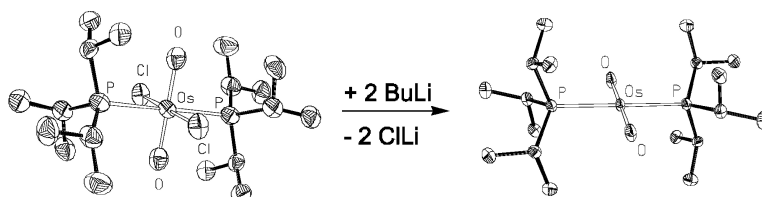


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J. Am. Chem. Soc., **2003**, 125 (44), 13344-13345 • DOI: 10.1021/ja037484u • Publication Date (Web): 10 October 2003

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Dioxygen Activation by an Osmium-dihydride: Preparation and Characterization of a d^4 Square-Planar Complex

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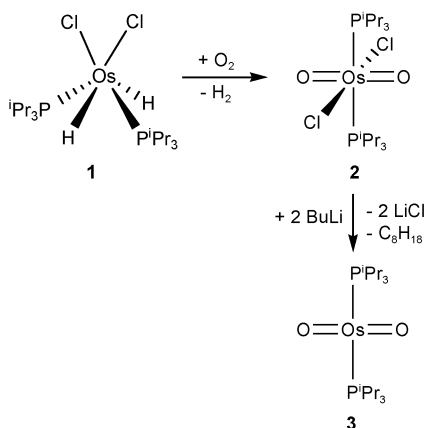
Received July 23, 2003; E-mail: maester@posta.unizar.es

Four-coordinate complexes are common, with a tetrahedral array of donor atoms being the most frequently observed. Square-planar derivatives are associated with d^8 configurations, where electronic factors strongly favor this arrangement. Thus, an almost unlimited number of Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III) compounds with a 16-electron configuration and general composition ML_4 (L = monodentate ligand) are known.¹ A few examples of corresponding Fe(0), Ru(0), and Os(0) derivatives have also been reported.²

Four-coordinate oxo complexes of the iron triad are tetrahedral d^0 or d^2 species.^{1,3} They are extremely important due to their applications for the *cis*-hydroxylation of alkenes to *cis*-diols.⁴ From a catalytic point of view, one of the major problems is the dioxygen activation. The reduction of the oxo compound by the organic substrate can directly occur. However, despite the advantage of air or dioxygen as the final oxidant, there are relatively few methods known which use homogeneous catalysts in the presence of oxygen under mild conditions.⁵ In general, the resultant reduced metallic species cannot be reoxidized by molecular oxygen but require stronger oxidants.⁶ In this context, the formation of oxo compounds by dioxygen activation is a reaction of general interest. In the iron triad, the formation of oxo derivatives from O_2 is common for the biomimetic systems based on the ferryl moiety, but is scarcely documented for ruthenium and osmium.⁷

We find now that for osmium not only it is possible to activate molecular oxygen but also to stabilize the first d^4 square-planar transition metal complex. The synthesis of this novel species, which is also a rare example of mononuclear osmium(IV)-oxo compound, takes place in a two-step procedure (Scheme 1). In toluene at room

Scheme 1



temperature, the dihydride $OsH_2Cl_2(PPr_3)_2$ (**1**) is capable of activating the oxygen–oxygen double bond of the molecular oxygen from the air or pure oxygen, to give the osmium(VI) dioxo *trans*- $OsO_2Cl_2(PPr_3)_2$ (**2**). Treatment of **2** in toluene with n BuLi affords

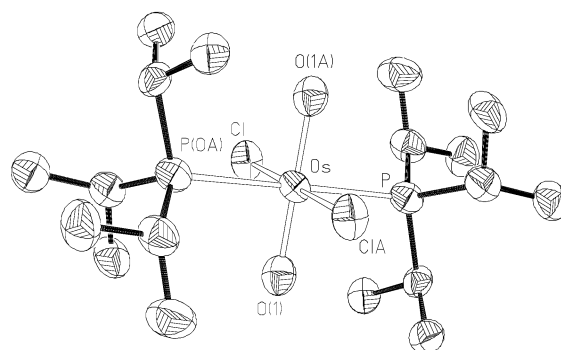


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Os–O(1) 1.767(6), Os–O(1A) 1.767(6), Os–Cl 2.3757(19), Os–Cl(A) 2.3757(19), Os–P 2.519(2), Os–P(OA) 2.519(2), O(1)–Os–O(1A) 180.00(15), P(OA)–Os–P 180.00(7), ClA–Os–Cl 180.00(7).

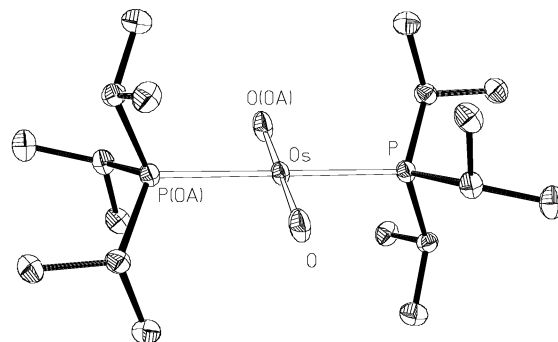


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Os–O(1) 1.743(2), Os–O(1A) 1.743(2), Os–P 2.4178(9), Os–P(OA) 2.4178(9), O(1)–Os–O(1A) 180.00(14), P(OA)–Os–P 180.00(4).

trans- $OsO_2(PPr_3)_2$ (**3**) and *n*-octane. Exposure of toluene solutions of **3** to air gives rise to the precipitation of an insoluble black solid. *trans*-Dioxoosmium(IV) compounds have been previously suggested as short-lived species in electrochemical studies of *trans*-dioxoosmium(VI) complexes.¹¹

Figures 1 and 2 show the molecular diagrams of **2** and **3**. The geometry of **2** is octahedral with O–Os–O, Cl–Os–Cl, and P–Os–P angles of 180°. The geometry of **3** can be described as derived from that of **2** by loss of two chlorine ligands and shortening of the Os–O and Os–P bonds. Thus, the O–Os–O and P–Os–P angles are also 180°, while the Os–O (1.743(2) Å) and Os–P (2.4178(9) Å) bond lengths are about 0.03 and 0.1 Å, respectively, shorter than the Os–O (1.767(6) Å) and Os–P (2.519(2) Å) distances found in **2**.

In agreement with the presence of *trans*-oxo ligands in these compounds, their IR spectra show a single Os–O stretch at 841 (**2**) and 838 (**3**) cm^{-1} . The NMR data reveal the high symmetry of

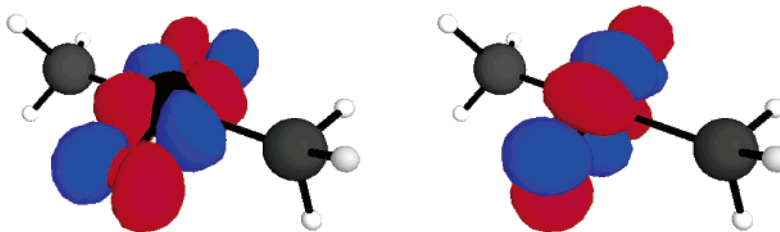


Figure 3. Schematic view of the LUMO (left) and LUMO+1 (right) orbitals of the model compound $\text{OsO}_2(\text{PH}_3)_2$.

the molecules. Thus, the ^1H NMR spectra contain a doublet of virtual triplets (δ 1.41; **2** and **3**) for the methyl protons of the phosphine ligands, whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra display singlets at 2.2 (**2**) and 30.1 (**3**) ppm.

To understand the stability of **3**, DFT calculations on the model complex $\text{OsO}_2(\text{PH}_3)_2$ have been carried out, without symmetry restrictions. The calculated geometry agrees well with that obtained by X-ray diffraction analysis, and it is similar to that calculated for the spectroscopically detected species $\text{OsO}_2(\text{CO})_2$.¹² The electron filling pattern is in agreement with a formal d^4 electron count for the metallic ion. The occupied HOMO and HOMO–1 orbitals have mainly d character of nonbonding nature. The three next empty orbitals (LUMO, LUMO+1, LUMO+2) are of metal–ligand antibonding character. The LUMO and LUMO+1 orbitals (Figure 3) result from π -antibonding interactions between π -donor p orbitals of the oxygen atoms and d orbitals of the metal, whereas LUMO+2 is a σ -phosphorus–osmium antibonding orbital. Their high energy leads to a sizable HOMO–LUMO gap, which reflects the stability of the molecule.

Acknowledgment. We thank MCYT of Spain for financial support (Projects RPQ2000-0488-94-02 and BQU2002-00606). E.R. thanks CSIC and the European Social Fond for funding through the I3P Program.

Supporting Information Available: Details of DFT calculations for model complexes $\text{OsO}_2\text{Cl}_2(\text{PH}_3)_2$ and $\text{OsO}_2(\text{PH}_3)_2$, as well as crystal structure determinations, including bond lengths and angles of compounds **2** and **3** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Synthesis of $\text{OsO}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$, **2**: A suspension of 2.70 g (4.60 mmol) of **1** in 10 mL of toluene was stirred at room temperature in an opened-air flask for 48 h; the black precipitate is separated by filtration, washed with pentane, and dried under vacuum. Yield: 74%. Anal. Calcd for $\text{C}_{18}\text{H}_{42}\text{O}_2\text{OsP}_2$: C, 35.23; H, 6.90. Found: C, 35.24; H, 7.07. MS (FAB^+): 614 (M^+). IR (PET): ν ($\text{Os}=\text{O}$) 841 cm^{-1} . UV–vis (λ nm/ ϵ_0 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 316/1221, 375/1179. ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 3.23 (m, 6H, PCH), 1.41 (dvt, 18H, $N = 14.1$, PCCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CDCl_3 , 293 K): δ 2.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.42 MHz, CD_2Cl_2 , 293 K): δ 22.4 (vt, $N = 22$, PCH), 18.2 (s, PCCH_3).
- (10) Synthesis of $\text{OsO}_2(\text{P}^i\text{Pr}_3)_2$, **3**: A toluene solution of **2** (0.70 g 1.10 mmol) was treated at room temperature with 0.9 mL (2.30 mmol) of a 2.5 M pentane solution of $n\text{BuLi}$ and stirred for 6 h. The solution was filtered and evaporated to dryness to afford **3** as a brown solid. Yield: 78%. Anal. Calcd for $\text{C}_{18}\text{H}_{42}\text{O}_2\text{OsP}_2$: C, 39.80; H, 7.80. Found: C, 40.02; H, 7.94. MS (FAB^+): 546 ($\text{M} + \text{H}^+$). IR (PET): ν ($\text{Os}=\text{O}$) 838 cm^{-1} . UV–vis (λ nm/ ϵ_0 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 288/2570, 316/1789. ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 2.25 (m, 6H, PCH), 1.41 (dvt, 18H, $N = 13.7$, PCCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, C_6D_6 , 293 K): δ 30.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.42 MHz, CD_2Cl_2 , 293 K): δ 24.9 (vt, $N = 22$, PCH), 20.5 (s, PCCH_3).
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JA037484U