

## Dioxygen Activation at $[\text{OsCl}(\text{dcpe})_2]^+$ Gives $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$ , the First Stable Oxo Complex of Osmium(IV)

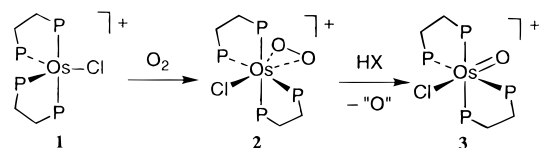
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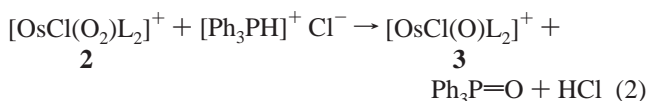
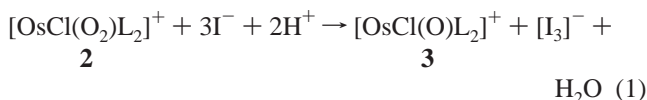
Dioxygen activation is one of the major issues in biochemistry<sup>1</sup> and in homogeneous catalysis.<sup>2</sup> Metal oxo complexes are involved in  $\text{O}_2$  activation and oxene transfer reactions<sup>3</sup> such as olefin epoxidation<sup>4</sup> and alkane hydroxylation.<sup>5</sup> In the iron triad, the formation of oxo complexes from  $\text{O}_2$  is common for the biomimetic systems based on the ferryl moiety,<sup>1</sup> but is scarcely documented for ruthenium and osmium.<sup>4a,6</sup> Oxo species of the latter metals are typically prepared by oxidation of aqua complexes<sup>7</sup> or using a terminal oxidant.<sup>3h,i,8</sup> The 16 electron complex  $[\text{OsCl}(\text{dcpe})_2]^+$  (**1**) is known to react with  $\text{O}_2$  to give *trans*- $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  (**2**) (dcpe = 1,2-bis(dicyclohexylphosphino)-

### Scheme 1



ethane).<sup>9</sup> We find now that the latter forms the paramagnetic  $d^4$  oxo complex *trans*- $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  (**3**) in the presence of anhydrous HCl and a reductant ( $\text{I}^-$  or  $\text{PPh}_3$ ) (Scheme 1). Although Os(IV) oxo species have been observed in solution,<sup>7a-c,g,h</sup> to the best of our knowledge  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  is the first mononuclear Os(IV) oxo complex to be isolated and fully characterized.

Addition of anhydrous HCl to  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  (**2**) and  $[\text{NBu}_4]\text{I}$  in  $\text{CH}_2\text{Cl}_2$  gives quantitatively  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  (**3**) and  $[\text{I}_3]^-$  within mixing time (eq 1), as determined by UV/visible spectroscopy. No reaction occurs without acid. The reaction of  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  (**2**) with  $[\text{Ph}_3\text{PH}]\text{Cl}$  (1:1) gives  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  (**3**) and  $\text{Ph}_3\text{P}=\text{O}$  (ca. 100% yield by  $^{31}\text{P}$  NMR) within 10 min (eq 2). The coordinated diphosphines are not oxidized.



The  $(d_{xy})^2(d_{xz})^1(d_{yz})^1$  configuration of  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  (**3**)<sup>10</sup> is supported by the  $\mu_{\text{eff}}$  of 3.05  $\mu_{\text{B}}$  at 300 K, near to the spin-only value for two unpaired electrons,<sup>7e,8a,b</sup> and by the small isotropic shifts of the  $^1\text{H}$  NMR signals.<sup>11</sup> The X-ray structure shows a distorted octahedral coordination (Figure 1). The Os–O distance of 1.834(3) Å is similar as in  $\text{Os}^{\text{IV}}\text{–O–Os}^{\text{IV}}$   $\mu^2$ -oxo-bridged species (1.78–1.83 Å),<sup>12</sup> but longer than in Os(VI) oxo complexes (ca. 1.72 Å),<sup>3a,6a,13</sup> due to the two  $\pi^*$  electrons in the  $(d_{xy})^2(d_{xz})^1(d_{yz})^1$  configuration.<sup>3a,7e,8b</sup>

Acid-promoted oxygen transfer has been proposed for other peroxo complexes.<sup>2d,e,14</sup> Contrary to what is observed for  $\text{M}(\eta^2\text{-O}_2)$  complexes ( $\text{M} = \text{Pt}, \text{Rh}$ ),<sup>15</sup> reactions 1 and 2 do not involve acid hydrolysis of  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  (**2**), since the use of aqueous HCl gives yet unidentified products instead of  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$ . Extraction of freshly prepared  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  with aqueous titanil sulfate does not reveal the presence of  $\text{H}_2\text{O}_2$ , and  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  does not reform

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(10)  $[\text{OsCl}(\text{O})(\text{dcpe})_2]\text{BPh}_4$ : MS-FAB<sup>+</sup>  $m/z$  1087 ( $\text{M}^+$ , 100).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  30 (vbr s, 4 H), 14.44 (br s, 4 H), 13.92 (br s, 4 H), 12.63 (br s, 8 H), 11.60 (br s, 4 H), 9.64 (br s, 4 H), 8.89 (d, 4 H,  $J(\text{H},\text{H}') = 9.4$  Hz), 8.27 (br s, 4 H), 7.39 (s, 8 H, PhH), 7.09 (t, 8 H, PhH,  $J(\text{H},\text{H}') = 7.4$  Hz), 6.93 (t, 4 H, PhH,  $J(\text{H},\text{H}') = 7.1$  Hz), 7.13 (br s, 4 H), 6.17 (s, 4 H), 4.02 (m), 3.24 (s), 2.1–1.22 (m), 0.94 (br s);  $-0.3$  to  $-1$  (m),  $-3$  (br s) ppm. X-ray: monoclinic,  $P2_1/c$ , brown,  $0.50 \times 0.20 \times 0.08$  mm,  $a = 23.605(4)$  Å,  $b = 12.824(2)$  Å,  $c = 25.648(4)$  Å,  $\beta = 104.0410(5)^\circ$ ,  $Z = 4$ ,  $R = 0.0462$  (on  $F_o$ ,  $I > 2\sigma(I)$ ), GOF = 0.979.

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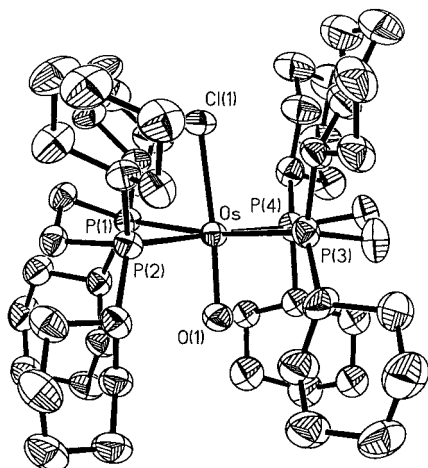
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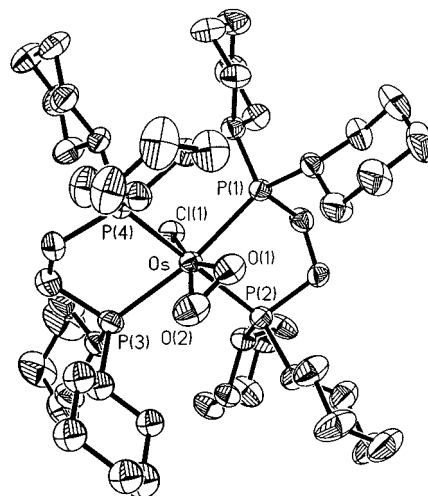
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**Figure 1.** ORTEP view of  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  (**3**) (50% probability ellipsoids). Selected interatomic distances (Å) and angles (deg): Os–O(1) 1.834(3), Os–Cl(1) 2.442(1), Os–P(1) 2.464(1), Os–P(2) 2.474(1), Os–P(3) 2.455(1), Os–P(4) 2.454(1); O(1)–Os–Cl(1) 175.1(1).

$[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  upon treatment with  $\text{H}_2\text{O}_2$ . Even without reductant,  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  forms  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  in the presence of anhydrous HCl in  $\text{CH}_2\text{Cl}_2$  in quantitative yield within 10 min.<sup>16</sup> Dissociation of  $\text{O}_2$  from  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  (**2**) followed by formation of a peroxo-bridged intermediate<sup>1f,5d</sup> is disfavored, since  $[\text{OsCl}(\text{dcpe})_2]^+$  does not react with the dioxygen complex **2** (1:1 ratio, in  $\text{CD}_2\text{Cl}_2$  over molecular sieves, NMR tube sealed in a vacuum,  $\text{OP}(\text{OMe})_3$  as internal standard).

Seeking a rationale for its reactivity, and in view of the few  $\text{Os}(\eta^2\text{-O}_2)$  complexes known,<sup>9a,17</sup> we determined the X-ray structure of  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]\text{BPh}_4$  (**2**) (Figure 2).<sup>18</sup> Despite



**Figure 2.** ORTEP view of  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$  (**2**) (50% probability ellipsoids). Selected interatomic distances (Å): O(1)–O(2) 1.315(5), Os–O(1) 2.006(3), Os–O(2) 2.041(4), Os–Cl(1) 2.380(1), Os–P(1) 2.5082(12), Os–P(2) 2.482(1), Os–P(3) 2.480(1), Os–P(4) 2.434(1).

structural analogies, **2** displays a much shorter O–O distance (1.315(5) Å) than that in  $[\text{OsH}(\eta^2\text{-O}_2)(\text{P–P})_2]^+$  (dcpe, 1.45(1) Å; dppe, 1.430(5) Å),<sup>9a,17a</sup> and among the shortest ever found for a dioxygen complex.<sup>13b,19</sup> This reflects the weaker  $\sigma$  donation of chloride vs hydride and is possibly related to the reactivity of **2**.

Oxo complexes with a  $d^4$  electron count are generally highly reactive or unstable toward disproportionation.<sup>7a–c,g</sup> A ruthenium analogue of  $\text{trans-}[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  (**3**) has been invoked as an intermediate in catalytic olefin epoxidation.<sup>20</sup>  $\text{trans-}[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  is surprisingly unreactive and does not transfer oxene to isonitriles, thioethers, or styrene. In conclusion,  $[\text{OsCl}(\text{dcpe})_2]^+$  promotes the four-electron reduction of  $\text{O}_2$  with the intermediacy of  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$ . Two bielectronic processes are involved, *i.e.* the overall metal-centered oxidation from  $[\text{OsCl}(\text{dcpe})_2]^+$  to  $[\text{OsCl}(\text{O})(\text{dcpe})_2]^+$  and the oxidation of  $\text{PPh}_3$  or  $\text{I}^-$  (2 equiv). Our efforts are directed toward developing productive oxene transfer to organic substrates.

**Supporting Information Available:** Details of experimental procedures and X-ray analyses (27 pages, PDF). See any current masthead page for Web access instructions.

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(18) X-ray of  $[\text{OsCl}(\eta^2\text{-O}_2)(\text{dcpe})_2]\text{BPh}_4$ : monoclinic,  $P2_1/c$ , green, 0.80 × 0.50 × 0.16 mm,  $a = 23.585(4)$  Å,  $b = 12.764(2)$  Å,  $c = 25.587(4)$  Å,  $\beta = 103.988(1)^\circ$ ,  $Z = 4$ ,  $R = 0.0462$  (on  $F_o$ ,  $I > 2\sigma(I)$ ),  $\text{GOF} = 0.973$ .

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