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Dihydroxylation of alkenes using a Tp–osmium complex

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Dedicated to Jerry Trofimenko for his inspiration and enthusiasm, and for the Tp ligands.

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ABSTRACT

The reaction of $TpOs^{VI}(N)(OH)_2$ (**1**) [Tp = hydrotris(1-pyrazolyl)borate], *m*-chloroperbenzoic acid (*m*-CPBA), and *trans*-stilbene in C_6H_6 at room temperature gives the diolate complex $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**) and *m*-chlorobenzoic acid (*m*-CBA). The *trans* configuration of the stilbene is retained in the diolate complex as shown in the crystal structure of **2**. Complex **2** is hydrolyzed by 2 equivalents of aqueous HCl in CD_2Cl_2 to give *rac*-hydrobenzoin, the product of *cis*-dihydroxylation, and $TpOs^{VI}(N)Cl_2$. *cis*-Stilbene, styrene, cyclohexene, *trans*-dimethyl fumarate, *trans*-methyl cinnamate, and *trans*-4-dimethylamino-4′-nitrostilbene are also converted to their corresponding free diol products by reaction with **1** and *m*-CPBA in CD_2Cl_2, and then aqueous HCl. In aqueous HBF_4, oxidation of the water-soluble olefin, 4-styrenesulfonic acid, by **1** is modestly catalytic (15 turnovers in 3 h) with excess PbO_2 as the oxidant. Under non-acidic conditions, the diolate complexes are inert and catalysis is precluded. Mechanistic experiments implicate an oxidizing osmium complex as an intermediate in these reactions.

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1. Introduction

Metal-catalyzed olefin oxidations are important reactions, from the chiral *cis*-dihydroxylation of olefins by ligated osmium tetroxide, $Os^{VIII}O_4(L)$ [1], to epoxidations with hydrogen peroxide over titanium silicalite TS1 [2] and many other processes [3]. While many metal systems perform various kinds of olefin oxidations, there are few complexes that accomplish dihydroxylation [4]. The classical examples of dihydroxylation are by osmium tetroxide, permanganate, and related simple polyoxo compounds [1,5]. In recent years, interesting dihydroxylating iron and manganese systems have also been developed [6]. For the reaction of $OsO_4(L)$ with alkenes to give Os^{VI} diolates, experimental and theoretical studies indicate a concerted [3+2] mechanism involving a pericyclic direct addition of the alkene to an O═Os═O unit [7–10]. The Os^{VI} diolate complex is then hydrolyzed to release the diol product and form an Os^{VI} hydroxide species such as osmate, $Os(O)_2(OH)_4^{2-}$. Oxidation of osmate by a terminal oxidant regenerates Os^{VIII} and completes the catalytic cycle.

We have been studying the oxidation chemistry of osmium compounds supported by a hydrotris(1-pyrazolyl)borate (Tp) ligand [11–16]. We have found that Tp is a good supporting ligand for oxidizing complexes despite the presence of the borohydride functionality [14,15]. As part of these studies, we reported the Tp–Os^{VI} complex $TpOs^{VI}(N)(OH)_2$ (**1**) [16] that has a *cis*-bis-hydroxide motif resembling osmate. Complex **1** is prepared from the dichloride complex $TpOs^{VI}(N)Cl_2$ [11], by initial chloride metathesis to acetate using AgOAc [12]. This is a rare example of a reaction of $TpOs^{VI}(N)Cl_2$ that does not occur at the electrophilic nitrido ligand [11,12,17]. Further reaction of $TpOs^{VI}(N)(OAc)_2$ with NaOH affords the bis-hydroxide complex **1**, by direct substitution of the acetates with hydroxides [16]. Complex **1** was prepared with the goal of oxidizing it to an Os^{VIII} species such as "$TpOs(N)(O)_2$". This paper presents our exploration of the oxidation chemistry of **1**, in particular the oxidations of olefins with **1** and *m*-chloroperbenzoic acid (*m*-CPBA) to give osmium(VI) diolate complexes. This is a new example of a system that accomplishes *cis*-dihydroxylation of alkenes.

2. Results and discussion

2.1. Synthesis and characterization of $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (2)

Stirring $TpOs^{VI}(N)(OH)_2$ (**1**) with 1 equivalent each of *m*-chloroperbenzoic acid (*m*-CPBA) and *trans*-stilbene in C_6H_6 at room temperature for 5 min yields *m*-chlorobenzoic acid (*m*-CBA) and the orange-red diolate complex $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**) (Eq. (1)). Complex **2** is isolated in 95% yield using silica gel chromatography. *Trans*-stilbene oxidation occurs with retention of the *trans* configuration as revealed by the ^1H NMR spectrum of **2**, which shows two different methinyl diolate protons (δ 5.40, 5.48 in

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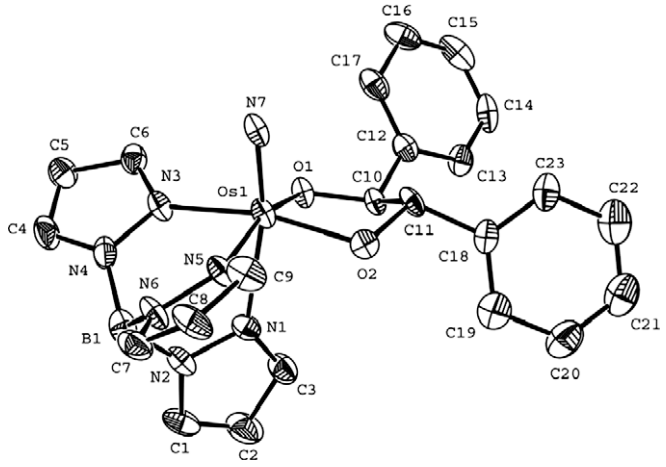
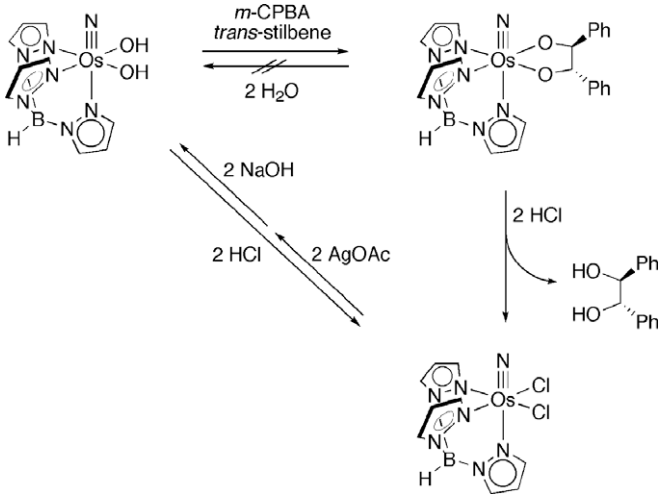
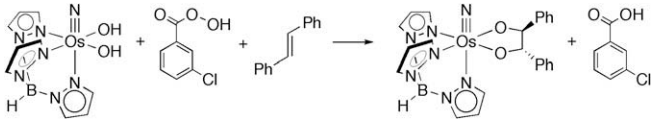


Fig. 1. ORTEP of $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**). Thermal ellipsoids are drawn at 30% probability level, and hydrogen atoms are omitted for clarity.



Scheme 1.

CD_2Cl_2) and nine pyrazole resonances (δ 6.11–8.19), indicating that **2** has C_1 symmetry. This is in contrast with the related complexes $TpOs^{VI}(N)X_2$ (X = Cl, OAc, or OH), which show C_s symmetry, with six pyrazole peaks in a 2:2:2:1:1:1 ratio in the ^{1}H NMR [11,12,14]. It should be noted that under the conditions of reaction 1, the oxidation of *trans*-stilbene by *m*-CPBA alone is negligible (see below).

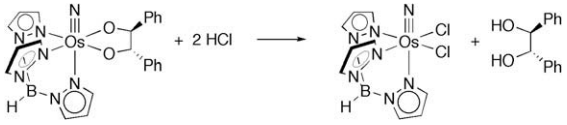


(1)

Crystals of **2** were grown from CH_2Cl_2/hexanes solutions, and the structure was solved by direct methods. The ORTEP of **2** is shown in Fig. 1, and the metrical parameters are shown in Table 1 (see Section 4.3 for selected crystallographic data). The ORTEP of **2** shows a distorted octahedral molecule with all of the ligands bent away from the nitrido ligand N(7), typical of complexes with a single nitrido or oxo group [18]. The Os≡N distance of 1.680(8) Å is within the 1.602(20)–1.70(2) Å range of such bond lengths in $TpOs^{VI}(N)X_2$ complexes (X = Cl, Me, Ph, O_2CCF_3, NO_3, or OH) [11a,12,14]. The Os–O distances in **2** (1.940(6) and 1.946(6) Å) are similar to those of **1** (1.956(7) and 1.941(8) Å) [14].

2.2. The reaction of $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**) with HCl

The reaction of **2** with 2 equivalents of aqueous HCl in CD_2Cl_2 yields the Os^{VI} nitrido-dichloride complex $TpOs^{VI}(N)Cl_2$ [11], and *rac*-hydrobenzoin (Eq. (2)), as observed by ^{1}H NMR. *Rac*-hydrobenzoin is the product of *cis*-dihydroxylation of *trans*-stilbene; its formation was confirmed by comparison of the NMR spectra with those of an authentic sample. Removal of the diolate from the osmium center requires strongly acidic conditions; no reaction is observed between **2** and H_2O in the absence of acid. Similar behavior has been observed for other $TpOs(N)(OR)_2$ compounds. The bis-acetate complex $TpOs^{VI}(N)(OAc)_2$ reacts with acids HX in which X is a coordinating anion to give $TpOs^{VI}(N)X_2$ [12]. The hydroxide and diolate complexes appear to react similarly. Thus catalytic oxidations could not be simply achieved by adding H_2O (Scheme 1); see Section 2.4.



(2)

2.3. Reactions with other olefins

The reaction of **1** with *m*-CPBA and other olefins also forms their corresponding diolate complexes. For example, reacting **1** with 1 equivalent each of *m*-CPBA and *cis*-stilbene in CD_2Cl_2 gives $TpOs^{VI}(N)(cis\text{-}O_2C_2H_2Ph_2)$ (**3**). ^{1}H NMR spectra of the reaction show that **3** is a roughly 1:1 mixture of two diastereotopic diolate products. Twelve pyrazole resonances are observed, in two sets of the characteristic peaks for C_s symmetry of the Tp compounds: 2 doublets + 1 triplet each of intensity two, and 2 doublets + 1 triplet of intensity one. The two isomers each have the phenyl

Table 1
Selected bond lengths and angles for $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**).

Bond	Length (Å) or Angle (°)	Bond	Length (Å) or Angle (°)
Os(1)–N(1)	2.296(8)	Os(1)–O(1)	1.946(6)
Os(1)–N(3)	2.084(8)	Os(1)–O(2)	1.940(6)
Os(1)–N(5)	2.080(8)	Os(1)≡N(7)	1.680(8)
N(3)–Os(1)–N(1)	78.2(3)	O(1)–Os(1)–N(1)	85.6(3)
N(5)–Os(1)–N(1)	78.2(3)	O(2)–Os(1)–N(1)	86.1(3)
N(3)–Os(1)–N(5)	91.2(3)	O(1)–Os(1)–N(3)	89.7(3)
N(1)–Os(1)–N(7)	166.1(3)	O(2)–Os(1)–N(3)	162.9(3)
N(3)–Os(1)–N(7)	93.3(3)	O(1)–Os(1)–N(5)	163.2(3)
N(5)–Os(1)–N(7)	91.2(3)	O(2)–Os(1)–N(5)	92.1(3)
O(1)–Os(1)–O(2)	82.3(3)	O(1)–Os(1)–N(7)	105.5(3)
		O(2)–Os(1)–N(7)	103.4(3)

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