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New Osmium-Based Reagent for the Dihydroxylation of Alkenes

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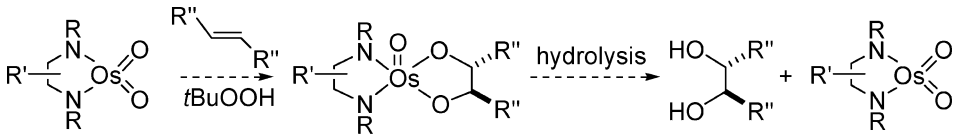

The cis dihydroxylation of alkenes is most efficiently accomplished by reaction with osmium tetroxide. Recently, the expense and toxicity of osmium tetroxide have led to a number of attempts to harness alternative osmium-based reagents, including microencapsulation and solid support techniques. We describe here the development of a new nonvolatile, stable, and recoverable osmium-based reagent devised for the stoichiometric cis dihydroxylation of alkenes. Although attempts to make this new dihydroxylation work with catalytic amounts of this reagent were unsuccessful, we did develop a sensitive test for free osmium tetroxide leached from the reagent in situ: this test may well have uses in probing future applications of derivatized osmium reagents.

Introduction

The syn-selective dihydroxylation of alkenes by osmium tetroxide has been known for almost 100 years.[1] More recently, the reaction has been developed into a highly efficient process using catalytic osmium tetroxide and a reoxidant,[2] most commonly *N*-methylmorpholine *N*-oxide (NMO) or potassium hexacyanoferrate. Moreover, the oxidation can also be accompanied by high levels of enantioselectivity in the product, and this variant of the reaction, the asymmetric dihydroxylation (AD), is one of the most powerful tools available to synthetic chemists.

However, as well as being difficult to recover, the disadvantages of using osmium tetroxide as a reagent include its expense, volatility, and toxicity. This has led to a large amount of research on the immobilization of osmium tetroxide using microencapsulation or solid support techniques in an attempt to overcome these disadvantages.[3] Our approach to this problem was to search for a new covalently bound osmium reagent to make the use and recovery of the transition metal more convenient.

In 2003, Muñiz published work on the first asymmetric diamination reaction based on diimidoosmium reagents originally developed by Sharpless.[4] The chiral (−)-8-phenylmenthol ester **1** reacted with osmium(VIII) species **2** at low temperature to give the stable complex **3** as a 94:6 ratio of diastereomers, separable by column chromatography (Scheme 1). Reduction of the major diastereomer with lithium aluminum hydride gave the enantiopure diamine **4**.

Recent work by Sharpless on the asymmetric aminohydroxylation reaction (AA) highlighted a class of compounds, namely, α-*β*-unsaturated carboxylic acids, that reacted remarkably ef-

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[||] Avlon Works.

(1) Makowka, O. *Chem. Ber*. **1908**, *41*, 943.

(2) (a) Hofmann, K. A. *Chem. Ber*. **1912**, *49*, 3329. (b) Hofmann, K. A.; Ehrhart, O.; Schneider, O. *Chem. Ber*. **1913**, *46*, 1657. (c) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1936**, *58*, 1302. (d) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1937**, *59*, 2345. (e) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *23*, 1973. (f) Byers, A.; Hickinbottom, W. J. *J. Chem. Soc*. **1948**, 1328. (g) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986. (h) Bucourt, R. U.S. Patent 3383385, 1968. (i) Minato, M.; Yamamoto, K.; Tsuji, J. *J. Org. Chem*. **1990**, *55*, 766. (j) Kwong, H.-L.; Sorato, C.; Ogino, Y.; Chen, H.; Sharpless, K. B. *Tetrahedron Lett*. **1990**, *31*, 2999.

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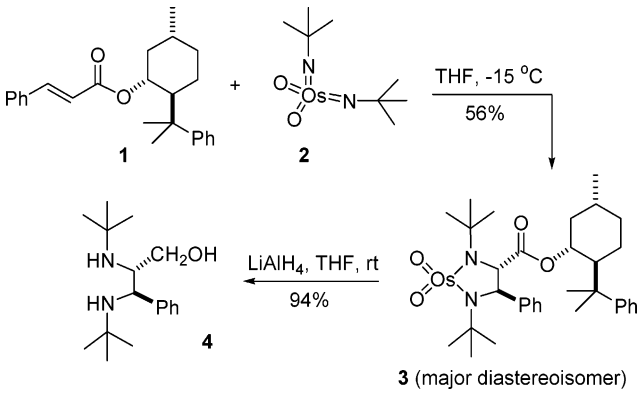
SCHEME 1. Asymmetric Diamination of Olefins



ficiently in the aminohydroxylation reaction yet perturbed the influence of the chiral ligands.[5] The reason for this observation was postulated to involve the second catalytic cycle (which is normally unresponsive to chiral amine ligands). In this second catalytic cycle, the amino-alcohol displaces the initially formed diol from the osmium glycolate, forming the persistent osmium(VI) intermediate **5** (Figure 1). This intermediate is then oxidized to osmium(VIII) species **6** before undergoing a cycloaddition reaction with the olefin. In fact, Sharpless has harnessed this mechanistic reasoning to design enantiopure amino-alcohols that do impart enantioselectivity onto the AD reaction through the second cycle.[2b,6]

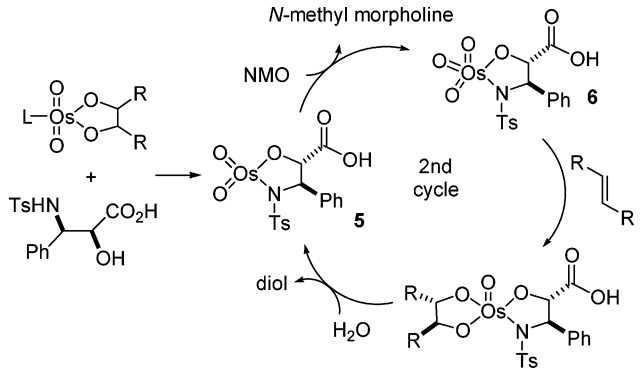


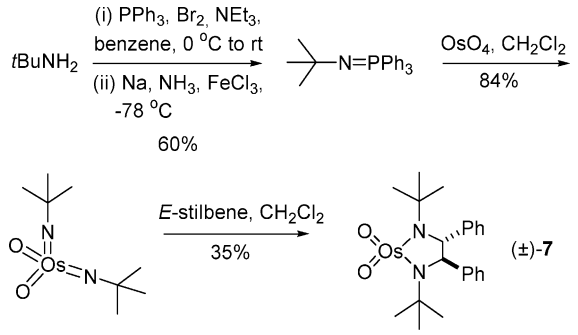
FIGURE 1. Second catalytic cycle for dihydroxylation.

We noticed that stable osmium(VI) complex **3** was comparable in structure to the putative osmium(VI) intermediate **5**. If complexes such as **3** could be oxidized to their corresponding osmium(VIII) species, then they may also undergo cycloadditions with olefins and could be used as a precursor to dihydroxylation rather than as an intermediate in diamination. The benefits of a new reagent of this sort include ease of use (including metal recovery) and the potential for development of a chiral osmium complex leading to enantioselective dihydroxylation.

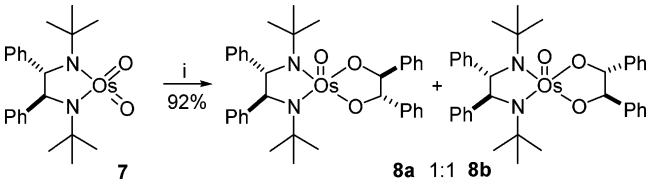
Results and Discussion

Therefore, we set out to make and investigate the crystalline osmium complex **7** following the method described by Sharpless

SCHEME 2. Synthesis of Dihydroxylation Precursor



SCHEME 3. Dihydroxylation of Stilbene[a]



[a] Reagents and conditions: (i) *E*-stilbene, *t*-BuOOH, CH_2Cl_2.

(Scheme 2).[7,8] The structure of **7** was confirmed by X-ray crystallography.

On addition of 1 equiv of **7** to a solution of *trans*-stilbene in CH_2Cl_2 with hydrogen peroxide or *tert*-butyl hydroperoxide (*t*BuOOH) as the oxidant, the solution turned from red to orange over a period of 5 min and intermediate **8** was isolated by chromatography in excellent yield (92%) and as a 1:1 mixture of diastereoisomers, **8a** and **8b** (Scheme 3). These intermediates were found to hydrolyze slowly in wet CH_2Cl_2 to regenerate **7** and give a stilbene diol.

This reaction sequence proved that **7** could indeed act as a reagent for dihydroxylation. Moreover, reaction of **7** with both *trans*-octene and cyclohexene, with *t*BuOOH as the oxidant, also gave the corresponding intermediates **9** and **10** in high yield and as a 1:1 and 2:1 mixture of diastereomers, respectively (Scheme 4, Table 1). Intermediates **8**−**10** were fully characterized, and the presence of the oxo ligand on osmium was confirmed by the characteristic Os═O stretches at 906, 910, and 907 cm^{-1}, respectively.[9]

We then examined ways of hydrolyzing the intermediates **8**−**10** to release the diols. After optimization, the best conditions for hydrolysis were found to be heating at 60 °C in a 4:1 acetone/water mixture. Chemoselective hydrolysis of **8**−**10** under these conditions gave the corresponding diols (and recovered **7**) cleanly and in good yield (Scheme 4, Table 1). As a control, the three diols were also prepared by reaction of the corresponding alkenes with osmium tetroxide using the Upjohn procedure (cat. OsO_4, NMO, acetone/water).[2e] In each case, both methods gave identical products proving that dihydroxylation by osmium complex **7** does represent a syn dihydroxylation. These experiments show that **7** can be used as a new reagent for the stoichiometric syn dihydroxylation of alkenes.

(5) (a) Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3455. (b) Andersson, M. A.; Epple, R.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 472.

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(7) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.

(8) Zimmer, H.; Singh, G. *J. Org. Chem.* **1963**, *28*, 483.

(9) Assuming a square-based pyramidal geometry (see Figure 2) and discounting the possibility of stereoisomeric chelate ring conformations, we deduced that the stereoisomers of **8** and **9** must arise from a different configuration at the newly formed carbinol centers. However, the stereoisomers of **10** arise from a different configuration at the osmium center.

SCHEME 4. Regeneration of the Osmium Reagent

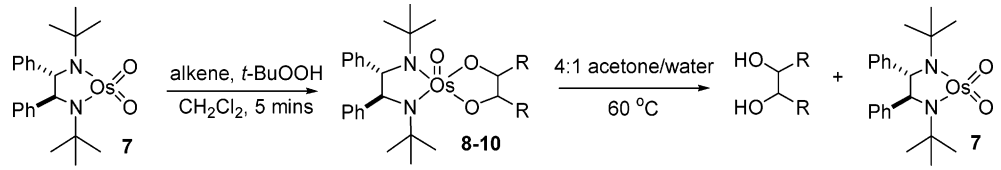
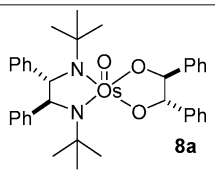
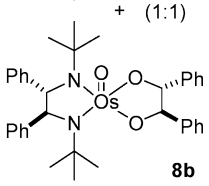
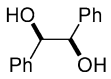
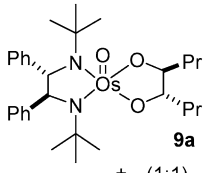
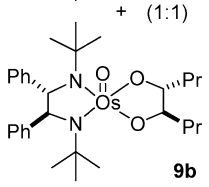
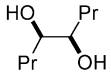
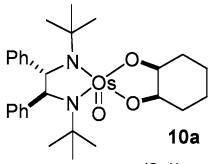
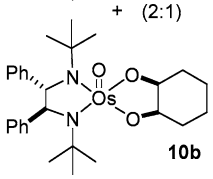
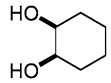


TABLE 1. Examples of the New Dihydroxylation Procedure

alkene	intermediate (from **7** + alkene)	yield of intermediate (%)	diol (from hydrolysis)	yield of diol (%)	recovered **7** (%)
E-stilbene	 **8a** + (1:1)  **8b**	92		87	88
E-octene	 **9a** + (1:1)  **9b**	96		91	94
cyclohexene	 **10a** + (2:1)  **10b**	96		60	89

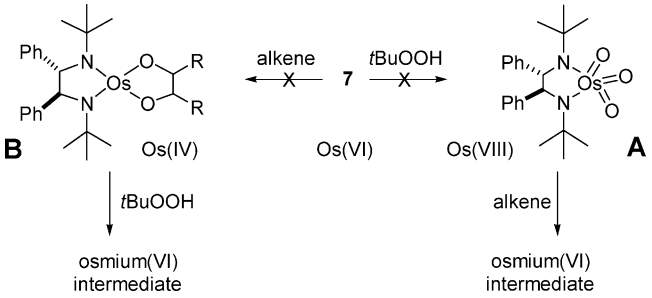
Mechanism of Dihydroxylation. The mechanism by which the alkene adds to the osmium reagent is unclear. However, two possible mechanisms can be ruled out by some control experiments (Scheme 5).

(1) Oxidation of **7** to an osmium(VIII) species prior to the cycloaddition does not occur on the time scale of the experiment because 99% of **7** can be recovered after reaction of **7** with excess *t*BuOOH over a 5 min period (the time it takes for intermediate formation to reach completion in the presence of an alkene).

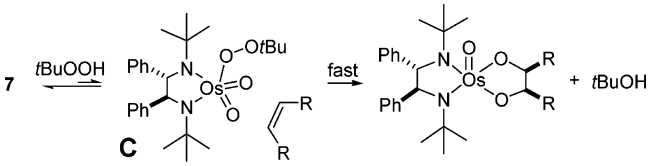
(2) A mixture of **7** and *E*-stilbene in $CDCl_3$ was monitored by NMR (no oxidant present), and these experiments showed that there was no discernible reaction between **7** and the alkene. If the osmium(IV) species **B** was formed, it should be readily oxidized to the osmium(VI) species not only by peroxides but also by other oxidizing agents. However, no intermediate is observed upon treatment of **7** and *E*-stilbene with NMO as the reoxidant (after 5 min). These results argue against irreversible direct cycloaddition of **7** and an alkene to give an osmium(IV) species prior to oxidation.

However, it is possible that either of the two reactions shown in Scheme 5 is reversible and that the equilibrium simply favors starting material **7**. In these cases, the small (and therefore unobserved) amount of **A** or **B** that is formed in solution could

SCHEME 5. Investigation into the Mechanism of Dihydroxylation



SCHEME 6. Potential Reactive Intermediate Formed in Situ

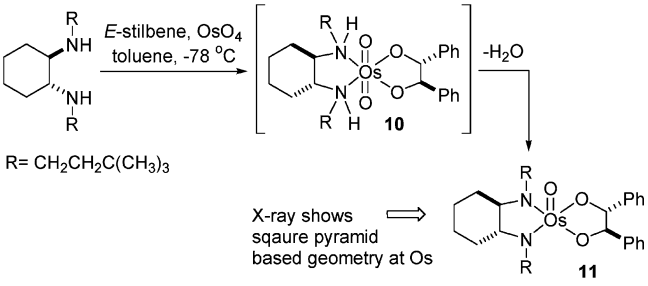


be removed irreversibly by reaction with an alkene (**A**) or an oxidant (**B**). We do not favor either of these possibilities because the reverse reaction of **A** to give **7** involves the oxidation of *tert*-butyl alcohol (which is a common and inert solvent for oxidations involving osmium(VIII)). The failure of NMO to oxidize a mixture of **7** and an alkene also mitigates against a reversible formation of **B** because we would expect NMO to rapidly oxidize the osmium(IV) intermediate even if it was formed in small amounts via a reversible process.

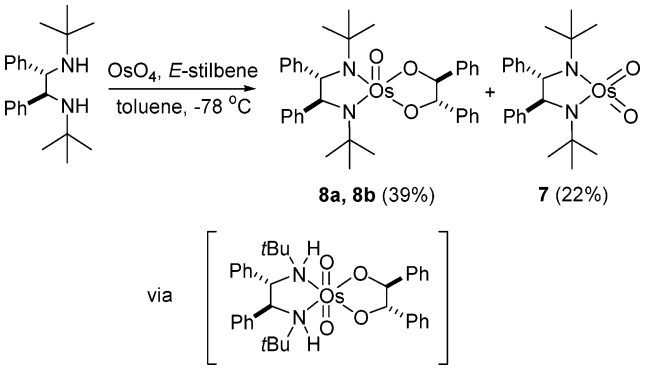
One other mechanism to be considered involves the formation of an adduct **C**, between **7** and *t*BuOOH, (Scheme 6). If this complex was reactive in the dihydroxylation reaction, then it would provide an explanation for the requirement that all three species (alkene, **7**, and peroxide) must be present before oxidation can occur. The formation of peroxy complexes of osmium has been invoked before to explain the extra oxidizing power that Oxone gives to osmium tetroxide during oxidative cleavage of alkenes.[10] However, attempts to find evidence for such a complex were unsuccessful. Mixtures of **7** and *t*BuOOH in chloroform were studied by IR and NMR spectroscopy; neither technique showed any new species formed when the two components interacted. However, it is worth pointing out that formation of a small amount of reactive intermediate (such as **C**) which is difficult to detect but is responsible for the progress of a reaction is commonplace in chemistry. An equilibrium between **7** and **C** that favored **7** by just 1−2 kcal mol^{-1} would be consistent with the observations that we have made (as long as **C** was much more reactive toward dihydroxylation). The relative inability of NMO to promote the dihydroxylation reaction may stem from a weaker binding constant or from a less-reactive intermediate analogous to **C**.

New Route to Osmium(VI) Diamine Complexes for Asymmetric Dihydroxylation. Unfortunately, investigation into osmium(VI) derivatives such as **7** is somewhat limited using Sharpless' method of preparation which cannot be used to make diimidodioxo osmium(VIII) complexes (e.g., **2**) which possess an (exocyclic) hydrogen β to nitrogen (decomposition ensues).[4] A further drawback is that this method involves a cycloaddition

SCHEME 7. Hanessian Route to the Dihydroxylation Reagents



SCHEME 8. Dihydroxylation Reagents from Diamines



of the diimidodioxo osmium(VIII) species to an alkene, and therefore (unless the alkene is chiral), the complexes thus prepared must be racemic. This had serious ramifications for the structures of oxidizing agents that we could access, and a new method of synthesis was sought.

While investigating the asymmetric dihydroxylation of olefins with simple chiral ligands, Hanessian observed the formation of osmium(VI) complex **11** arising from the dehydration of osmate ester **10** (Scheme 7).[11]

This dehydration method offers a new route into the osmium(VI) intermediates detailed above but with one major advantage. The intermediates made via the Hanessain route are derived from 1,2-diamines rather than from alkenes and are, therefore, no longer restricted to having *tert*-alkyl groups on nitrogen. It also means that enantiopure reagents should be accessible from reaction of the corresponding enantiopure diamines.

To test the validity of this route, (±)-1,2-diphenyl-*N*,*N*-1,2-di-*tert*-butylamine (prepared by $LiAlH_4$ reduction of **7**) was reacted with osmium tetroxide and stilbene in toluene at −78 °C. The reaction afforded intermediate **8** in 39% yield with 22% of **7** also isolated (presumably originating from in situ hydrolysis of **8**, Scheme 8). Both compounds **7** and **8** were identical to the compounds prepared by the method outlined previously, and so the Hanessian method does provide a quick and versatile route to the intermediates we sought directly from secondary 1,2-diamines.

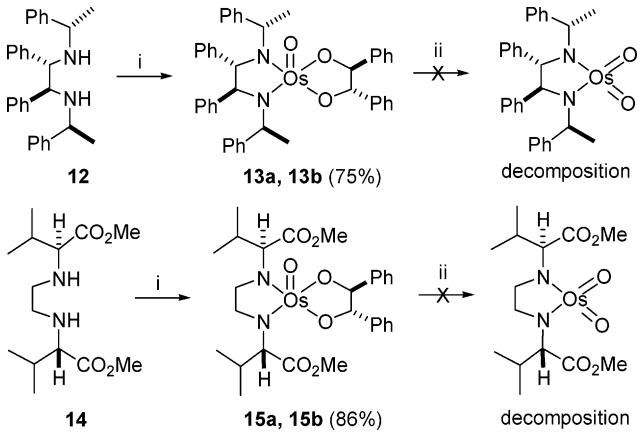
The new route meant that it might be possible to prepare dioxo complexes such as **7** with β-hydrogens on the exocyclic alkyl group next to nitrogen; therefore, intermediates **13** and **15** were made (from **12** and **14**, respectively, both as a 1:1 mixture of diastereomers)[12,13] using the Hanessian route (Scheme 9).

(10) Travis, B. R.; Narayan, R. S.; Borhan, B. *J. Am. Chem. Soc.* **2002**, *124*, 3824.

(11) Hanessian, S.; Meffre, P.; Girard, M.; Beaudoin, S.; Sanceau, J. Y.; Bennani, Y. *J. Org. Chem.* **1993**, *58*, 1991.

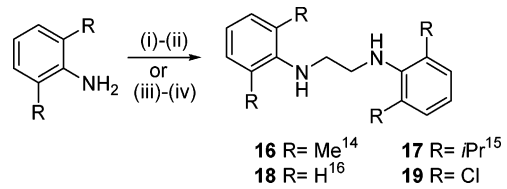
(12) Martelli, G.; Morri, S.; Savoia, D. *Tetrahedron* **2000**, *56*, 8367.

SCHEME 9. Enantiopure Dihydroxylation Precursors[a]



[a] Reagents and conditions: (i) OsO_4, *E*-stilbene, toluene, −78 °C; (ii) H_2O, acetone, △.

SCHEME 10. *N*-Aryl-Substituted Diamines for Complexation to Osmium[a]



[a] Reagents and conditions: (i) glyoxal, HCO_2H, CH_2Cl_2 (83% R = Me[14], 33% R = *i*Pr[16]); (ii) $NaBH_4$, THF, reflux (99% R = Me[15], 83% R = *i*Pr[16]); (iii) oxalyl chloride, NEt_3, CH_2Cl_2 (55% R = H) or oxalyl chloride, NaH, THF, −78 °C to room temperature, (32% R = Cl); (iv) $LiAlH_4$, THF, reflux (87% R = H[17], 45% R = Cl).

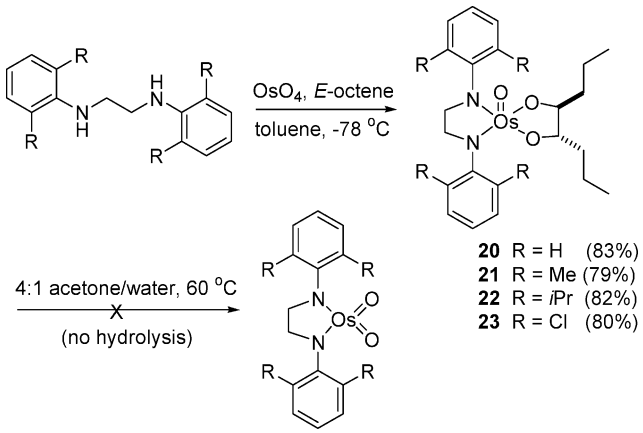
Unfortunately, no hydrolysis of either **13** or **15** to stilbene diol and dioxo osmium reagents was observed on heating in 4:1 acetone/water. Instead, only decomposition occurred suggesting that, like imidoosmium(VIII) complex **2**, the corresponding dioxo osmium(VI) reagents are only stable when there are no hydrogens on the exocyclic alkyl groups β to the nitrogens; this observation reveals the limits of this chemistry and how it is necessary to control carefully the groups on nitrogen to avoid decomposition.

To circumvent this problem, it was decided to investigate the formation of dioxo osmium(VI) reagents such as **7** with *N*-aryl groups, instead of with *tert*-butyl, using the Hanessian route. Substitution of the *tert*-butyl groups with an aryl unit offers the possibility of making an osmium reagent with different electronic properties and with the potential of introducing axial chirality.

Therefore, a series of appropriate *N*-aryl 1,2-diamines were prepared using standard literature methods (Scheme 10).[14−17]

The four diamines were then reacted with osmium tetroxide and *E*-octene at low temperature to yield the corresponding

SCHEME 11. *N*-Diaryl Osmium(VI) Precursors for Dihydroxylation



intermediates **20**−**23** in good yields (Scheme 11). However, under the optimized hydrolysis conditions, no hydrolysis of **20**−**23** to the osmium(VI) dioxo reagents was observed, and only starting material could be recovered. This contrasts with the behavior of **13** and **15** under the same conditions when decomposition was observed (implying that hydrolysis did occur but gave an unstable osmium complex); clearly, the *N*-aryl complexes **20**−**23** are much less reactive toward hydrolysis. An X-ray crystal structure of **21** was obtained (Figure 2), and this shows the two nitrogen atoms to be in a planar environment with the aryl rings close to orthogonal to the plane of the five-membered ring (dihedral angle is 80°).[18] The aryl rings are, therefore, greatly increasing the steric bulk around the osmium center hindering the approach of the water molecule necessary for hydrolysis to occur.

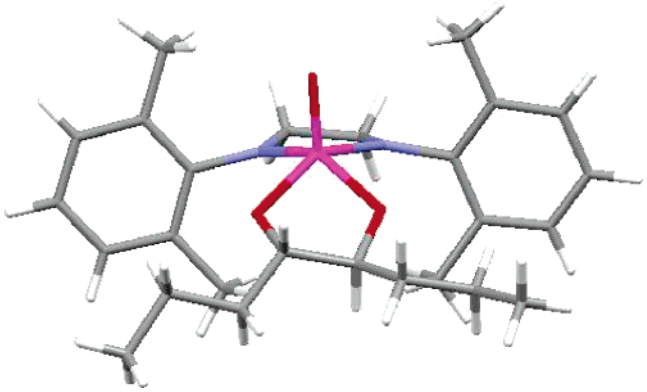


FIGURE 2. X-ray structure of complex **21**.

Clearly, one of the long-term goals of this project is to develop new catalytic reagents for dihydroxylation and asymmetric dihydroxylation; this is likely to be impeded by the poor rates of hydrolysis of compounds such as **8**−**10** and **20**−**23**. Therefore, we decided to prepare an intermediate with less steric

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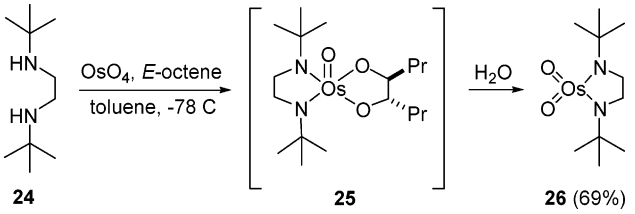
(17) Denk, M. K.; Krause, M. J.; Niyogi, D. F.; Gill, N. K. *Tetrahedron* **2003**, *59*, 7565.

(18) Compound **21** crystallized as a mixture of two distinct types of crystals. The structure described in this report is that of the minority phase, which formed large red−brown prismatic single crystals. The majority phase consisted of brown needles, mostly as polycrystalline aggregates; it was found to be possible to determine the unit cell of this material (at 150 K, triclinic, $a = 8.4846(3)$, $b = 9.1792(4)$, $c = 16.5417(8)$ Å, $\alpha = 95.9657(17)$, $\beta = 90.7644(19)$, $\gamma = 95.109(2)$°). However, because of the poorly defined positioning of the two propyl groups, the crystallographic data did not lead to publishable results.

SCHEME 12. Sterically Less-Hindered Osmium Intermediate 25 Undergoing Rapid Hydrolysis



bulk around the osmium center in the hope that the rate of hydrolysis (and diol liberation) would be increased. Consequently, *N*,*N*′-bis(*tert*-butyl)ethylenediamine, **24**, prepared by reaction of *tert*-butylamine with dibromoethane,[15] was reacted with osmium tetroxide and octene in toluene (Scheme 12) in an attempt to form intermediate **25**. However, compound **25** was not observed from this reaction and the new osmium reagent, **26**, was formed exclusively instead. The X-ray structure of **26** is shown in Figure 3.

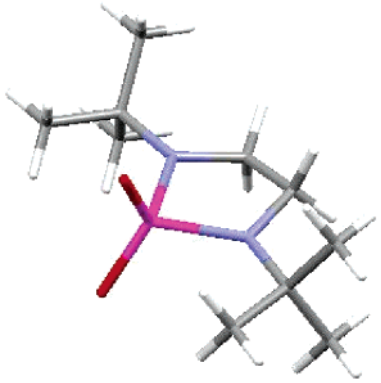


FIGURE 3. X-ray structure of complex **26**.

We presume that **25** was formed in situ but then hydrolyzed rapidly upon workup to give **26**. The increased rate of hydrolysis was promising for the use of **26** as a catalytic dihydroxylation reagent because the problem of the slow hydrolysis, apparent when **7** was used as the reagent, had been overcome.

Attempted Catalytic Dihydroxylation Using 1,2-Diamine-dioxo-osmium(VI) Complexes. Because of the expense and toxicity of the osmium tetroxide required in the preparation of the osmium reagents shown above, the use of catalytic amounts of these reagents in the cis dihydroxylation of alkenes would be desirable. It is clear that in a proposed catalytic cycle (as outlined in Figure 4) there are two parameters that need to be controlled: step 1, the cycloaddition to form an intermediate, followed by step 2, chemoselective ester hydrolysis of that intermediate to yield the diol and recovered osmium reagent.

In the stoichiometric dihydroxylation outlined previously, the cycloaddition step was shown to be rapid (5 min) using osmium reagent **7** with *t*BuOOH as the oxidant. The hydrolysis, however, was much slower, and heating was required. Nevertheless, the two steps were found to be high yielding and so the potential for the use of **7** in a catalytic cycle was clear.

Regrettably, dihydroxylation of *E*-stilbene with 10 mol % of **7** and *t*BuOOH in 4:1 acetone/water at 60 °C (the optimized hydrolysis conditions) led to a poor yield of diol and a large number of side products including some overoxidation to benzaldehyde. This was not too surprising because it is well-known that the use of peroxides to reoxidize osmium (in

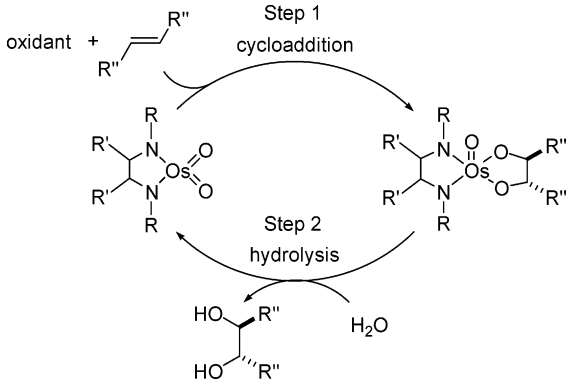
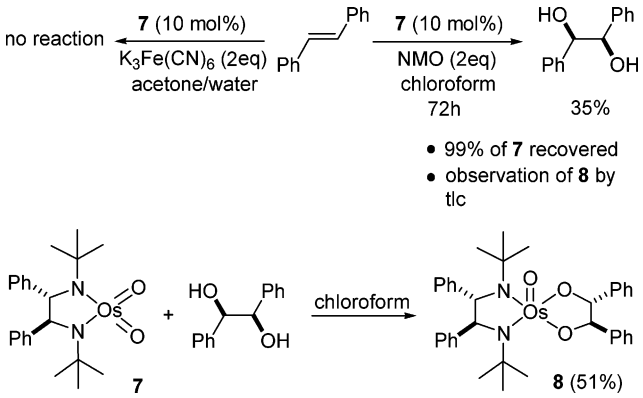


FIGURE 4. Potential catalytic cycle.

SCHEME 13. Catalytic Dihydroxylation?



dihydroxylation reactions) often leads to overoxidation.[2c] Another problem was that prolonged exposure of **7** to peroxides led to a small amount of decomposition of the reagent. Any decomposition of the osmium complex itself may result in osmium being leached which could (via osmium tetroxide) be responsible for any alkene dihydroxylation observed. Reaction of complex **26** with *t*BuOOH showed that decomposition was much faster than for **7** suggesting that this less-hindered complex is itself unstable and again raising concerns of osmium leaching in situ. Leached osmium tetroxide is incompatible with the proposed new catalytic reaction as the free metal oxide can compete with these new osmium reagents to produce diol; as a result of these studies, peroxides were deemed poor oxidants for catalytic oxidation and alternative reoxidants were sought.

Other reoxidants commonly used in dihydroxylation reactions include NMO and potassium hexacyanoferrate. These oxidizing reagents are milder than peroxides, so they would hopefully be more compatible with a catalytic cycle. Initial experiments using *trans*-stilbene and a catalytic amount of complex **7** showed that use of potassium hexacyanoferrate as the reoxidant gave only recovered starting materials (Scheme 13).

However, using NMO as the reoxidant, we obtained a 35% yield of the stilbene diol after 72 h, and moreover, complex **7** could be recovered in 99% yield, suggesting that it was acting as a catalyst for dihydroxylation (albeit slowly).

We decided to investigate this reaction more closely to rule out leaching of a small amount of osmium tetroxide which could be responsible for some, or all, of the stilbene diol observed. We might not detect this loss of osmium from the reagent **7** if it is a very small amount (≤1%). One observation that was initially encouraging was the formation (by TLC) of intermediate **8** in the catalytic reaction described above.

TABLE 2. Enantioselective Dihydroxylation

entry	acetone/water	$(DHQD)_2PHAL$ (10 mol %)	time (h)	diol (%)	ee (%)
1	4:1	yes	48	20	20
2	4:1	yes	72	30	19
3	4:1	yes	168	62	60
4	4:1	no	48	7	n/a
5	2:1	no	72	37	n/a

A control experiment was performed to test whether the stilbene diol would react with **7** in CH_2Cl_2 (Scheme 13). The reaction was slow with 51% of **8** and 40% of recovered **7** isolated after 6 days; however, **8** was formed in reasonable yield. It is, therefore, possible that NMO is not acting as an oxidant for **7** at all and that osmium tetroxide leaching can explain the formation of both the diol and intermediate **8**. The leaching problem was examined by another route.

A set of experiments were designed which would detect even minute amounts of osmium tetroxide in solution and thus rule out (or otherwise) osmium leaching from **7**. The chiral ligand $(DHQD)_2PHAL$ (10 mol %) was added to the reaction of catalytic **7** (10 mol %), *E*-stilbene, and NMO in 4:1 acetone/water at 60 °C. With the important proviso that the chiral ligand does not impart any enantioselectivity to the addition of **7** to the alkene, the resulting diol should only be racemic if there is no osmium tetroxide free in solution. Any enantiomeric excess (ee) in the diol product must have its origins in free osmium tetroxide.

A set of experiments with 10 mol % of **7**, *E*-stilbene (1 equiv), and NMO (2 equiv) in 4:1 acetone/water at 60 °C were then undertaken (Table 2), and the ee of the diol product was determined by chiral HPLC.

Unfortunately, it is clear that addition of a chiral ligand to the reaction does result in the formation of an enantioenriched stilbene diol, and this strongly suggests that osmium tetroxide is being leached from **7**. The lower ee's for entries 1 and 2 suggest that some diol may come from the reaction of stilbene with **7** (via intermediate **8**), but after heating for 7 days (entry 3), sufficient osmium tetroxide has been leached to enhance the background reaction and increase the ee to 60. It also appears that lowering the acetone/water ratio increases the osmium tetroxide leaching (entries 2 and 5).

It should be pointed out that this is a highly sensitive test for free osmium tetroxide in solution because the $(DHQD)_2PHAL$ ligand is known to accelerate the rate of dihydroxylation by approximately 4 orders of magnitude relative to the ligand-free system.[19] This effect is evident in entries 1 and 4 where the difference in diol yield is likely to be due to this ligand-accelerated dihydroxylation by osmium tetroxide.

Two important control experiments must be reported. First, the assumption that $(DHQD)_2PHAL$ does not impart enantioselectivity upon the reaction of **7** was tested (Scheme 14). Thus, the reaction of **7** and *E*-stilbene to give the diol (via **8**) was conducted in the presence of stoichiometric $(DHQD)_2PHAL$: the product diol was racemic.

In addition, the ee of the stilbene diol, resulting from dihydroxylation of stilbene (1 equiv) with osmium tetroxide and NMO (2 equiv) as the reoxidant (acetone/water at 60 °C), was measured with $(DHQD)_2PHAL$ (10 mol %) as the ligand (Table 3).

(19) Anderson, P. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 7047.

SCHEME 14. Control Experiment

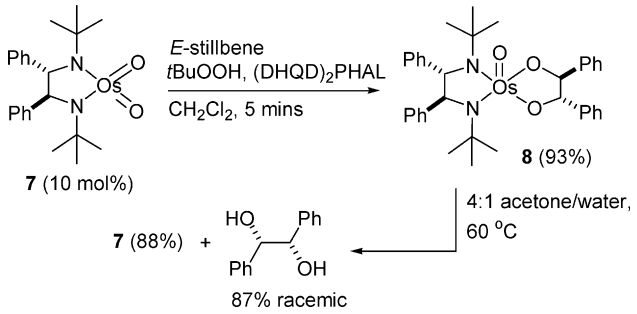


TABLE 3. Asymmetric Dihydroxylation of *E*-Stilbene with Osmium Tetroxide

OsO_4 (mol %)	time (h)	diol (%)	ee (%)
10	4	71	80
1	4	82	66
0.1	16	72	63
0.01	24	15	72

These results show that even a minute amount of osmium tetroxide free in solution can be responsible for diol formation and for enantioenriched products.

These results were not encouraging for the formation of diols using catalytic amounts of reagent **7** as they prove that it decomposes slowly under aqueous conditions and that even <1% decomposition is enough to liberate another oxidant (osmium tetroxide) that is more adept at catalytic dihydroxylation.

We briefly examined the reaction of complex **26** because it was shown to participate in both the oxidation and hydrolysis steps (but with vastly increased rates of hydrolysis relative to **7**).

Dihydroxylation of cyclohexene with 10 mol % of osmium reagent **26** and NMO in 4:1 acetone/water at room temperature yielded 76% cylohexane-1,2-diol. Unfortunately, a small amount of decomposition of **26** was also observed. This result suggests that **26** leaches osmium tetroxide more readily than **7**. Indeed, dihydroxylation of stilbene with 10 mol % of **26** and $(DHQD)_2PHAL$ (10 mol %) in 4:1 acetone/water at room temperature gave the stilbene diol with an ee of 50% confirming the presence of free osmium tetroxide.

Conclusion

In conclusion, we have developed a stable, nonvolatile, recoverable osmium reagent for the stoichiometric (syn) dihydroxylation of alkenes using *t*BuOOH as the oxidant; however, attempts to make the reaction catalytic in an osmium reagent were unsuccessful. The problem with developing the catalytic reaction is one of compatibility of the two steps: the oxidation is only fast in the presence of peroxides, which are themselves not suitable as reoxidants for catalytic dihydroxylation. Switching to amine-*N*-oxides means that the initial oxidation is slow, and so competitive hydrolysis of the osmium reagent occurs. It is possible that further studies will identify an osmium reagent with the correct balance of stability and reactivity and also a reoxidant that does promote cycloaddition without causing overoxidation. The results of our test for free osmium tetroxide serve as a warning that very small amounts of free osmium in solution can be responsible for the outcome of a dihydroxylation

reaction; these may be virtually undetectable by standard analytical techniques.

Experimental Section

Osmium(VI) Complex 7. Method 1: A solution of osmium(VIII) complex **2** (0.18 g, 0.51 mmol) and *E*-stilbene (0.46 g, 2.6 mmol) in dry CH_2Cl_2 (20 mL) was heated at reflux for 70 h. The reaction mixture was evaporated under reduced pressure, and the product was isolated by flash column chromatography (SiO_2, petrol → petrol-Et_2O, 80:20) to furnish **7** as a red solid (0.22 g, 52%). Method 2: 1,2-Diphenyl-1,2-*N*,*N*-di-*tert*-butylamine (0.02 g, 0.06 mmol) was subjected to procedure B with *E*-stilbene. The reaction furnished **8** (1:1 mixture of stereoisomers) as an orange solid (0.02 g, 39%) and **7** as a red solid (0.01 g, 22%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.25 (m, 10 H), 4.99 (s, 2 H), 1.23 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 129.2, 128.1, 126.7, 87.6, 68.8, 31.1; IR (KBr disk) 2970, 1740, 1464, 1452, 893 cm^{-1}; ESIMS *m*/*z* (rel intensity) 1112 (100%, 2M + NH_4^+); $C_{22}H_{31}N_2O_2{}^{192}$Os requires M + H 547.2000, found M + H^+ 547.2004; mp 155−158 °C.

Osmium Intermediate 8. *E*-Stilbene (0.026 g, 0.14 mmol) was subjected to procedure A (see Supporting Information) with osmium(VI) reagent **7**. Compound **8** was furnished as an orange solid (0.05 g, 92%) as a 1:1 mixture of stereoisomers. Spectroscopic data for the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2 H), 7.40−7.23 (m, 16 H), 6.96−6.92 (m, 2 H), 6.01, 5.96 (2 × s, 1 H), 5.62, 5.55 (2 × d, *J* = 10.0, 1 H), 5.17−4.94 (m, 2 H), 1.45, 1.41 (2 × s, 9 H), 1.36, 1.34 (2 × s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 149.0, 145.9, 145.1, 141.3, 140.9, 128.8, 128.6, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.2, 127.1, 126.9, 126.9, 126.3, 98.1, 97.3, 96.5, 92.6, 89.5, 87.9, 82.1, 82.0, 69.9, 69.6, 69.5, 68.4, 31.7, 31.4, 30.9, 30.2; IR (KBr disk) 2972, 1600, 1451, 906 cm^{-1}; ESIMS *m*/*z* (rel intensity) 1485 (15%, 2M + H^+), 743 (100%, M + H^+); $C_{36}H_{43}N_2O_3{}^{192}$Os requires M + H 743.2889, found M + H^+ 743.2896; mp 132−135 °C.

Osmium Intermediate 9. *E*-Octene (0.023 mL, 0.12 mmol) was subjected to procedure A with osmium(VI) reagent **7**. Compound **9** was furnished as an amorphous orange solid (0.04 g, 96%) as a 1:1 mixture of stereoisomers. Spectroscopic data for the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.45 (m, 2 H), 7.37−7.21 (m, 6 H), 6.83−6.80 (m, 2 H), 5.83, 5.78 (2 × s, 1 H), 4.90, 4.84 (2 × s, 1 H), 4.58−4.50 (m, 0.5 H), 4.32−4.24 (m, 1 H), 4.00−3.90 (m, 0.5 H), 1.82−1.40 (m, 8 H), 1.37−1.31 (m, 18 H), 1.02 (t, *J* = 6.8, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.7, 145.5, 145.2, 128.8, 128.5, 128.1, 128.0, 127.6, 127.4, 127.4, 127.1, 127.0, 126.7, 126.5, 126.4, 89.3, 88.6, 81.9, 81.9, 68.9, 68.5, 68.4, 67.9, 37.6, 35.7, 31.5, 30.6, 30.4, 29.9, 19.8, 18.8; IR (KBr disk) 2960, 1452, 910 cm^{-1}; ESIMS *m*/*z* (rel intensity) 675 (100%, M + H^+); $C_{30}H_{47}N_2O_3{}^{192}$Os requires M + H 675.3202, found M + H^+ 675.3225.

Osmium Intermediate 10. Cyclohexene (0.017 mL, 0.17 mmol) was subjected to procedure A with osmium(VI) reagent **7**. Compound **10** was furnished as an orange solid (0.05 g, 96%) as a 2:1 mixture of stereoisomers. Spectroscopic data for the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.24 (m, 9 H), 6.98−6.96 (m, 1 H), 5.82 (s, 1 H_{minor}), 5.74 (s, 1 H_{major}), 4.96−4.85 (m, 2 H_{major} and 1 H), 4.61−4.56 (m, 1 H_{minor}), 4.48−4.45 (m, 1 H_{minor}), 2.33−2.20 (m, 1 H), 2.08−1.96 (m, 3 H), 1.81−1.20 (m, 22 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.8, 145.0, 144.9, 128.6, 128.5, 128.2, 127.7, 127.4, 127.1, 127.0, 126.7, 126.7, 126.3, 89.9, 89.5, 87.5, 86.7, 84.8, 82.5, 82.2, 81.9, 69.5, 69.3, 69.2, 68.7, 31.7, 31.6, 31.2, 30.9, 30.7, 30.3, 30.0, 28.5, 23.5, 22.8, 21.2, 21.1; IR (KBr disk) 2932, 1740, 1450, 907 cm^{-1}; ESIMS *m*/*z* (rel intensity) 645 (100%, M + H^+); $C_{28}H_{41}N_2O_3{}^{192}$Os requires M + H 645.2732, found M + H^+ 645.2736; mp 130−131 °C.

Osmium Intermediate 13. Diamine **12** (0.10 g, 0.24 mmol) was subjected to procedure B (see Supporting Information) with *E*-stilbene. The reaction furnished **13** as an amorphous orange solid (0.15 g, 75%) as a separable 1:1 mixture of stereoisomers. Stereoisomer α: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−6.88 (m, 26 H), 6.82−6.79 (m, 2 H), 6.67 (q, *J* = 6.8, 1 H), 6.54−6.51 (m, 2 H), 5.92 (q, *J* = 6.8, 1 H), 5.72 (d, *J* = 9.2, 1 H), 5.24−5.19 (m, 2 H), 4.59 (s, 1 H), 1.99 (d, *J* = 6.8, 3 H), 1.38 (d, *J* = 7.2, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.5, 143.0, 141.8, 141.6, 140.3, 128.8, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.5, 127.3, 127.2, 127.2, 127.0, 127.0, 126.8, 126.6, 126.4, 97.1, 96.6, 86.8, 81.2, 67.8, 65.8, 23.5, 18.2. Stereoisomer *β*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−6.86 (m, 29 H), 6.32−6.30 (m, 2 H), 6.08 (q, *J* = 6.8, 1 H), 5.72 (d, *J* = 9.2, 1 H), 5.35 (s, 1 H), 5.22 (d, *J* = 9.6, 1 H), 4.88 (s, 1 H), 1.59 (d, *J* = 6.8, 3 H), 1.53 (d, *J* = 6.8, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.8, 142.1, 141.3, 140.7, 140.5, 129.3, 128.6, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.6, 127.6, 127.3, 127.2, 127.1, 127.0, 126.9, 126.5, 125.4, 97.0, 96.8, 87.5, 82.0, 69.2, 66.8, 18.9, 16.7; IR (KBr disk) 2929, 1494, 1453, 923 cm^{-1}; ESIMS *m*/*z* (rel intensity) 897 (100%, M + CH_3CN + NH_4^+), 839 (100%, M + H^+); $C_{44}H_{43}N_2O_3{}^{192}$Os requires M + H 839.2889, found M + H^+ 839.2896.

Osmium Intermediate 15. Diamine **14** (0.038 g, 0.13 mmol) was subjected to procedure B with *E*-stilbene. The reaction furnished **15** as an amorphous orange solid (0.08 g, 86%) as a 1:1 mixture of stereoisomers. Spectroscopic data for the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.08 (m, 10 H), 5.87, 5.86 (2 × d, *J* = 10.4, 1 H), 5.55−5.51 (m, 1.5 H), 5.43 (d, *J* = 10.4, 0.5 H), 4.91, 4.82 (2 × d, *J* = 9.0, 1 H), 4.47−4.36 (m, 1 H), 4.24−4.03 (m, 3 H), 3.73, 3.73, 3.67, 3.42 (4 × s, 6 H), 2.60−2.43 (m, 2 H), 1.11−1.01 (m, 7.5 H), 0.93, 0.80, 0.67 (3 × d, *J* = 6.4, 4.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.8, 172.0, 171.9, 141.5, 140.9, 140.8, 140.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.2, 126.9, 126.9, 97.4, 96.6, 95.9, 95.7, 76.5, 75.2, 74.7, 74.3, 61.7, 61.5, 61.4, 61.2, 51.8, 51.7, 51.3, 51.1, 32.1, 31.9, 28.0, 27.4, 20.5, 20.5, 20.3, 20.0, 19.8, 19.8, 18.9, 18.7; IR (KBr disk) 1734, 941 cm^{-1}; ESIMS *m*/*z* (rel intensity) 729 (20%, M + Na^+), 707 (100%, M + H^+); $C_{28}H_{39}N_2O_7{}^{192}$Os requires M + H 707.2372, found M + H^+ 707.2368.

***N*,*N*′-Diphenylethylenediamine 18.** Triethylamine (0.77 mL, 5.5 mmol) was added dropwise to a solution of aniline (0.25 mL, 2.8 mmol) in CH_2Cl_2 (20 mL) and cooled to −78 °C. Oxalyl chloride (0.11 mL, 1.3 mmol) was added dropwise and stirred at room temperature for 20 h. The precipitate was filtered off, and the solution was evaporated under reduced pressure. The product was isolated by flash column chromatography (SiO_2, CH_2Cl_2) to furnish *N*,*N*′-diphenyloxalamide as a white solid (0.17 g, 55%): ^{1}H NMR (400 MHz, DMSO) δ 10.84 (br s, 2 H), 7.87 (d, *J* = 7.7, 4 H), 7.38 (app. t, 4 H), 7.16 (t, *J* = 7.4, 2 H); ^{13}C NMR (100 MHz, DMSO) δ 159.4, 138.5, 129.6, 125.5, 121.3; IR (KBr disk) 3307, 1662, 1437 cm^{-1}; CIMS *m*/*z* (rel intensity) 258 (45%, M + NH_4^+), 241 (100%, M + H^+); $C_{14}H_{13}N_2O_2$ requires M + H 241.0977, found M + H^+ 241.0968; mp 235−236 °C.

Lithium aluminum hydride (0.16 g, 4.2 mmol) was then added to a solution of *N*,*N*′-diphenyloxalamide (0.17 g, 0.69 mmol) in dry THF (15 mL) and heated at reflux for 18 h. The reaction mixture was quenched with 1 M NaOH, extracted with CH_2Cl_2 (× 3), dried ($MgSO_4$), and evaporated under reduced pressure, and the product was purified by flash column chromatography (SiO_2, CH_2Cl_2-petrol, 5:4) to furnish **18** as a white solid (0.13 g, 87%). The spectroscopic data for this compound matched that in the literature.[31]

***N*,*N*′-Bis(2,6 dichlorophenyl)ethylenediamine 19.** Sodium hydride, 60% dispersion in mineral oil (0.729 g, 18.2 mmol), was added to a solution of 2,6-dichloroaniline (1.23 g, 7.59 mmol) in dry THF (15 mL) at 0 °C and cooled to −78 °C. A solution of oxalyl chloride (0.07 mL, 0.85 mmol) in dry THF (5 mL) was added dropwise and stirred at room temperature for 50 h. The reaction was quenched with cold water, and the THF was evaporated under reduced pressure. The product was extracted with CH_2Cl_2 (× 3), dried ($MgSO_4$), evaporated under reduced pressure, and isolated by flash column chromatography (SiO_2, CH_2Cl_2) to furnish *N*,*N*′-bis(2,6-dichlorophenyl)oxalamide as a white solid (0.37 g, 32%):

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.89 (br s, 2 H), 7.61 (d, J = 8.0, 4 H), 7.42 (app. t, 2 H); ^{13}C (100 MHz, DMSO-d_6) δ 159.2, 134.4, 133.0, 130.8, 129.5; IR (KBr disk) 3228, 1674, 1487 cm^{-1}; CIMS *m*/*z* (rel intensity) 394 (60%, M + NH_4^+), 377 (50%, M + H^+), 341 (100%, M − Cl^-); $C_{14}H_9N_2O_2{}^{35}Cl_4$ requires M + H 376.9418, found M + H^+ 377.9409; mp 264−265 °C.

Lithium aluminum hydride (0.24 g, 6.2 mmol) was then added to a solution of *N*,*N*′-bis(2,6-dichlorophenyl)oxalamide (0.20 g, 0.52 mmol) in dry THF (20 mL) and heated at reflux for 20 h. The reaction mixture was quenched with 1 M NaOH and the THF was evaporated under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 (× 3), dried ($MgSO_4$), and evaporated under reduced pressure, and the product was purified by flash column chromatography (SiO_2, CH_2Cl_2-petrol, 1:1) to furnish **19** as a white solid containing a minor impurity (0.08 g, 45%): ^{1}H (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.2, 4 H), 6.81 (t, J = 8.2, 2 H), 3.99 (br s, 2 H), 3.56 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.9, 126.5, 122.0, 47.6. The minor impurity could not be removed, so **19** was carried through without further purification.

Osmium Intermediate 20. Diamine **18** (0.045 g, 0.21 mmol) was subjected to procedure B with *E*-octene. The reaction furnished **20** as a red solid (0.10 g, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.34 (m, 8 H), 7.19−7.11 (m, 2 H), 4.54−4.38 (m, 2 H), 4.35−4.23 (m, 3 H), 3.92 (q, J = 6.4, 1 H), 1.59−1.03 (m, 8 H), 0.81 (t, J = 7.2, 3 H), 0.72 (t, J = 7.2, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 155.5, 128.3, 128.3, 125.2, 124.8, 124.5, 123.9, 92.9, 92.9, 65.3, 63.2, 37.6, 36.8, 18.8, 18.6, 14.1, 14.0; IR (KBr disk) 2978, 1478, 925 cm^{-1}; ESIMS *m*/*z* (rel intensity) 620 (100%, M + CH_3CN + NH_4^+), 563 (80%, M + H^+); $C_{22}H_{31}N_2O_3{}^{192}Os$ requires M + H 563.1950, found M + H^+ 563.1951; mp 148−149 °C.

Osmium Intermediate 21. Diamine **16** (0.11 g, 0.39 mmol) was subjected to procedure B with *E*-octene. The reaction furnished **21** as an orange solid (0.19 g, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.10 (m, 6 H), 4.29−4.14 (m, 4 H), 4.04 (td, J = 7.6 and 3.6, 1 H), 3.77 (ddd, J = 9.2, 7.6, and 3.6, 1 H), 2.33 (s, 3 H), 2.29 (s, 3 H), 1.95 (s, 3 H), 1.92 (s, 3 H), 1.50−1.29 (m, 4 H), 1.24−0.98 (m, 4 H), 0.72 (app. q, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 152.3, 137.0, 136.9, 134.7, 134.2, 128.8, 128.7, 128.2, 129.0, 126.9, 126.7, 92.4, 92.1, 66.7, 66.5, 37.4, 36.6, 18.9, 18.7, 18.4, 18.3, 17.7, 17.7, 14.2, 13.8; IR (KBr disk) 2954, 2866, 1466, 930 cm^{-1}; ESIMS *m*/*z* (rel intensity) 677 (100%, M + MeCN + NH_4^+); $C_{26}H_{39}N_2O_3{}^{192}Os$ requires M + MeCN + NH_4 619.2576, found M + MeCN + NH_4^+ 619.2571; mp 137−138 °C.

Osmium Intermediate 22. Diamine **17** (0.14 g, 0.36 mmol) was subjected to procedure B with *E*-octene. The reaction furnished **22** as a red-orange solid (0.21 g, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.27 (m, 2 H), 7.23−7.15 (m, 4 H), 4.34−4.21 (m, 4 H), 4.06 (td, J = 9.2 and 2.8, 1 H), 3.77 (td, J = 9.2 and 2.8, 1 H), 3.41 (sp, J = 6.8, 2 H), 2.39 (sp, J = 6.8, 1 H), 2.30 (sp, J = 6.8, 1 H), 1.52−1.43 (m, 2 H), 1.32−1.23 (m, 19 H), 1.10−1.00 (m, 11 H), 0.63 (app. q, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.2, 147.4, 147.3, 145.2, 144.3, 127.4, 127.4, 124.2, 124.1, 123.7, 123.5, 93.6, 92.8, 70.0, 69.7, 37.0, 35.9, 28.6, 28.4, 27.4, 27.2, 25.0, 24.5, 24.4, 24.3, 24.2, 24.0, 23.9, 19.0, 18.8, 14.1, 13.7; IR (KBr disk) 2961, 2867, 1462, 936 cm^{-1}; ESIMS *m*/*z* (rel intensity) 731 (100%, M + H^+); $C_{34}H_{55}N_2O_3{}^{192}Os$ requires M + H 731.3828, found M + H^+ 731.3840; mp 165−166 °C.

Osmium Intermediate 23. Diamine **19** (0.035 g, 0.10 mmol) was subjected to procedure B with *E*-octene. The reaction furnished **23** as an orange solid (0.06 g, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.35 (m, 4 H), 7.21−7.16 (m, 2 H), 4.44−4.18 (m, 4 H), 4.07 (td, J = 8.4 and 3.2, 1 H), 3.81 (td, J = 8.4 and 3.2, 1 H), 1.51−1.21 (m, 4 H), 1.10−0.95 (m, 4 H), 0.71 (td, J = 7.6 and 2.8, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 149.0, 135.7, 135.6, 134.3, 134.0, 128.7, 128.4, 128.1, 128.1, 127.9, 127.9, 93.0, 92.6, 65.1, 64.9, 36.6, 36.1, 18.9, 18.6, 14.2, 13.6; IR (KBr disk) 2929, 2869, 1435, 950 cm^{-1}; ESIMS *m*/*z* (rel intensity) 757 (100%, M + CH_3CN + NH_4^+), 699 (100%, M + H^+); $C_{22}H_{27}N_2O_3{}^{35}Cl_4{}^{192}Os$ requires M + H 699.0391, found M + H^+ 699.0405; mp 189−190 °C.

Osmium(VI) Complex 26. Diamine **24** (0.420 g, 2.44 mmol) was subjected to procedure B with *E*-octene. The reaction furnished osmium(VI) reagent **26** as a dark purple solid (0.61 g, 69%): ^{1}H MNR (400 MHz, $CDCl_3$) δ 3.79 (s, 4 H), 1.45 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.5, 62.4, 29.4; IR (KBr disk) 2969, 1465, 885 cm^{-1}; ESIMS *m*/*z* (rel intensity) 395 (100%, M + H^+); $C_{10}H_{23}N_2O_2{}^{192}Os$ requires M + H 395.1374, found M + H^+ 395.1373; mp 153−155 °C.

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Supporting Information Available: General experimental procedures and spectra for all new compounds and X-ray crystallographic files (CIF) for compounds **7**, **21**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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