Oxo Complexes of Osmium(IV) Formed via Dioxygen Activation. X-ray Structures of $[OsX(dcpe)_2]PF_6$ (X = Cl, Br), $[OsCl(\eta^2 - O_2)(dcpe)_2]BPh_4$, and $[OsCl(O)(dcpe)_2]BPh_4$ (dcpe = 1,2-Bis(dicyclohexylphosphino)ethane)

Peter Barthazy, Michael Wörle,[†] Heinz Rüegger,[‡] and Antonio Mezzetti*

Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland

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Dioxygen addition to the 16-electron complexes $[OsX(P-P)_2]^+$ (3) gives the dioxygen adducts $[OsCl(\eta^2-O_2) (P-P)_2$ ⁺ (3), which in turn react with HCl gas to give the novel osmium(IV) oxo complexes trans-[OsX(O)- $(P-P)_2^+$ (5) (X = Cl, Br; P-P = 1,2-bis(dicyclohexylphosphino)ethane (dcpe), 1,2-bis(diethylphosphino)ethane (depe), 1,2-bis((2R,5R)-2,5-dimethylphospholano)benzene (Me-duphos)). The complexes $[OsX(dcpe)_2]^+$ (X = Cl, Br) (3) are studied by X-ray crystallography and are shown to have a "Y-shaped" coordination geometry in the equatorial plane. The X-ray structural analysis of $[OsCl(\eta^2-O_2)(dcpe)_2]^+$ (4a) reveals an exceptionally short O-O bond (1.315(5) Å). trans-[OsCl(O)(dcpe)₂]⁺ (5a), the first oxo complex of osmium(IV) investigated crystallographically, exhibits a long Os–O distance of 1.834(3) Å. The reactivity of 4 and 5 as oxidants is described. The dioxygen complex 4a transfers one oxygen atom to PPh₃ (to give Ph₃PO) or oxidizes iodide ions to triiodide ions in the presence of anhydrous HCl. In both reactions, the corresponding oxo species 5a is quantitatively formed as the only metal-containing product. Oxo complexes 5 are surprisingly stable and unreactive toward standard reducing agents such as phosphines.

Introduction

Despite its enormous potential, the use of molecular oxygen in transition-metal-catalyzed oxidation reactions is relatively rare.¹ Rather than dioxygen, most industrial processes exploit partially reduced forms of this molecule, e.g., peroxides, as well as catalysts based on metal centers in high oxidation states, often with d⁰ or d² configurations, which easily form oxo complexes.² Nature instead uses processes where the metal centers are in low oxidation states, typically with d⁶ configurations, and operates with the most readily available oxidant, i.e., dioxygen.³ As several natural systems are based on the heme ferryl moiety, much effort has been directed toward developing biomimetic catalytic systems based on iron porphyrin complexes.⁴ Replacement of the central atom with other members of the iron triad along with retention of the d⁶ electronic configuration of the central atom offers an opportunity to vary the catalytic species. This approach was developed by Groves in his pioneering work

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on dioxygen activation by ruthenium porphyrin complexes⁵ and has found applications in catalytic oxidation reactions.⁶ However, because of the intrinsic difficulties associated with dioxygen activation,¹ advancements in this area have been much slower than those for alternative methods utilizing single-oxygen donors as oxidants in "shunt" pathways, such as those in Mnsalen catalytic systems.7,8

Despite the large variety of transition metals and ligands employed, all catalytic processes cited above have a number of features in common. The active species is often a five-coordinate complex [MXL₄] containing four ligands L (often incorporated in chelating ligands favoring a planar geometry). The ligand X trans to the active site fine-tunes the reactivity of the system. The catalytic cycle is generally thought to involve an oxo species of the type $[MX(O)L_4]^+$. However, although the involvement of oxo complexes² in olefin epoxidation⁹ and alkane hydroxylation¹⁰ reactions is an established fact, well-documented examples of the formation of oxo complexes from molecular

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^{*} Corresponding author. E-mail: mezzetti@inorg.chem.ethz.ch.

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Scheme 1





oxygen are rare in nonbiomimetic systems of the iron triad.^{5,11} Indeed, most oxo complexes of ruthenium and osmium are formed by oxidation of coordinated water¹² or oxene transfer from a terminal oxidant.^{4,13}

We recently found that the five-coordinate, 16-electron complexes $[OsX(dcpe)_2]^+$, 3 (X = H, Cl; dcpe = 1,2-bis-(dicyclohexylphosphino)ethane),14 activate molecular oxygen,15 and that the resulting complex *trans*-[OsCl(η^2 -O₂)(dcpe)₂]⁺ (4a) forms the oxo species *trans*- $[OsCl(O)(dcpe)_2]^+$ (5a) (Scheme 1).¹⁶ Complexes 3–5 belong to the series $[OsXO_nP_4]^+$, which features a variable number of oxygen atoms n (n = 0, 1, 2) with the same ligand set. These species share all the commonalities mentioned above, as they are five-coordinate complexes of the iron triad, contain an ancillary ligand X that tunes their electronic properties, and include an oxo species formed from molecular oxygen. We show herein that this chemistry can be generalized to other five-coordinate complexes [OsX- $(P-P)_2$ ⁺ (2) (X = Cl, Br; P-P = diphosphine; Chart 1) and report their reactions with O_2 to give trans-[OsX(η^2 -O₂)(P- P_{2}^{+} (4) and, eventually, the oxo complexes *trans*-[OsX(O)- $(P-P)_2$]⁺ (5).

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Results and Discussion

The Six-Coordinate Complexes [OsX₂(P-P)₂]. The sixcoordinate complexes trans- $[OsX_2(P-P)_2]$ (1) and cis- $[OsX_2-P)_2$ $(P-P)_2$ (2) are the precursors for the five-coordinate, 16electron species $[OsX(P-P)_2]^+$ (3). By a variation of the published procedures, the dcpe¹⁴ and depe (depe = 1,2-bis- $(diethylphosphino)ethane)^{17}$ derivatives $trans-[OsX_2(P-P)_2]$ (P-P = dcpe, X = Cl (1a), Br (1b); P-P = depe, X = Cl(1c)) were prepared by ligand metathesis from $[OsX_2(PPh_3)_3]^{18}$ and the appropriate diphosphine ligand (2 equiv) in refluxing toluene. However, this synthetic method failed with Me-duphos (Me-duphos = (-)-1, 2-bis((2R, 5R)-2, 5-dimethylphospholano)benzene),19 giving a monosubstituted binuclear species, most likely [(Me-duphos)(PPh₃)Os(µ-Cl)₃Os(PPh₃)(Me-duphos)]Cl, instead of the disubstituted mononuclear complex. Therefore, cis-[OsCl₂(depe)₂] (**2c**) and cis-[OsCl₂(Me-duphos)₂] (**2d**) were prepared by heating $[(PEt_2Ph)_3Os(\mu-Cl)_3Os(PEt_2Ph)_3]Cl$ with the neat diphosphine ligand.¹⁷ In this series, the Me-duphos derivative 2d is new. It shows two pseudotriplets (AA'XX' spin system) in the ³¹P NMR spectrum, indicating that a single diastereomer (either Δ or Λ) is formed.

The Five-Coordinate Complexes $[OsX(P-P)_2]PF_6$. The five-coordinate dcpe derivatives are easily prepared by reacting *trans*- $[OsX_2(dcpe)_2]$ (X = Cl (1a), Br (1b)) with a strong halide scavenger (Scheme 2). Thus, 1a,b smoothly form $[OsCl(dcpe)_2]$ -PF₆ ($[3a]PF_6$) and $[OsBr(dcpe)_2]PF_6$ ($[3b]PF_6$) upon addition of TlPF₆. When dry, the five-coordinate species $[3a,b]PF_6$ are air-stable in the solid state for months.

In the case of the least bulky diphosphine, depe, dissociation of chloride from *trans*-[OsCl₂(depe)₂] (**1c**) does not occur under the above conditions, whereas the more labile *cis*-[OsCl₂(depe)₂] (**2c**) reacts with TIPF₆ in CH₂Cl₂ or CHCl₃. However, instead of the 16-electron species [OsCl(depe)₂]⁺ (**3c**), the dioxygen complex [OsCl(η^2 -O₂)(depe)₂]⁺ (**4c**) is isolated when standard Schlenk techniques are employed under argon. The putative intermediate [OsCl(depe)₂]⁺ is so reactive toward traces of O₂ that we were not able to observe it by monitoring the reaction between *cis*-[OsCl₂(depe)₂] and TIPF₆ with ³¹P NMR spectroscopy in CD₂Cl₂ solutions under argon. Thus, in view of the extreme reactivity of **3c** and its structural analogy to **3a,b,d**, its isolation was not further pursued.

In the case of Me-duphos, *cis*-[OsCl₂(Me-duphos)₂] (2d) smoothly reacts with TlPF₆, giving [OsCl(Me-duphos)₂]PF₆ ([3d]PF₆). The new compound was characterized by ³¹P and ¹H NMR spectroscopy and elemental analysis. The ³¹P room-temperature NMR spectrum, consisting of two sharp triplets at δ 76.1 and 42.6 (J = 5.5 Hz), suggests that the complex has a stereochemically rigid TBP structure and is present as a single diastereomer (either Δ or Λ) under these conditions.

In general, halide dissociation is apparently favored in the sterically crowded dcpe complexes **1a,b**. In the other cases, the

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Figure 1. ORTEP view of $[OsCl(dcpe)_2]^+$ (3a) (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Os-Cl, 2.371(1); Os-P(1), 2.282(1); Os-P(3), 2.321(1); Os-P(2), 2.422(1); Os-P(4), 2.417(1); Cl-Os-P(1), 122.38(4); P(1)-Os-P(3), 92.58-(4); Cl-Os-P(2), 88.05(4); P(1)-Os-P(4), 102.06(4); Cl-Os-P(3), 144.86(4); P(2)-Os-P(3), 101.50(4); Cl-Os-P(4), 85.78(4); P(2)-Os-P(4), 173.75(4); P(1)-Os-P(2), 82.08(4); P(3)-Os-P(4), 83.10-(4).

more labile cis isomer **2** has to be used, exploiting the stronger trans effect of P as compared to Cl. The reactivity trend also suggests that the increasing basicity of the P–P ligand labilizes the halide, as observed for *trans*-[OsCl₂(dcpe)₂] as compared to *trans*-[OsCl₂(dppe)₂] (dppe = 1,2-bis(diphenylphosphino)-ethane). The latter species, which contains a less basic and less bulky diphosphine, does not react with TIPF₆, and the corresponding five-coordinate complex has been prepared from *cis*-[OsCl₂(dppe)₂].²⁰ Steric and electronic effects apparently coordinate in stabilizing the Lewis-acidic 16-electron complexes containing the more basic and more bulky phosphines.

X-ray Structures of $[OsX(dcpe)_2]PF_6$ (X = Cl, Br). The five-coordinate nature of **3a** and **3b** was confirmed by X-ray analysis (Figure 1 and Figure S1 (Supporting Information)). Selected interatomic distances and angles of 3a and 3b are given in the caption to Figure 1 and in Table S2 (Supporting Information), respectively. The five-coordinate cations [OsX- $(dcpe)_2$ ⁺ (X = Cl (**3a**), Br (**3b**)) have a Y-shaped, distorted trigonal bipyramidal structure, similar to that found in [OsCl- $(dppe)_2$ ⁺,²¹ as well as in the ruthenium analogues with dcpe²² and other diphosphines.^{23,24} This is as expected for π -stabilized 16-electron complexes.²⁵ The "Y-plane" is further distorted, with two largely different P-Os-X angles, as already observed in the ruthenium analogues.^{22–24} Support for the role played by the π -donation from the chloride ligand comes from the Os-Cl distance of 2.371(1) Å, which is ca. 0.06 Å shorter than those in *trans*-[OsCl₂(dppe)₂] (2.434(1) Å).^{26,27} Similarly, the Os-

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Br distance in the bromo derivative **3b** is 2.481(2) Å, shorter than the 2.5738(6) Å distances in the reference compound *trans*- $[OsBr_2(dppe)_2]$.²⁸ Taking into account the unsaturated nature of these complexes, the axial Os-P distances in both **3a** and **3b** appear exceptionally long with respect to literature values.^{21,26,29} An interesting feature in both **3a** and **3b** is the envelope conformation of the chelate rings with the flap on a C atom.

Reaction of [OsX(P-P)_2]PF_6 with O₂. The 16-electron species **3a,b** reacted quantitatively with O₂ in CH₂Cl₂, forming the dioxygen complexes $[OsX(\eta^2-O_2)(dcpe)_2]^+$ (X = Cl (4a), Br (4b)) within hours. The dependent derivative $[OsCl(\eta^2-O_2) (depe)_2$ ⁺ (4c) was prepared directly from six-coordinate 2c by reaction with TIPF₆ and O₂ in CH₃OH. The light green complexes 4a-c were characterized by ³¹P and ¹H NMR spectroscopy, mass spectrometry (FAB⁺), and elemental analysis. Although the $\nu(O-O)$ stretching band was unassignable owing to the crowding of the 800-900 cm⁻¹ IR spectral region, the X-ray structure of 4a reported below gives definitive evidence of the η^2 -O₂ linkage. The ³¹P NMR spectra of **4a**-c consist of one sharp singlet in the range δ +10 to -10, consistent with rapid internal reorientation rendering all P atoms equivalent. In contrast, the ³¹P NMR spectra of the related complexes $[MH(\eta^2-O_2)(P-P)_2]$ (M = Ru, Os) show broad signals at room temperature, possibly due to the hindered propeller-like rotation of the η^2 -O₂ ligand.^{15,30,31}

The dioxygen complex $[OsCl(\eta^2-O_2)(depe)]^+$ (**4**c) is probably the cationic species observed by Chatt and Hayter upon dissolution of *cis*- $[OsCl_2(depe)_2]$ in water.¹⁷ In the series, the Me-duphos derivative $[OsCl(Me-duphos)_2]^+$ (**3d**) is the least reactive toward O₂. Upon exposure to air of a CDCl₃ solution, the five-coordinate complex **3d** remains unchanged to a great extent and no diamagnetic η^2 -O₂ complex is formed, as indicated by the ³¹P NMR spectrum. The ¹H NMR spectrum of the solution indicates that traces (~1%) of a paramagnetic complex are formed, which we tentatively formulate as the corresponding oxo complex by analogy with the other $[OsX(O)(P-P)_2]^+$ species (see below). The latter probably derives from an undetected dioxygen adduct present at low concentration in equilibrium with **3d**. Finally, for the dppe complex, no reaction with O₂ was observed.²⁰

X-ray Structure of [OsCl(η^2 -O₂)(dcpe)₂]BPh₄ ([4a]BPh₄). X-ray-quality crystals of [4a]BPh₄ were grown from CH₂Cl₂/ Pr^{*i*}OH. The complexes [OsBr(η^2 -O₂)(dcpe)₂]⁺ (4b) and [OsCl-(η^2 -O₂)(depe)₂]⁺ (4c) decomposed to the oxo complexes during the crystallization process. This prevented growing crystals of their salts with [PF₆]⁻, [BPh₄]⁻, or [BAr₄]⁻ (BArF, Ar = 3,5bis(trifluoromethyl)phenyl).

The formally seven-coordinate cation $[OsCl(\eta^2-O_2)(dcpe)_2]^+$ can be described as a distorted pentagonal bipyramid, with two P atoms, the Cl atom, and the two O atoms approximately in the equatorial plane and with two mutually trans axial P atoms (Figure 2, Table S3 (Supporting Information)).³² The Os-Cl

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Figure 2. ORTEP view of *trans*- $[OsCl(\eta^2-O_2)(dcpe)_2]^+$ (4a) (30% probability ellipsoids).

Table 1. O–O and Os–O Bond Distances (Å) in $[OsX(\eta^2-O_2)(P-P)_2]PF_6$

	0-0	Os-O	ref
$[OsCl(\eta^{2}-O_{2})(dcpe)_{2}]PF_{6} \\ [OsH(\eta^{2}-O_{2})(dcpe)_{2}]PF_{6} \\ [OsH(\eta^{2}-O_{2})(dppe)_{2}]PF_{6} \\ \label{eq:eq:expansion}$	1.315(5)	2.006(3), 2.041(4)	this work
	1.45(1)	2.045(8), 2.037(8)	15
	1.430(5)	2.061(4), 2.064(3)	33a

distance in the (formally seven-coordinate) **4a** (2.380(1) Å) is similar to that in five-coordinate **3a** (2.371(1) Å), whereas the Os-P distances are even longer than those in **3a,b**. The Os-P₄ arrangement shows a tetrahedral distortion, with the P(1) and P(3) atoms bent away from the coplanar dioxygen ligand (P(1)-Os-P(3) = 162.46(4)°). The axial P atoms are only slightly bent toward the dioxygen (P(2)-Os-P(4) = 175.91(4)°). Both chelate rings show an envelope conformation with the flap on a C atom.

Despite structural analogies, **4a** displays a much shorter O–O distance (1.315(5) Å) than $[OsH(\eta^2-O_2)(P-P)_2]^+$ (dcpe,¹⁵ 1.45-(1) Å; dppe,^{33a} 1.430(5) Å; Table 1) and among the shortest ever found for a dioxygen complex.^{29,34} Unfortunately, the Os–O distances are not a reliable probe of the Os–O bond strengths in **4a**, as the η^2 -coordination mode of the dioxygen ligand is slightly distorted. Thus, the Os–O(2) distance is longer by 0.035(4) Å than Os–O(1) and the O(2)–O(1)–Os angle (72.5(2)°) is larger than O(1)–O(2)–Os (69.6(2)°). Comparison with $[OsH(\eta^2-O_2)(P-P)_2]^+$ (Table 1) shows an enhanced interaction between Os and one of the O atoms of η^2 -O₂. Although these features invite speculation about distortion of the η^2 -coordination toward η^1 , their magnitudes are so small that they could be the effect of crystal packing as well.

Bonding in $[MX(\eta^2-O_2)(P-P)_2]^+$. Examples of dioxygen adducts of d⁶ complexes of Ru(II)^{30,31,35} and Os(II)^{33,36} have been increasing in number, in particular since the recent

discovery of $[\text{RuH}(\eta^2-\text{O}_2)(\text{P}-\text{P})_2]^+$.³⁰ Most of these new $\eta^2-\text{O}_2$ derivatives are complexes of the type $[\text{MH}(\eta^2-\text{O}_2)(\text{P}-\text{P})_2]^+$ (M = Ru, Os)^{30–33} or $[\text{Ru}(\eta^2-\text{O}_2)(\text{Cp}^*)(\text{P}-\text{P})]^+$ (Cp* = C₅Me₅).³⁵ The present investigation contributes to the assessment of the electronic requirements for dioxygen activation by relatively electron-rich but coordinatively unsaturated Ru(II) and Os(II) complexes of the $[\text{MX}(\text{P}-\text{P})_2]^+$ series. In this class of compounds, the osmium derivatives show a higher tendency to bind O₂ than the ruthenium analogues. As the five-coordinate complexes $[\text{MX}(\text{P}-\text{P})_2]^+$ generally react rapidly with both neutral and anionic donors, such as halide, CO, H₂, and nitriles,^{14,22,37} this is probably a thermodynamic effect, as supported by the following considerations.

Dioxygen adducts of ruthenium are formed only when several strong σ -donors (the hydride and basic P–P ligands) enhance the electron density at the metal. Thus, the five-coordinate [RuH- $(P-P)_2$ ⁺ complexes form $[RuH(\eta^2-O_2)(P-P)_2]^+$ $(P-P = dcpe^{31})$ or 1,2-bis(diisopropylphosphino)ethane³⁰ (dippe)), whereas the chloro analogue [RuCl(dcpe)₂]⁺ is stable in solutions exposed to air for short periods of time and does not form a (detectable) dioxygen adduct.²² In the case of [OsX(dcpe)₂]⁺, O₂ activation occurs also when less basic X and P-P ligands are combined, as in $[OsH(dppe)_2]^{+33a}$ and $[OsCl(dcpe)_2]^{+.15}$ Indeed, the higher energy of the d orbitals of Os as compared to Ru favors the shift of electron density from the metal to the dioxygen ligand that stabilizes the M(η^2 -O₂) linkage. The effect of the donor properties of the anionic ligand X is clearly visible in the series $[OsX(\eta^2-O_2)(P-P)_2]^+$, where the O-O distance increases on going from chloride (a weak donor) to hydride (a strong donor) (Table 1). In this class of compounds, the chloro derivatives $[OsCl(\eta^2-O_2)(P-P)_2]^+$ (4a-c) reported herein are the dioxygen complexes that are stabilized by the least basic ligands. However, some stable dioxygen adducts of osmium are formed even in the presence of a π -acid ligand, as in [OsHCl(η^2 -O₂)- $(CO)(PR_3)_2$] (R = c-C₆H₁₁, Pr^{*i*}).^{36b}

Besides the nature of the metal M (M = Ru or Os) and the donor properties of the ligand X (X = halide or H), the electronic and steric properties of the diphosphine fine-tune the reactivity of $[MX(P-P)_2]^+$ toward O₂. As described above, the reactivity of the five-coordinate species $[OsCl(P-P)_2]^+$ toward dioxygen increases with increasing basicity and decreasing steric bulk of the P–P ligand along the series dppe < Me-duphos « dcpe < depe.

The structural data available for $[MX(\eta^2-O_2)(P-P)_2]^+$ (M = Ru, Os; X = Cl, H) in the solid state and in solution provide further insight into the bonding in **4a**-**c**, taking into account that the η^2 -O₂ ligand is a π -acceptor and the chloride a weak π -donor. The P_{eq}-Os-P_{eq} angle is much larger in **4a** (162.46-(4)°) than in the hydride analogue $[OsH(\eta^2-O_2)(dcpe)_2]^+$ (136.3-(1)°). As the steric crowding in chloro derivatives **4** is higher than that in the hydride analogues, this effect is more likely electronic than steric. For the related $[MH(\eta^2-H_2)(P-P)_2]^+$

⁽³²⁾ This is largely formal and implies that 4b could be described as a peroxo complex of Os(IV). However, the alternative description as a six-coordinate dioxygen complex of Os(II) (featuring a distorted octahedral coordination) seems more appropriate in view of the short O–O distance and is normally used throughout this paper.

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Figure 3. Partial (π -bonding) correlation diagram of the Cl–Os– η^2 -O₂ fragment. Only the d_{xz} orbital has the correct symmetry for interacting with $\pi^*(O_2)$.

complex, it has been shown that the bending of two trans P atoms away from the dihydrogen ligand enhances the $d_{\pi^-}(M) \rightarrow \sigma^*(\eta^2-H_2)$ back-bonding.³⁸ This is because closing the equatorial P–Ru–P angle rehybridizes the d_{xz} orbital and raises its energy. Such a distortion is necessary in $[OsH(\eta^2-O_2)-(dcpe)_2]^+$, where it improves the overlap with the π^* orbitals of O₂. In $[OsCl(\eta^2-O_2)(P-P)_2]$, closing one P–Ru–P angle is both unfavorable (because Cl is larger than H) and unnecessary, as the d_{xz} orbital is destabilized by the p_{π} orbital of the chloro ligand (Figure 3).²⁵ This is consistent with a weaker $d_{\pi}(Os) \rightarrow \pi^*$ - (η^2-O_2) binding component in **4a** than in $[OsH(\eta^2-O_2)(dcpe)_2]^+$ due to Cl being an overall weaker donor than hydride, as discussed above for the O–O and Os–O bond distances.

Variable-temperature NMR spectroscopy data support the above interpretation. Thus, the hydride analogues $[MH(\eta^2-O_2)-(P-P)_2]^+$ (M = Ru, Os) show fluxional behavior in solution that is possibly due to the hindered propeller-like rotation of the η^2 -O₂ ligand.^{15,30,31} Their room-temperature ³¹P NMR spectra show two broad humps that resolve into two pseudotriplets at low temperature. In contrast, the ³¹P NMR spectra of the halo derivatives **4a**-**c** consist of one sharp singlet, indicating rapid rotation of η^2 -O₂ on the NMR time scale due to lower energy barriers. This is contrary to expectation based on steric arguments and consistent with a larger $d_{\pi}(Os) \rightarrow \pi^*(\eta^2-O_2)$ binding component in chloro derivative **4a** than in $[OsH(\eta^2-O_2)(dcpe)_2]^+$.

The overall bonding pattern in the Cl–Os– (η^2-O_2) moiety features a three-orbital, four-electron push–pull interaction between the chloro ligand and the dioxygen ligand analogous to the case of the Cl–M–CO moiety (Figure 3).²⁵ Accordingly, the Os–Cl distance in the formally seven-coordinate **4a** (2.380-(1) Å) is similar to that in the five-coordinate **3a** (2.371(1) Å). This is again contrary to the expectation based on steric effects and suggests that π -donation plays similar roles in both complexes.

In conclusion, the stronger Os–O bonds (and weaker O–O bond) in $[OsH(\eta^2-O_2)(P-P)_2]^+$ than in **4a** are due to hydride being a much stronger donor than Cl. As the Os– (η^2-O_2) electron transfer is mediated by a π -effect, the $d_{\pi}(Os)-\pi^*(O_2)$ overlap is maximized by the distortion of the equatorial P–M–P angle in the hydride complexes and by the $d_{\pi}(Os)-p_{\pi}(Cl)$ fourelectron destabilization in the case of **4**. The weaker Os– (η^2-O_2) bonding and smaller $d_{\pi}-\pi^*$ overlap in **4** are possibly reflected in the distortion of the η^2 -coordination toward η^1 . This could explain the unusual reactivity of **4** as compared to the hydride analogues.

Reactivity of $[OsX(\eta^2-O_2)(P-P)_2]^+$. We investigated the reversibility of dioxygen addition to five-coordinate **3a**. Photolysis of **4a** (Xe lamp) in CH₂Cl₂ solution gives small amounts of five-coordinate **3a** (20%) together with other (uncharacter-



Figure 4. UV-visible monitoring of the reaction of 4a with I⁻ in the presence of anhydrous HCl.

ized) products. Heating under vacuum mainly produces dcpe dioxide. A similar behavior has been observed for $[OsH(\eta^2-O_2)(dcpe)_2]^+$.¹⁵ Complex **4a** reacts slowly with carbon monoxide in CH₂Cl₂ solution, but ³¹P NMR spectroscopy and stripping of the effluent gases in aqueous Ba(OH)₂ indicated that neither the carbonyl complex $[OsCl(CO)(dcpe)_2]^+$ nor CO₂ was formed.

All of the dioxygen complexes $4\mathbf{a}-\mathbf{c}$ are stable in the solid state, but decomposition to the oxo species *trans*-[OsX(O)(P-P)₂]⁺ slowly occurs in CH₂Cl₂ solution. Simple storing of $4\mathbf{a}-\mathbf{c}$ in CH₂Cl₂ solution yields the corresponding oxo complexes within 3 d. As independent experiments show that traces of acids greatly accelerate this reaction, we conclude that the reaction is triggered by traces of HCl formed by the decomposition of the chlorinated solvent over time (Scheme 1) or, alternatively, by traces of water incorporated during the preparation of 4. Accordingly, as the [PF₆]⁻ anion is always associated with small amounts of acids (or water), changing the anion Y⁻ in [OsCl-(P-P)₂]Y to [BPh₄]⁻ or [BAr₄]⁻ substantially increases the stability of the dioxygen complex. In contrast, [OsH(η^2 -O₂)-(dcpe)₂]⁺ is stable in solution for longer periods of time.¹⁵

Neither the fate of the "lost" oxygen atom nor the mechanism of this reaction could be assessed. However, we rule out that the above reaction occurs by dissociation of O₂ from [OsCl- $(\eta^2$ -O₂)(dcpe)₂]⁺ (**4a**) followed by formation of a peroxo-bridged intermediate, ^{3,6c,d} as O₂ coordination in **4a** is essentially irreversible, as discussed above, and five-coordinate **3a** does not react with the dioxygen complex **4a**.¹⁶

Oxidation Reactions with $[OsX(\eta^2-O_2)(P-P)_2]^+$ (4). The oxygen-transfer reactivity of 4a with a number of substrates was studied. The test reactions were generally performed with $[OsCl(\eta^2-O_2)(dcpe)_2]^+$ (4a), but 4b and 4c showed similar reactivity when used in selected instances. [4a]BPh₄ oxidizes I^- (as $[NBu_4]I$) to triiodide, forming *trans*- $[OsCl(O)(dcpe)_2]^+$ (5a) in the presence of anhydrous HCl in CH₂Cl₂ according to eq 1. Monitoring of the reaction by UV-visible spectroscopy

$$[\text{OsCl}(\eta^2\text{-}\text{O}_2)(\text{dcpe})_2]^+ + 3\text{I}^- + 2\text{H}^+ \rightarrow$$

trans-[OsCl(O)(dcpe)_2]^+ + I_3^- + H_2O (1)

at 365 nm shows quantitative formation of $[I_3]^-$ and **5a** based on the absorbance trace of the reaction after correction for the absorbance of the oxo complex (Figure 4). The ³¹P NMR spectrum of the reaction solution indicates quantitative disappearance of **4a**, whereas only the typical signals of **5a** are visible

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in the ¹H NMR spectrum. No reaction occurs without acid. Complex **4a** also oxidizes triphenylphosphine in the presence of HCl under argon (eq 2). The stoichiometry of reaction 2 is

$$[OsCl(\eta^2-O_2)(dcpe)_2]^+ + [Ph_3PH]Cl \rightarrow$$

trans-[OsCl(O)(dcpe)_2]^+ + Ph_3PO + HCl (2)

well-defined, as [Ph₃PH]Cl is added to **4a** (1:1 mole ratio) to give **5a** and Ph₃PO in almost quantitative yields, as measured by ³¹P NMR spectroscopy. The reaction is complete within 10 min, and the coordinated diphosphines are not oxidized.³⁹

Acid-promoted oxygen transfer has been proposed for other peroxo complexes.^{1,40} In contrast to what is observed for $M(\eta^2 - O_2)$ complexes (M = Pt, Rh),⁴¹ it seems unlikely that reaction 1 involves acid hydrolysis of **4a**, since the use of aqueous HCl gives yet unidentified products instead of **5a** and extraction of freshly prepared CH₂Cl₂ solutions of **5a** with aqueous titanyl sulfate does not reveal the presence of H₂O₂. Finally, **5a** does not re-form **4a** upon treatment with H₂O₂.

The oxidation of a number of organic substrates has been attempted. Complex 4a does not epoxidize olefins (styrene) or quinone-like substrates (menadione), oxidize aldehydes (benzaldehyde) or alcohols (PriOH, tert-butyl alcohol, CH3OH), or hydroxylate alkanes (adamantane). In contrast, the dioxygen ligand of the ruthenium analogue [RuH(η^2 -O₂)(dcpe)₂] displays moderate nucleophilic behavior and oxidizes aldehydes to the corresponding carboxylic acids.³¹ With TCNE an immediate reaction occurs, but the TCNE radical anion is formed instead of the epoxide. We also tested whether 5a shows haloperoxidase reactivity in the presence of bromide ions.⁴² However, the acidic hydrolysis of the dioxygen complex 4a in the presence of [NBu4]-Br and 1,3,5-trimethoxybenzene or 2,3-dimethoxytoluene does not give the corresponding brominated derivatives (not even traces). This also disfavors the possibility that HOCl is formed in the reaction of 4a with HCl (Scheme 1).

trans-[OsX(O)(P-P)2]BPh4. The osmium(IV) complexes $[OsX(O)(P-P)_2]^+$ (X = Cl, P-P = dcpe, 5a; X = Br, P-P = dcpe, **5b**; X = Cl, P-P = depe, **5c**) were prepared from the corresponding dioxygen complexes 4a-c and fully characterized. As mentioned above, the d^4 oxo complexes 5a-c are formed by oxygen transfer from the dioxygen adducts 4a-c(Scheme 1) and the reaction is accelerated by gaseous HCl. The light green or brownish complexes 5a-c are stable in the solid state and in solution. The Me-duphos analogue [OsCl(O)(Meduphos)₂]⁺ is formed only in traces, as discussed above. We have previously reported that 5a is paramagnetic with an effective magnetic moment μ_{eff} of 3.05 μ_B at 300 K,¹⁶ a value near the spin-only value for two unpaired electrons. This is explained by the molecular orbital ordering of octahedral oxo complexes with a d⁴ configuration based on C_{4v} symmetry as discussed by Mayer (Figure 5).43 In the case of the d4 complexes $[OsX(O)(P-P)_2]^+$, two d electrons fill the d_{xy} orbital, and the remaining two occupy the two degenerate d_{xz} and d_{yz} orbitals with parallel spins.



Figure 5. Partial correlation diagram of a d^4 [Os(O)L₅] complex.

 Table 2.
 ¹H and ¹³C NMR Data (Obtained in CDCl₃) for trans-[OsCl(O)(depe)₂]BPh₄ ([5c])BPh₄)

assignt ^a	$\delta(^{1}\text{H})$	$R_2(^1\text{H}),^b \text{s}^{-1}$	$\delta(^{13}\text{C})$
CH ₃ (Cl)	1.5	45	-26.6
$CH_3(O)$	29.0	240	+34.2
$CH_2(Cl)$	6.9, -4.1	195, 350	-122.2
$CH_2(O)$	34.0, 12.3	320, 635	+173.8
$CH_2(BB)$	15.1, 8.1	155, 205	-85.4

^{*a*} (Cl) and (O) denote the chloride and oxo hemispheres, respectively; (BB) denotes the diphosphine backbone. ^{*b*} Transverse relaxation rates R_2 estimated from line widths.

NMR Spectroscopy. Although no ³¹P NMR signals can be observed (at least at room temperature), the ¹H and ¹³C NMR spectra are sufficiently resolved in the diamagnetic areas and feature well-defined paramagnetic regions with relatively small isotropic shifts. Most of the signals could be assigned by a combination of one- and two-dimensional NMR techniques (Table 2). In the dependerivative *trans*- $[OsCl(O)(depe)_2]^+$ (5c), there are two inequivalent methyl groups belonging to the two hemispheres in which the oxo and the chloro substituents reside, respectively. On the basis of the assumptions (i) that most of the unpaired spin density is located either on the oxo ligand or between it and the metal and (ii) that the dipolar term dominates the relaxation behavior of the adjacent protons, we assign the slowly relaxing methyl protons resonating in the diamagnetic region of the spectrum at δ 1.5 to the group in the Cl hemisphere.

Despite the considerable transverse relaxation rates R_2 (Table 2) of the diastereotopic protons in the ethyl CH₂ groups, it proved possible to relate these to their respective CH₃'s by means of a 2D TOCSY experiment. The backbone CH₂ protons are consequently assigned to the remaining two signals. All ¹³C resonances were assigned on this basis by means of ¹H-¹³C 2D-heteronuclear multiple-quantum coherence spectroscopy. It is interesting to note that the chemical shifts of the carbons residing in the oxo hemisphere are isotropically shifted toward higher frequency, whereas those of the carbons belonging to the chloride hemisphere and the chelate backbone are below the TMS frequency.

The dcpe derivatives **5a** and **5b** are completely analogous in structure and spectroscopic properties to **5c**. However, the interpretation process is more demanding in view of 12 and 22 inequivalent C and H atoms to be assigned, requiring the use of 2D methods. A contour plot of a section of the ${}^{1}\text{H}{-}{}^{13}\text{C}$ heteronuclear multiple-quantum coherence spectrum for *trans*-[OsBr(O)(dcpe)_2]BPh_4 ([**5b**]BPh_4) (Figure 6) in CDCl_3 at room temperature shows the wide spread of shifts in the carbon dimension. Indeed, with the exception of that of one α -carbon,

⁽³⁹⁾ Although [OsCl(Me-duphos)₂]⁺ (3d) probably forms a very labile dioxygen adduct, PPh₃ is not oxidized in the presence of 3d (1 equiv) under O₂ in CDCl₃.

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Figure 6. ${}^{1}\text{H}{-}{}^{13}\text{C}$ heteronuclear multiple-quantum coherence spectrum of [**5b**]BPh₄. Cross-peaks labeled with an asterisk are vertically expanded by a factor of 8; BB denotes the chelate backbone resonances. The dashed wavy line separates signals assigned to ${}^{1}\text{H}$ and ${}^{13}\text{C}$ nuclei in the two hemispheres (see text).

all resonances can be unambiguously assigned. It is again to be noted that the signals belonging to carbons in the two different hemispheres of the complex are in well-separated shift regions, whereas no such distinction can be made for the respective hydrogens. This allows structural assignments, as the ¹³C chemical shifts of both (equivalent) C atoms of the chelate backbone are in the negative range as are those of the α -carbons of the cyclohexyl groups in the chloride hemisphere (α CH(Cl), Table S4 (Supporting Information)). Indeed, the chelate ring present in the solid phase for **5a** exhibits an envelope conformation with a tip into this part of the molecule (see below).

X-ray Structure of [5a]BPh4. Crystals of trans-[OsCl(O)-(dcpe)₂]BPh₄ ([**5**a]BPh₄) were grown from CH₂Cl₂/Pr^{*i*}OH. An ORTEP view of 5a is shown in Figure 7, and structural data are provided in Table S5 (Supporting Information). The complex cation features a slightly distorted octahedral geometry with an O(1)-Os-Cl angle of 175.1(1)°. The OsP₄ arrangement shows a tetrahedral distortion with P(1) and P(3) below the mean plane (both by -0.12 Å) and P(2) and P(4) above it (both by 0.09 Å). In agreement with the higher oxidation state of 5a, the Os-P distances are significantly shorter than those in 4a. The bite angles of about 82° are normal for dcpe. As already observed for **3a**,**b** and **4a**, the chelate rings have an envelope conformation. The Os, P(1), P(2), and C(14) atoms are nearly coplanar $(\pm 0.04 \text{ Å})$, and C(13) is displaced 0.71 Å from their mean plane toward Cl. In the second chelate ring, Os, P(3), P(4), and C(39) are coplanar within ± 0.1 Å and C(40) is displaced 0.44 Å from their mean plane in the Cl hemisphere.



Figure 7. ORTEP view of trans-[OsCl(O)(dcpe)₂]⁺ (5a) (30% probability ellipsoids).



Figure 8. Correlation diagram of the Cl–Os=O fragment.

The Os-oxo linkage deserves discussion. The Os-O(1) distance in **5a** (1.834(3) Å) is much longer than those in osmium(VI) oxo complexes (ca. 1.72 Å),^{2,29,44} e.g., in the (*E*)-styryl complex [OsCl(O)₂((*E*)-CH=CHPh)(PPrⁱ)₂] (d(Os-O) = 1.70(1), 1.72(1) Å).^{11a} The lengthening of the Os-O bond in **5a** is due to the two additional electrons in the $(d_{xy})^2(d_{xz})^1(d_{yz})^1$ configuration as compared to the d² osmium(VI) systems. A partial, qualitative correlation diagram (Figure 8) indicates that the degenerate d_{xz} and d_{yz} orbitals have antibonding character with respect to the Os-O bond.² Their partial occupation by parallel spins is confirmed by the magnetic data.^{2,12d,13b}

Oualitative MO considerations explain further structural features. The Os-Cl bond is much longer in **5a** (2.442(1) Å) than in five-coordinate **3a** (2.371(1) Å) and in the η^2 -O₂ complex **4a** (2.380(1) Å). The opposite trend is expected on the basis of the ionic radius contraction upon going from Os(II) to Os(IV). The straightforward explanation is that both the dioxygen complex 4a and the 16-electron species 3a are stabilized by p_{π} \rightarrow d_{π} donation from the halide, although via different mechanisms, as discussed above.^{25,45} In contrast, **5a** contains two π -donors, a strong one, the oxo ligand,² and a much weaker one, the chloro ligand (Figure 8),²⁵ and the d⁴ metal center has two electrons occupying the antibonding d_{xz} and d_{yz} orbitals. This results in a 2-fold five-electron $p_{\pi}-d_{\pi}$ destabilizing interaction between the oxo and chloro lone pairs and the halffilled d_{xz} and d_{yz} orbitals of osmium (Figure 8), which possibly explains the longer Os-Cl bond. Although it has been suggested that $p_{\pi}-d_{\pi}$ destabilization energies are very small,⁴⁶ the present

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structural data show that such effects are sizable, at least when a strong donor, such as an oxo ligand, is involved.⁴⁷

Reactivity of *trans*-[**OsX(O)**(**P**–**P**)₂]⁺. Most of the reactions were performed with *trans*-[OsCl(O)(dcpe)₂]⁺ (**5a**), but *trans*-[OsBr(O)(dcpe)₂]⁺ (**5b**) and *trans*-[OsCl(O)(depe)₂]⁺ (**5c**) show very similar reactivity. The oxo complexes **5** do not react with CO (1 atm, 20 °C), transfer oxene to isonitriles, thioethers, and styrene, or react with these substrates in other ways. Stoichiometric oxidation of alcohols does not take place in CDCl₃ at room temperature. However, some [OsH₃(dcpe)₂]^{+ 37} is formed in refluxing methanol, together with decomposition products. This suggests that the protic solvent is able to protonate the oxygen and reduce the complex under forcing conditions. To test the possibility of reoxygenating the oxo species **5a**, we treated it with H₂O₂ or O₂, but the η^2 -O₂ complex **4a** was not formed in either case.

The d⁴ osmium oxo complexes reported to date have been prepared by oxidation of the corresponding aquo complexes of the general formula $[Os(OH_2)N_5]^{2+}$ (N = sp² or sp³ N-donor).^{12a-c,f} These species are highly reactive or unstable toward disproportionation to the point that the osmium(IV) oxidation state is sometimes considered as "missing".^{12a-c,f} Also, a high reactivity is expected for octahedral d⁴ oxo complexes owing to their reduced Os–O bond order (Figure 5).² Thus, we were surprised to find that **5a** reacts with nucleophiles (PR₃ and SR₂) sluggishly or does not react at all. Complex **5a** reacts with PPh₃ (in an NMR tube sealed under vacuum to exclude traces of O₂), giving Ph₃PO (20%) and a small amount of **3a** (ca. 5% by ³¹P NMR), together with other unidentified products after 14 d (eq 3). The ¹H NMR spectrum of the reaction solution

 $trans - [OsCl(O)(dcpe)_2]^+ + Ph_3P \rightarrow [OsCl(dcpe)_2]^+ + Ph_3PO (3)$

indicates that **5a** is still present after this time, but other unidentified paramagnetic complexes are formed. The reaction with PMe₃ is not significantly faster. As a comparison, the d⁴ oxo species [Ru(O)(TMP)] (TMP = the 5,10,15,20-tetramesi-tylporphyrin dianion) readily oxidizes PPh₃ under analogous conditions.⁴⁸

The above results suggest that the dissociation energy of the Os=O bond is lower than 125 kcal mol⁻¹, the dissociation energy of the P–O bond in PPh₃.⁴⁹ This appears reasonable also in view of the long Os–O distance (1.834(3) Å) and the presence of two π -antibonding electrons discussed above. Provided that reaction 3 is thermodynamically favored, its low rate points to the existence of a kinetic barrier. As the dcpe and depe analogues **5a** and **5c** react similarly, we suspect that the nature of the kinetic barrier is electronic rather than steric. A possible explanation is that the attack of the incoming nucleophile on the LUMO's of **5**, the degenerate d_{xz} and d_{yz} orbitals, must be preceded by electron pairing (Figure 5).⁵⁰ Thus, the attack on complexes **5** requires either geometrical rearrangement or the involvement of the high-energy d_z² orbital.

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Although the oxo complexes **5** are not useful oxidants, the discovery of stable phosphine oxo complexes is important, as ruthenium analogues of *trans*- $[OsCl(O)(P-P)_2]^+$ have been invoked as intermediates in catalytic olefin epoxidation. It has been suggested that complexes of the type $[RuCl(P-P)_2]^+$ and the related $[RuCl(PNNP)]^+$ complexes (PNNP = tetradentate ligands with P and N donors) catalyze the asymmetric epoxidation of olefins with hydrogen peroxide and PhIO as oxidants and with the involvement of oxo species of Ru(IV).⁵¹

Conclusion

The main reaction of the dioxygen complexes $[OsX(\eta^2-O_2) (dcpe)_2$ ⁺ (4) is the loss of one oxygen atom to form *trans*- $[OsX(O)(P-P)_2]^+$ (5). The reactivity of coordinated dioxygen is analogous to that of peroxide. The investigations concerning the reactivity of the oxo species 5 show clearly that these osmium complexes are much less reactive than their Fe and Ru analogues. This can be qualitatively explained by considering that the metal center becomes softer (and the oxo species less electrophilic) upon going from 3d to 5d metals. This effect is reinforced upon going from iron porphyrins to [RuCl(PNNP)]⁺ and $[OsCl(P-P)_2]^+$ as the ligand set is changed from N₄ to P₂N₂ (a drastic change as the extensive π interactions in the metalloporphyrin are lost) and, finally, to P₄. Besides the significance of *trans*- $[OsX(O)(P-P)_2]^+$ with respect to nonbiomimetic dioxygen activation, its isolation and characterization lend support to previous mechanistic speculations regarding the catalytic epoxidation of olefins catalyzed by $[RuCl(P-P)_2]^+$.

Experimental Section

General Details. All operations were carried out under argon using standard Schlenk techniques or in a glovebox (Braun) under purified nitrogen. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. 1,2-Bis((2R,5R)-2,5dimethylphospholano)benzene (Me-duphos) was purchased from Strem. The ligand dcpe and *trans*-[OsCl₂(dcpe)₂] were prepared as previously reported (see ref 14). Yields are based on the metal. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer, and UV-visible spectra, on a Kontron Instruments Uvikon 922 spectrophotometer. Microanalyses were performed by the Laboratory of Microelemental Analysis at the Organic Laboratories of the ETH Zürich. ¹H, ¹³C{¹H}, and ³¹P{¹H} and 2D correlation NMR spectra were obtained with Bruker Avance 250, 300, 400, and 500 spectrometers. ¹H (and ¹³C) and ³¹P chemical shifts are relative to TMS and external 85% H₃PO₄, respectively. Mass spectrometry was carried out by the Analytic Service of the Organic Laboratories at the ETH Zürich. NaBArF was prepared by a literature method.52

cis-[OsCl₂(depe)₂], 2c. An improved synthesis for 2c was as follows: [(PEt₂Ph)₃Os(μ -Cl)₃Os(PEt₂Ph)₃]Cl (1.021 g, 0.672 mmol) and depe (1.24 g, 6.0 mmol) were heated together without solvent for 12 h. The resulting colorless solid was extracted with boiling hexane (50 mL) to remove diethylphenylphosphine. The resulting white microcrystals were filtered off and washed twice with hexane. Yield: 829 mg (92%). ¹H NMR (CDCl₃): δ 1.0–32.7 (m, 48 H, *CH*₂, *CH*₃). ³¹P NMR: δ 19.4 (t, 2 P, ²J_{PP'} = 8.8 Hz), 10.9 (t, 2 P). Other data are as in ref 17.

cis-[OsCl₂(Me-duphos)₂], 2d. [(PEt₂Ph)₃Os(μ -Cl)₃Os(PEt₂Ph)₃]Cl (541 mg, 0.356 mmol) and Me-duphos (459 mg, 1.50 mmol, 1.05 equiv) were heated together without solvent for 12 h. Diethylphenylphosphine

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was separated from the resulting pale yellow oil by distillation under reduced pressure at 200 °C. The solid residue was then crushed and vacuum-dried, yielding a pale-yellow powder. Yield: 612 mg (98%). ¹H NMR (CDCl₃): δ 9.79 (br, 2 H, Ph *H*), 9.58 (br, 2 H, Ph *H*), 9.3 (br, 4 H, Ph *H*), 5.40–5.30 (m, 2 H, C*H*), 4.98–4.78 (m, 6 H, C*H*, C*H*₂), 4.77–4.59 (m, 2 H, C*H*), 4.41–4.25 (m, 2 H, C*H*), 4.09–3.30 (m, 18 H, C*H*₂, wherefrom δ 3.73 (dd, 6 H, C*H*₃, *J*_{HH'} = 7 Hz, *J*_{PH} = 14 Hz)), 3.13 (dd, 6 H, C*H*₃, *J*_{HH'} = 7 Hz, *J*_{PH} = 13 Hz), 2.49 (dd, 6 H, C*H*₃, *J*_{HH'} = 7 Hz, *J*_{PH} = 14 Hz), 2.14 (dd, 6 H, C*H*₃, *J*_{HH'} = 7 Hz, *J*_{PH} = 16 Hz). ³¹P NMR (CDCl₃): δ 40.2 (t, 2 P, ²*J*_{PP'} = 9.0 Hz), 37.5 (t, 2 P). MS (FAB⁺): *m*/*z* 874 (M⁺, 16), 839 ([M – Cl]⁺, 100). Anal. Calcd for C₃₆H₅₆Cl₂OsP₄: C, 49.48; H, 6.46. Found: C, 49.49; H, 6.43.

[OsCl(dcpe)₂]BPh₄, [3a]BPh₄. A simplified synthesis was employed: *trans*-[OsCl₂(dcpe)₂] (3.04 g, 2.75 mmol) and TlPF₆ (960 mg, 2.75 mmol) were suspended in CH₂Cl₂ (50 mL), and the mixture was stirred overnight at room temperature. The thallium chloride that formed was filtered off, Pr'OH (40 mL) was added, and CH₂Cl₂ was removed under vacuum to yield a dark brown precipitate of [**3a**]PF₆. Yield: 2.38 g (71%). A slurry of [**3a**]PF₆ (121.6 mg, 0.10 mmol) and NaBPh₄ (171 mg, 0.50 mmol) was stirred for 10 min in CH₂Cl₂ under vacuum gave brown [**3a**]BPh₄, which was filtered off and vacuum-dried. Yield: 119 mg (86%). Analytical and spectroscopic data were as reported in ref 14.

[OsBr(dcpe)₂]PF₆, [3b]PF₆. An improved synthesis was again employed: *trans*-[OsBr₂(dcpe)₂] (4.20 g, 3.5 mmol) and TlPF₆ (1.22 g, 3.5 mmol) were suspended in CH₂Cl₂ (50 mL), and the mixture was stirred overnight at room temperature. The thallium bromide that formed was filtered off, PrⁱOH (40 mL) was added, and CH₂Cl₂ was removed under vacuum, yielding an almost black precipitate. Yield: 3.99 g (87%).³¹P NMR (CDCl₃): δ 40.8 (t, 2 P, ²*J*_{PP'} = 1.8 Hz), 26.7 (t, 2 P, ²*J*_{PP'} = 1.8 Hz). Analytical data were as in ref 14.

[OsCl(Me-duphos)_]PF₆, [3d]PF₆. Complex **2d** (87 mg, 0.1 mmol) was dissolved in CH₂Cl₂ (10 mL), TIPF₆ (34 mg, 0.15 mmol) was added, and the solution was stirred overnight. TICl was then filtered off, and Pr'OH (20 mL) was added. Evaporation of CH₂Cl₂ under vacuum afforded red microcrystals. Yield: 71 mg (72%). ¹H NMR (CDCl₃): δ 7.85 (br, 2 H, Ph *H*), 7.54–7.33 (m, 6 H, Ph *H*), 3.24 (s br, 2 H, CH), 3.08 (br, 2 H, CH), 2.48–2.32 (m, 4 H, CH), 2.20–2.03 (m, 8 H, CH₂), 1.94–1.53 (m, 8 H, CH₂), 1.47 (dd, 6 H, CH₃, J_{HH'} = 8 Hz, J_{PH} = 18 Hz), 1.28 (dd, 6 H, CH₃, J_{HH'} = 7 Hz, J_{PH} = 17 Hz), 0.45 (dd, 6 H, CH₃, J_{HH'} = 7 Hz, J_{PH} = 15 Hz). ³¹P NMR (CDCl₃): δ 76.1 (t, 2 P, ²J_{PP'} = 5.5 Hz), 42.6 (t, 2 P), -143 (septet, 1 P, PF₆, ¹J_{PF} = 710 Hz). MS (FAB⁺): *m*/z 839 (M⁺, 100), 755 ([M - C₆H₁₂]⁺, 8). Anal. Calcd for C₃₆H₃₆ClF₆OsP₅: C, 43.97; H, 5.74. Found: C, 43.71; H, 5.91.

[OsCl(η²-O₂)(dcpe)₂]BPh₄, [4a]BPh₄. A slurry of [3a]PF₆ (0.846 g, 0.70 mmol) and NaBPh4 (1.195 g, 3.5 mmol) in CH2Cl2 (50 mL) and PriOH (10 mL) was stirred for 10 min, after which more PriOH (100 mL) was added. CH₂Cl₂ was then removed under vacuum, and the precipitate was filtered off and dissolved in CH2Cl2/PriOH (200 mL, 1:1 v/v). This solution was stirred under O₂ (1 atm) at room temperature for 1 h. The CH₂Cl₂ was then removed under vacuum, and the resulting light green [4a]BPh₄ was filtered off. Yield: 0.751 g (87%). The presence of CH₂Cl₂ (0.5 equiv) was supported by ¹H NMR spectroscopy. ¹H NMR (CDCl₃): δ 7.39 (s, 8 H, Ph H), 7.09 (t, 8 H, Ph H, $J_{\text{HH}'} = 7.4 \text{ Hz}$), 6.93 (t, 4 H, Ph H, $J_{\text{HH}'} = 7.1 \text{ Hz}$), 2.5–2.2 (m, 12 H, PCH₂, PCH), 2.2-1.7 (m, 44 H, C₆H₁₁), 1.7-1.2 (m, 40 H, C_6H_{11}). ³¹P NMR (CDCl₃): δ -4.0 (s, 4 P). UV-vis (CH₂Cl₂) λ_{max} , nm (ϵ_{max} , M⁻¹ cm⁻¹): 345 (sh), 435 (sh). MS (FAB⁺): m/z 1104 ([M $([M - O]^+, 100), 1071 ([M - 2O]^+, 11), 921 ([M - 2O]^+, 12))$ $- O - 2C_6H_{11}]^+$, 14), 665 ([M - O - dcpe]⁺, 8). Anal. Calcd for C₇₆H₁₁₆BCl₃O₂OsP₄•0.5CH₂Cl₂: C, 62.74; H, 8.05. Found: C, 62.87; H, 8.09.

[OsBr(η^2 -O₂)(dcpe)₂]**BPh**₄, [4b]**BPh**₄. A CH₂Cl₂ solution of [OsBr-(dcpe)₂]PF₆ (56.3 mg, 45 μ mol) was stirred under an O₂ atmosphere for 3 h, after which PrⁱOH (30 mL) and NaBPh₄ (70 mg, 200 μ mol) in CH₂Cl₂ (20 mL) were added. CH₂Cl₂ was removed under vacuum, and the resulting precipitate was filtered off and vacuum-dried. Yield: 56 mg (85%). ¹H NMR (CDCl₃): δ 7.85 (s, 8 H, Ph *H*), 7.4–7.3 (m, 8 H, Ph *H*), 7.1–7.0 (m, 4 H, Ph *H*), 2.4–0.9 (m, 96 H, PCH₂, PCH, C₆H₁₁).

³¹P NMR: δ -8.6 (s, 4 P). MS (FAB⁺): m/z 1148 ([M + H]⁺, 100), 1131 ([M - O]⁺, 48), 1115 ([M - 2O]⁺, 20), 965 ([M - O - 2C₆H₁₁]⁺, 4), 709 ([M - O - dcpe]⁺, 8). Anal. Calcd for C₇₆H₁₁₆BBrO₂OsP₄: C, 62.24; H, 7.97; O, 2.18. Found: C, 62.27; H, 8.11; O, 2.46.

[OsCl(η^2 -**O**₂)(**dep**)₂]**PF**₆, **[4c**]**BPh**₄. Complex 2c (67 mg, 0.1 mmol) and TlPF₆ (35 mg, 0.1 mmol) were dissolved in MeOH (10 mL). After 10 min of stirring, the TlCl that formed was filtered off, the volume of the solution was reduced under vacuum, and hexane (10 mL) was added. The resulting precipitate was then filtered off and treated with NaBPh₄ as described for **[4b**]BPh₄. Yield: 49 mg (60%). This substance contained traces of **[5c**]BPh₄. ¹H NMR (CDCl₃): δ 2.54–1.85 (m, 24 H, CH₂), 1.55–0.86 (m, 24 H, CH₃). ³¹P NMR: δ 9.6 (s, 4 P). MS (FAB⁺): m/z 671 (M⁺, 95), 656 ([M – O + H]⁺, 64), 640 ([M – 2O + H]⁺, 100), 205 ([depe – H]⁺, 10). Anal. Calcd for C₄₄H₆₈BClO₂-OsP₄: C, 53.42; H, 6.93. Found: C, 53.52; H, 6.89.

trans-[OsCl(O)(dcpe)₂]PF₆, [5a]PF₆, [3a]PF₆ (1.286 g, 1.06 mmol) was dissolved in CH₂Cl₂ (50 mL) and PrⁱOH (100 mL), and the solution was was stirred in air for 2 d. Evaporation of the CH₂Cl₂ under vacuum yielded [5a]PF₆ as a light brown solid. Yield: 1.04 g (80%). ¹H NMR: see Table 2. ³¹P NMR (CDCl₃): δ –143 (septet, 1 P, PF₆, ¹J_{PF} = 710 Hz). MS (FAB⁺): *m*/z 1087 (M⁺, 100), 1071 ([M – O]⁺, 12), 921 ([M – 2C₆H₁₁]⁺, 19), 665 ([M – dcpe]⁺, 9). Anal. Calcd for C₅₂H₉₆-ClF₆OOsP₅: C, 50.70; H, 7.85; O, 1.30; Cl, 2.88. Found: C, 50.46; H, 7.99; O, 1.53; Cl, 3.09.

trans-[OsCl(O)(dcpe)₂]BPh₄, [5a]BPh₄. [5a]PF₆ (123.1 mg, 0.10 mmol) and NaBPh₄ (171 mg, 0.50 mmol) were dissolved in CH₂Cl₂ (10 mL). Addition of CH₃OH (40 mL) and evaporation of CH₂Cl₂ under vacuum yielded a light brown precipitate, which was filtered off and vacuum-dried. Yield: 125 mg (89%). ¹H NMR (CDCl₃): δ 7.39 (s, 8 H, Ph *H*), 7.09 (t, 8 H, Ph *H*, *J*_{HH'} = 7.4 Hz), 6.93 (t, 4 H, Ph *H*, *J*_{HH'} = 7.1 Hz); for **5a** data, see Table 2. UV–vis (CH₂Cl₂) λ_{max} , nm (ϵ_{max} , M⁻¹ cm⁻¹): 350 (2200), 410 (sh), 480 (sh), 575 (sh). MS (FAB⁺): *m*/*z* 1087 (M⁺, 100), 1071 ([M – O]⁺, 12), 921 ([M – 2C₆H₁₁]⁺, 19), 665 ([M – dcpe]⁺, 9). Anal. Calcd for C₇₆H₁₁₆BClOOsP₄: C, 64.92; H, 8.31; O, 1.14; Cl, 2.52. Found: C, 64.74; H, 8.38; O, 1.13; Cl, 2.43.

trans-[**OsBr(O)(dcpe)**₂]**BArF**, [**5b**]**BArF**. [**3b**]**P**F₆ (1.00 g, 0.80 mmol) was dissolved in CH₂Cl₂ (50 mL), and the solution was stirred in air for 2 d. The resulting complex $[OsBr(\eta^2-O_2)(dcpe)_2]PF_6$ was treated with gaseous HCl for 1 min. After 12 h of stirring, the mixture was filtered, and the filtrate was treated with NaBArF (710 mg, 0.80 mmol). Addition of ⁱPrOH (100 mL) and removal of CH₂Cl₂ under vacuum gave a brown product. Yield: 1.03 g (66%). ¹H NMR (CDCl₃): δ 7.79 (s, 8 H, Ph *o*-H), 7.63 (s, 4 H, Ph *p*-H); for **5b** data, see Table 2. MS (FAB⁺): m/z 1131 (M⁺, 100), 1115 ([M – O]⁺, 84), 1049 ([M – HBr]⁺, 31), 965 ([M – 2C₆H₁₁]⁺, 27). Anal. Calcd for C₈₄H₁₀₈BBrF₂₄OOsP₄: C, 49.63; H, 5.35. Found: C, 49.63; H, 5.19.

trans-[OsCl(O)(dep)₂]PF₆, [5c]BPh₄. This complex was prepared similarly to [4c]BPh₄, but stirring was prolonged to 12 h before filtration and precipitation. Yield: 67 mg (84%). ¹H NMR: see Table 2. ³¹P NMR δ –143 (septet, 1 P, PF₆, ¹J_{PF} = 710 Hz). MS (FAB⁺): *m*/*z* 656 ([M + H]⁺, 100). Anal. Calcd for C₄₄H₆₈BClOOsP₄: C, 54.29; H, 7.04. Found: C, 54.22; H, 6.88.

Oxidation of Iodide with [4a]BPh4. A CH_2Cl_2 solution of [**4a**]BPh4 (0.2 mM, 1 mL) and a CH_2Cl_2 solution of [NBu4]I (2.0 mM, 1 mL) were mixed in a UV cuvette. The reaction was initiated by the addition of one drop of a saturated solution of anhydrous HCl in CH_2Cl_2 . The spectrum of the reaction solution recorded immediately after the addition and corrected for the absorbance of **5a** indicated that [I₃]⁻ was formed on the basis of the reference for the triiodide ion. Quantitative conversion (within experimental error) was calculated from absorbance data at 365 nm. Two measurements gave the same results. No reaction occurred without addition of acid. Blank experiments omitting HCl gave no reaction.

X-ray Structure Determinations. Crystals of $[OsCl(dcpe)_2]PF_6$ ([**3a**]PF₆), $[OsBr(dcpe)_2]PF_6$ ([**3b**]PF₆), $[OsCl(\eta^2-O_2)(dcpe)_2]BPh_4$ ([**4a**]-BPh₄), and *trans*- $[OsCl(O)(dcpe)_2]BPh_4$ ([**5a**]BPh₄) were obtained by slow evaporation of concentrated CH₂Cl₂/PrⁱOH solutions of the respective complexes. Crystals of [**3a**]PF₆ and [**3b**]PF₆ were grown in a glovebox under purified N₂. Data were collected on a Siemens CCD SMART area detector system equipped, except for the [**3b**]PF₆ study (four-circle diffractometer Syntex P2₁), with a normal-focus Mo-target X-ray tube. Unit cell dimension determinations and data reductions were performed by standard procedures. An empirical absorption correction (SADABS) was applied for **3a**, **4a**, and **5a**. The structures were solved with SHELXS-96 using direct methods and refined by full-matrix least-squares calculations based on F^2 with anisotropic displacement parameters for all non-H atoms. Disordered atoms were refined isotropically. Hydrogen atoms (bound to nondisordered C atoms) were introduced at calculated positions and refined with a riding model using individual isotropic thermal parameters for each group. Further details of the crystallographic determinations are given in the Supporting Information.

Maximum and minimum difference peaks for $[3a]PF_6$ were +0.71and -0.55 e Å⁻³; the largest and the mean Δ/σ values were -0.638and +0.007. In $[3b]PF_6$, cyclohexyl C(15)–C(20) is disordered and was split between two chair conformations with 64:36 refined occupancies. Maximum and minimum difference peaks were +3.834 and -1.907 e Å⁻³ (at 1.18 Å from Os); the largest and the mean Δ/σ values were -0.002 and 0.000. In [4a]BPh₄, cyclohexyl C(27)–C(32) is disordered and was split between two conformations with 7:3 refined occupancies. Maximum and minimum difference peaks were +1.765 and -1.851 e Å⁻³; the largest and the mean Δ/σ values were +0.014 and 0.000. In [5a]BPh₄, cyclohexyl C(47)–C(52) and phenyl C(71)–C(76) are disordered and were split between two conformations with equal refined occupancies and isotropic displacement parameters. Complete results are reported in the Supporting Information.

Supporting Information Available: A listing of NMR data for **5a** and **5b**, an ORTEP drawing of **3b**, and tables of crystal data, X-ray experimental details, atomic coordinates, thermal parameters, bond distances, and bond angles along with X-ray crystallographic files, in CIF format, for [**3a**]PF₆, [**3b**]PF₆, [**4a**]BPh₄, and [**5a**]BPh₄. This material is available free of charge via the Internet at http://pubs.acs.org.

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