, 193 K): ^{1}H{^{31}P} NMR (600 MHz, [D_8]toluene, 193 K): $\delta = 1.87$ (m, 6H, PCH_aH_b), 1.74 (m, 6H, PCH_aH_b), 1.21 (s, 12H, CH_3, Bpin), 0.85 (t, $^3J(H,H) = 7.3$ Hz, 18H, PCH_2CH_3,), 0.76 (s, 9H, $NC(CH_3)_3$), −8.72 ppm (m (q in the ^{1}H{^{19}F} NMR spectrum), $^2J(H,Rh) = {}^2J(H,P) = 11.5$ Hz, 1H, RhH); ^{19}F NMR (564.7 MHz, [D_8]toluene,

193 K): $\delta = -99.3$ (m, 1F), −99.9 (m, 1F), −112.0 (m, 1F), −115.3 ppm (m, 1F); $^{31}P\{^{1}H\}$ NMR (242.9 MHz, [D$_8$]toluene, 193 K): $\delta = 30.4$ ppm (d, ^{1}J(P,Rh) = 92 Hz); Raman (THF, 223 K): $\tilde{\nu} = 2175$ (C≡N), 1934 cm^{-1} (Rh-H).

Analytical data for **3**: Elemental analysis calcd (%) for $C_{28}H_{52}BF_4N_2P_2O_2Rh$: C 47.98, H 7.48, N 4.00; found: C 47.68, H 7.36, N 3.72; $^{1}H\{^{31}P\}$ NMR (600 MHz, [D$_8$]toluene, 253 K): $\delta = 1.84$ (m, 6H, PCH_aH$_b$), 1.64 (m, 6H, PCH$_a$$H_b$), 1.19 (s, 12H, CH$_3$, Bpin), 0.80 (t, 18H, ^{3}J(H,H) = 8.1 Hz, PCH$_3$CH_3), 0.87 (s, 9H, NC(CH$_3$)$_3$), −8.62 ppm (m (q in the $^{1}H\{^{19}F\}$ NMR spectrum), ^{2}J(H,Rh) = ^{2}J(H,P) = 11.5 Hz, 1H, RhH); $^{11}B\{^{1}H\}$ NMR (192.6 MHz, [D$_8$]toluene, 253 K): $\delta = 22.8$ ppm (br s, $\Delta\nu_{1/2} \approx 1200$ Hz); ^{19}F NMR (564.7 MHz, [D$_8$]toluene, 253 K): $\delta = -97.4$ (m, 1F), −98.5 (m, 1F), −110.7 (m, 1F), −116.5 ppm (m, 1F); $^{31}P\{^{1}H\}$ NMR (242.9 MHz, [D$_8$]toluene, 253 K): $\delta = 28.5$ ppm (br d, ^{1}J(P,Rh) = 89 Hz); Raman (THF, 223 K) $\tilde{\nu} = 2181$ (C≡N), 1967 cm^{-1} (Rh-H).

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