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## Reactivity of rhodium and iridium peroxido complexes towards hydrogen in the presence of $B(C_6F_5)_3$ or $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]^{\dagger}$

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The peroxido complexes trans- $[M(4-C_5F_4N)(O_2)(CNtBu)(PR_3)_2]$  (**1**: M = Rh, R = Et; **2a**: M = Ir, R = iPr) can be used in the metal-mediated hydrogenation of  $O_2$ . The reaction of trans-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)  $(PEt_3)_2$  (1) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and H<sub>2</sub> gave trans-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(CNtBu)(PEt\_3)<sub>2</sub>] (3), OPEt\_3 and (H<sub>2</sub>O)·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, whereas treatment of  $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$  with **1** in the presence of H<sub>2</sub> yielded trans- $[Rh(4-C_5F_4N)(CNtBu)(PEt_3)_2]$  (3) and  $H_2O_2$ . The reactivity of 2a towards  $B(C_6F_5)_3$  and  $BClCy_2$  was also studied and an intermediate was detected which is assigned to be  $trans-[Ir(4-C_5F_4N)(CI)(OOBCy_2)(CNtBu)$ (PiPr<sub>3</sub>)<sub>2</sub>] (4a).

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### Introduction

The transition metal-mediated hydrogenation of dioxygen is an interesting subject in oxygenation chemistry.<sup>1</sup> The two feasible products are water and hydrogen peroxide. The reduction of dioxygen to H2O is an important process, for instance in fuel cells.<sup>1</sup> H<sub>2</sub>O<sub>2</sub> is an economically crucial industrial product for the manufacture of a wide range of everyday items.<sup>2</sup> The development of a transition metal-mediated selective process, as an alternative to the energy intensive anthraquinone process to access water or hydrogen peroxide from dihydrogen and dioxygen, can be considered a fundamental challenge.

Late transition metal complexes have been reported to reduce molecular oxygen to water, but only a couple of conversions proceed with dihydrogen as reductant.<sup>3-6</sup> The reaction of the amido amine hydrido complex  $[Ir(Cp^*)(H)]{\kappa^2-(N,N)-rac-$ NTsCHPhCHPhNH<sub>2</sub>] (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; Ts = SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) with dioxygen led to the formation of water and the bisamido complex  $[Ir(Cp^*)]{\kappa^2-(N,N)-rac-NTsCHPhCHPhNH}].^{4a,b}$  In the presence of dihydrogen and catalytic amounts of the Brønsted acidic borane additive  $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$ , the bisamido complex is converted back to the amido amine hydrido complex to close a putative cycle. A comparable reaction sequence can be found for the reaction of the bisamido

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bridged binuclear rhodium complex [Rh(Cp\*)(µ-NHTs)]<sub>2</sub>.<sup>5</sup> Mechanistic steps might include dioxygen activation, followed by protonation to form hydroperoxido complexes.<sup>3–5,7</sup> However, the water formation step and the fate of the second oxygen atom of the O<sub>2</sub> molecule is unknown. Moreover the iridium(III) pincer peroxido complex  $[Ir{C_6H_3(CH_2PtBu_2)_2}(O_2)]$ reacts with H<sub>2</sub> to yield H<sub>2</sub>O and  $[Ir{C_6H_3(CH_2PtBu_2)_2}(H)_4]$ .

A variety of catalytic investigations have been carried out to access H<sub>2</sub>O<sub>2</sub> from dioxygen and appropriate reducing agents. For example, alcohols can be oxidized with  $O_2$  using transition metal complexes,<sup>8</sup> mainly palladium and copper,<sup>9</sup> while  $H_2O_2$ is produced as an additional product. Palladium-catalyzed transformations of mixtures of CO, O2, and H2O provide CO2 and  $H_2O_2$  in the presence of an excess of a Brønsted acid.<sup>10</sup> At rhodium, we found in model reactions that the peroxido complex trans-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (1) reacts with dihydrogen sources to yield hydrogen peroxide and trans- $[Rh(4-C_5F_4N)(CNtBu)(PEt_3)_2]$  (3).<sup>11</sup> The metal-bound dioxygen can be reduced in a catalytic experiment where H2O2 was generated at ambient temperature and atmospheric pressure from dioxygen and ammonium formate.<sup>11</sup> A key step in such transformations is the protonation of a peroxido entity to form hydroperoxido complexes like trans-[Rh(4-C5F4N){OC(O)H}- $(OOH)(CNtBu)(PEt_3)_2]^{11}$  which subsequently react further to give H<sub>2</sub>O<sub>2</sub>. Similarly, the iridium peroxido complex trans- $[Ir(4-C_5F_4N)(O_2)(CNtBu)(PiPr_3)_2]$  (2a) releases hydrogen peroxide when reacted with various Brønsted acids like HCl, CF<sub>3</sub>COOH or HF.<sup>12</sup> Note also that *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)- $(CNtBu)(PEt_3)_2$  (1) reacts with HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane) to yield trans- $[Rh(H)(OBpin)(4-C_5F_4N)(CNtBu)(PEt_3)_2]$  and trans- $[Rh(4-C_5F_4N)-$ 





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 $(CNtBu)(PEt_3)_2$  (3) with presumably *trans*-[Rh(H)(OOBpin)-(4-C<sub>5</sub>F<sub>4</sub>N)(CNtBu)(PEt\_3)\_2] as an intermediate.<sup>13</sup>

In this paper, we describe that the dioxygen moiety of the peroxido complexes *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CN*t*Bu)(PEt<sub>3</sub>)<sub>2</sub>] (1) and *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CN*t*Bu)(PiPr<sub>3</sub>)<sub>2</sub>] (2a),<sup>12,14</sup> which are generated from O<sub>2</sub> and are inert towards dihydrogen, can be activated by boranes. The peroxido complexes can be hydrogenated with H<sub>2</sub> in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. In contrast, *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CN*t*Bu)(PEt<sub>3</sub>)<sub>2</sub>] (1) forms hydrogen peroxide with dihdyrogen in presence of the Brønsted acid [H(OEt<sub>2</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}].<sup>15</sup>

#### **Results and discussion**

The reaction of *trans*- $[Rh(4-C_5F_4N)(O_2)(CNtBu)(PEt_3)_2]$  (1) with the borane  $B(C_6F_5)_3$  and dihydrogen afforded the rhodium(1) complex trans- $[Rh(4-C_5F_4N)(CNtBu)(PEt_3)_2]$  (3), OPEt<sub>3</sub> and the water adduct  $(H_2O) \cdot B(C_6F_5)_3$ . There is no indication for the formation of  $H_2O_2$ . In addition to the signal for 3, the  ${}^{31}P{}^{1}H{}$ NMR spectrum of the reaction mixture shows a doublet signal for a minor compound (ratio 7 : 1) at  $\delta$  = 20.2 ppm with a coupling constant of  ${}^{1}/(Rh,P) = 134.0$  Hz. We were not able to isolate or identify the unknown rhodium(1) complex. However, the formation of this compound can be suppressed in the presence of one equivalent of triethylphosphine (Scheme 1). The latter forms an adduct with the Lewis acidic borane (see ESI<sup>†</sup>).<sup>16</sup> After 2d the conversion of **1** was about 80% and the ratio of 3 to phosphine oxide to  $(H_2O) \cdot B(C_6F_5)_3$  was 3.4:6.7:1. The water adduct  $(H_2O) \cdot B(C_6F_5)_3$  was identified by a comparison of the <sup>1</sup>H and <sup>19</sup>F NMR data with an authentic sample and shows a broad signal for  $(H_2O) \cdot B(C_6F_5)_3$  at  $\delta = 4.66$  ppm in the <sup>1</sup>H NMR spectrum.<sup>17</sup> This signal cannot be detected when D<sub>2</sub> is used as the reducing agent.

It seems to be plausible, that a pre-coordination of the borane at the peroxido entity of **1** may lead to a weakening or even a cleavage of a rhodium oxygen bond to generate a vacant coordination site (Scheme 2).<sup>18,19</sup> In the presence of dihydrogen this might result in the formation of a non-classical dihydrogen complex.<sup>20</sup> Then several reactions pathways are conceivable to generate ( $H_2O$ )·B( $C_6F_5$ )<sub>3</sub> and phosphine oxide. The



Scheme 1 Reduction of 1 with dihydrogen in the presence of  $B(C_6F_5)_3$  or  $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$ .



Scheme 2 Possible mechanism for the reaction of complex 1 with  ${\sf H}_2$  and  ${\sf B}({\sf C}_6{\sf F}_5)_3.$ 

transfer of an oxygen atom of a putative RhOOB-moiety to PEt<sub>3</sub> may lead to the formation of OPEt<sub>3</sub> and the borato complex trans- $[Rh(4-C_5F_4N){OB(C_6F_5)_3}(H_2)(CNtBu)(PEt_3)_2]$ . It is known that complexes containing a RhOOR group can oxygenate phosphines.<sup>11,21</sup> As mentioned above, the intramolecular oxygenation of the phosphine ligand in the perborate complex trans-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(H){OOBpin}(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] at low temperature has been described.<sup>13</sup> A stepwise transfer of hydrogen atoms<sup>22</sup> to the {Rh-OB( $C_6F_5$ )<sub>3</sub>} entity may then lead to *trans*- $[Rh(4-C_5F_4N)(H){HOB(C_6F_5)_3}(CNtBu)(PEt_3)_2]$  and subsequently to 3 and the water adduct  $(H_2O) \cdot B(C_6F_5)_3$ . Alternatively, the reaction could proceed via the formation of an ion pair trans- $[Rh(4-C_5F_4N)(OOH)(CNtBu)(PEt_3)_2][HB(C_6F_5)_3]$  in a first step. The heterolytic cleavage of H<sub>2</sub> using frustrated Lewis pairs is well established.<sup>23</sup> However, the NMR and IR data of the reaction of 1 with the borane  $B(C_6F_5)_3$  and dihydrogen did not show any evidence for the presence of the borate  $[HB(C_6F_5)_3]^{-24}$  In addition, treatment of the peroxido complex 1 with  $[2,6-(CH_3)_2C_5H_3NH][HB(C_6F_5)_3]^{23a}$  led to the formation of an unstable compound which decomposed to OPEt<sub>3</sub> and 2,3,5,6-tetrafluoropyridine. A rhodium species could not be identified. Therefore, we consider a mechanism involving  $[HB(C_6F_5)_3]^-$  to be unlikely.

The reaction of the iridium peroxido complex trans- $[Ir(4-C_5F_4N)(O_2)(CNtBu)(PiPr_3)_2]$  (2a) with the borane  $B(C_6F_5)_3$ in a dihydrogen atmosphere also afforded the water adduct  $(H_2O)$ ·B $(C_6F_5)_3$ , similar to the analogous reaction at rhodium. However, at iridium, no distinct metal species could be isolated, even in the presence of additional phosphine, but the NMR studies support the assumption of a pre-coordination of the Lewis acid at the peroxido ligand. Addition of  $B(C_6F_5)_3$  to a solution of 2a in argon atmosphere resulted initially in a broad signal for a new species in the  ${}^{31}P{}^{1}H$  NMR spectrum at  $\delta$  = 83 ppm. This might indicate the formation of a Lewis acidbase adduct between the nucleophilic oxygen moiety of the iridium complex<sup>12</sup> and the acidic borane. When the reaction solution was cooled down to -50 °C and a base (pyridine or lutidine) was added, the starting compound 2a was isolated again after work-up.

The chlorinated and less Lewis acidic borane BClCy<sub>2</sub> was chosen to get more information on the reactivity of Lewis acidic boranes towards the oxygen moiety of the peroxido complex 2a. The reaction of the iridium complex trans- $[Ir(4-C_5F_4N)(O_2)(CNtBu)(PiPr_3)_2]$  (2a) with BClCy<sub>2</sub> afforded the literature known dichlorido complex trans-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)-(Cl)<sub>2</sub>(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (5) as the main product as well as Cy<sub>2</sub>BOBCy<sub>2</sub> and (CyBO)<sub>3</sub> as oxygenated boron species.<sup>12a</sup> The identification of the latter was done by <sup>11</sup>B NMR spectroscopy and GC-MS measurements. If the reaction is carried out in presence of PiPr<sub>3</sub>, an intermediate 4a was detected in the reaction mixture. We assign it to be trans- $[Ir(4-C_5F_4N)(Cl)(OOBCy_2)(CNtBu) (PiPr_3)_2$ ]. However, we cannot exclude *trans*- $[Ir(4-C_5F_4N)]OO\cdots B$  $(Cl)(Cy_2)$  (CNtBu)(PiPr<sub>3</sub>)<sub>2</sub> as a possible alternative entirely. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture displays a singlet at  $\delta = -5.9$  ppm for the iridium species 4a as well as the signal for 5. The <sup>19</sup>F NMR spectrum for 4a shows four multiplets of equal intensity at  $\delta = -99.3$ , -100.1, -112.8 and -122.0 ppm for the inequivalent fluorine atoms of the tetrafluoropyridyl ligand. A low temperature NMR study of the reaction mixture shows two broad resonances in the <sup>11</sup>B NMR spectrum at  $\delta$  = 4 and 0 ppm. Possibly, one resonance results from the boron atom of 4a and the other from Cy<sub>2</sub>BOOBCy<sub>2</sub>. The peroxoborane Cy2BOOBCy2 could not be detected at room temperature anymore. It is presumably not stable and undergoes decomposition. Stable neutral peroxoboranes are rather unusual and a subporphyrinato derivative was described.<sup>25</sup> For the molybdenum complex  $[Mo(O)(O_2)]{B(C_6F_5)_3}{\eta^2-PhN(O)C(O) Ph_{2}$ , the authors propose the coordination of the Lewis acid at the peroxido moiety and observe a resonance in the <sup>11</sup>B NMR spectrum at  $\delta = 4$  ppm.<sup>26</sup> The IR spectrum of the reaction mixture provided evidence for iridium in the oxidation state +III for 4a and exhibits a strong absorption band at  $\tilde{\nu}$  = 2160 cm<sup>-1</sup> for the stretching vibration of the CNtBu ligand.<sup>27</sup> In addition, an absorption band at  $\tilde{\nu} = 821 \text{ cm}^{-1}$  was detected. This area is characteristic for O-O stretching vibrations of peroxido compounds.<sup>14,21,25a,28</sup> For the reaction of the isotopologue trans- $[Ir(4-C_5F_4N)(^{18}O_2)(CNtBu)(PiPr_3)_2]$  (2b) with BClCy<sub>2</sub>, this absorption band shifts to  $\tilde{\nu} = 787 \text{ cm}^{-1}$  for the proposed trans-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(Cl)(<sup>18</sup>O<sup>18</sup>OBCy<sub>2</sub>)(CNtBu)intermediate  $(PiPr_3)_2$  (4b). The HR-FT-ESI mass spectra gave m/z = 991.405and m/z = 995.400 for the ions  $[M + H]^+$  of the isotopologues.

Note that only very few metallaperoxoborane species were structurally characterized.<sup>13,25,29</sup> A conceivable intermediate, *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(Cl)(OOBCy<sub>2</sub>)(CN*t*Bu)(PiPr<sub>3</sub>)<sub>2</sub>] (**4a**) supports the suggested mechanism, which involves an activation of the peroxido complexes **1** and **2a** at the oxygen moiety by  $B(C_6F_5)_3$ .<sup>18,26</sup> With  $BClCy_2$  the metal-oxygen bond is cleaved and the chloride anion binds at the resulting free coordination site to give **4a** (Scheme 3). The reaction with another equivalent of  $BClCy_2$  would then afford the dichlorido complex *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(Cl)<sub>2</sub>(CN*t*Bu)(PiPr<sub>3</sub>)<sub>2</sub>] (**5**) and the peroxoborane  $Cy_2BOOBCy_2$  as observed (Scheme 3).

For the protonation reaction of the peroxido units of 1 or 2a with HCl or HCOOH at low temperature, the formation of hydroperoxido complexes like *trans*- $[M(4-C_5F_4N)(X)(OOH)-$ 



Scheme 3 Proposed mechanism for the reaction of 2a with BClCy<sub>2</sub>.

 $(CNtBu)(PR_3)_2$  (X = Cl, {OC(O)H}; M = Rh, R = Et; M = Ir, R = iPr) is discussed.<sup>11,12a,14a</sup> In all cases, the corresponding anion of the Brønsted acid is bound to the metal center. Therefore, the utilization of a weakly coordinating anion may open up a pathway for further reactions. Indeed, treatment of the Brønsted acid  $[H(OEt_2)_2][B{3,5-(CF_3)_2C_6H_3}_4]^{15}$  with 1 in the presence of dihydrogen yielded the rhodium(1) complex trans- $[Rh(4-C_5F_4N)(CNtBu)(PEt_3)_2]$  (3) and  $H_2O_2$ . The latter was identified by a positive peroxide test (see ESI<sup>†</sup>). A broad signal at  $\delta$  = 2.89 ppm in the <sup>1</sup>H NMR spectrum of the reaction mixture is also attributed to H<sub>2</sub>O<sub>2</sub>. This signal cannot be detected when D<sub>2</sub> is used as the reducing agent. When equimolar amounts of  $[H(OEt_2)_2][B{3,5-(CF_3)_2C_6H_3}_4]$  were used, after two days the reaction mixture showed signals in the NMR spectrum for 3 and trans-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][B{3,5- $(CF_3)_2C_6H_3_4$  in a ratio of 3:2, along with some OPEt<sub>3</sub> and 2,3,5,6-tetrafluoropyridine. The generation of the latter is due to a competing protonation of the Rh-C bond in 3. This was confirmed in an independent experiment by protonation of 3 with  $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$ . However, the formation of the ionic rhodium compound was diminished when catalytic amounts of  $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$  were applied (Scheme 1). NMR spectroscopic analyses of the reaction mixture revealed small amounts of OPEt<sub>3</sub> and 2,3,5,6-tetrafluoropyridine (approx. 10%), the rhodium(1) complex 3 and trans- $[Rh(CNtBu)_2(PEt_3)_2][B{3,5-(CF_3)_2C_6H_3}_4]$  with a ratio of the latter complexes of 8:1. In case of the iridium complex trans- $[Ir(4-C_5F_4N)(O_2)(CNtBu)(PiPr_3)_2]$  (2a), no defined reaction with  $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$  was observed. Instead, decomposition occurred and no iridium species could be identified.

#### Conclusions

In conclusion we have demonstrated that the peroxido ligand in the rhodium complex *trans*- $[Rh(4-C_5F_4N)(O_2)(CNtBu)-(PEt_3)_2]$  (1) can be reduced using dihydrogen. In the presence of the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> the water adduct (H<sub>2</sub>O)·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was generated. With catalytic amounts of the Brønsted acid [H(OEt\_2)\_2][B{3,5-(CF\_3)\_2C\_6H\_3}\_4] hydrogen peroxide is produced in case of the rhodium complex **1**. The Rh(1) product *trans*-[Rh (4-C<sub>5</sub>F<sub>4</sub>N)(CN*t*Bu)(PEt<sub>3</sub>)<sub>2</sub>] (3) can again be converted into the peroxido derivative **1** with  $O_2$ .<sup>14*a*</sup> The latter reaction is very slow which hampers the development of a catalytic process. To the best of our knowledge, **3** is the only transition metal complex that produces water or hydrogen peroxide from  $O_2$  and  $H_2$  using the same complex by varying the acid which is required as additive. Other systems use Brønsted acids instead of  $H_2$  and often require an additional reducing agent like decamethylferrocene.<sup>3d,30</sup>

#### Conflicts of interest

There are no conflicts to declare.

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