reactions. Infrared spectra were recorded using either a Perkin-Elmer 137 Infracord or a 237 grating spectrometer. NMR spectra were obtained with a Varian T-60 spectrometer with tetramethylsilane as an internal standard. Mass spectral analyses and elemental analyses were obtained from the Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

(14) This direct procedure was first reported by Professor N. C. Yang and his associates at the University of Chicago.
(15) B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, 169 (1965).
(16) H. C. Brown and C. P. Grag, *J. Am. Chem. Soc.*, **83**, 2952 (1961).
(17) K. Gollnick and G. Schade, *Tetrahedron*, 123 (1966).
(18) G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *J. Am. Chem. Soc.*, **90**, 173 (1968).
(19) Prepared by the method of A. S. Dreiding and S. N. Nickel, *J. Am. Chem. Soc.*, **76**, 3965 (1954). This material was shown to be the *E* isomer using NMR data of J. E. Dubois and M. Dubois, *C. R. Acad. Sci.* **256**, 715 (1963).
(20) L. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Am. Chem. Soc.*, **94**, 7761 (1972).
(21) Prepared by refluxing of mixture of 3-methylcyclohexanone and NaOD in D_2O for 4 h.

Synthesis of Dioxobis(*tert*-alkylimido)osmium(VIII) and Oxotris(*tert*-alkylimido)osmium(VIII) Complexes. Stereospecific Vicinal Diamination of Olefins[1]

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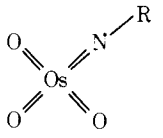
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received December 6, 1976*

Abstract: The synthesis and properties of dioxobis(*tert*-butylimido)osmium(VIII) (**5**) and oxotris(*tert*-butylimido)osmium(VIII) (**6**) are described. Other *tert*-alkylimido derivatives (*tert*-alkyl = *tert*-amyl, 1-adamantyl) were also prepared. These di- and triimido complexes were prepared by reaction of osmium(VIII) oxo compounds with *N*-*tert*-alkylphosphinimines, and are stable, yellow, crystalline compounds. Both the diimido complex **5** and the triimido complex **6** were found to react with monosubstituted and trans-disubstituted olefins to give cis vicinal diamines as the major products on reductive workup. Cyclic diamido complexes of osmium(VI) were isolated in the case of dimethyl and diethyl fumarate. Improved conditions are described for the synthesis of trioxo-*tert*-butylimidoosmium(VIII) and trioxo-*tert*-amylimidoosmium(VIII) from osmium tetroxide and the corresponding amine using water as solvent.

We have reported the vicinal oxyamination of olefins by *tert*-alkylimidoosmium(VIII) complexes **1**,[2] and the allylic amination of olefins by imido selenium reagents **2**.[3] Both



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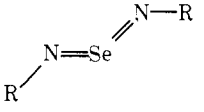

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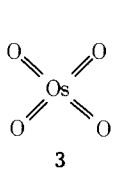
transformations are aza analogues of known oxygen insertion processes and represent a new class of reactions. More recently, we developed a catalytic oxyamination procedure[4] using chloramine-T and a catalytic amount of osmium tetroxide which has greatly increased the synthetic utility of the oxyamination reaction. It occurred to us that, by replacing more than one of the oxo groups of osmium tetroxide with imido groups, we might be able to extend this new class of reactions to include the direct vicinal diamination of olefins. Such a transformation is potentially of considerable value to synthetic chemists.

Thus, our aim was to complete the oxoimido series



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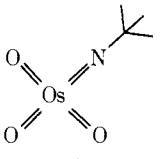

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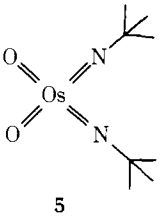

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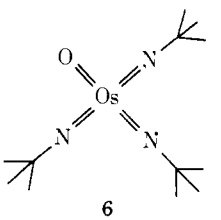

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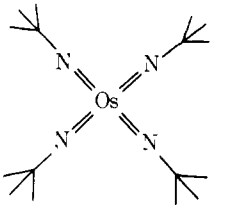

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and to investigate the reactions of the new osmium imido compounds with olefins. Prior to our work, the only known members of the oxoimido series were osmium tetroxide (**3**) and the monoimido complex **4**. In this paper we report the first synthesis and characterization of dioxobis(*tert*-butylimido)osmium(VIII) (**5**) and oxotris(*tert*-butylimido)osmium(VIII) (**6**), and their reactions with olefins to give primarily vicinal diamines. We also report a simplified procedure for the preparation of the monoimido complex **4**.

Results and Discussion

Preparation and Characterization of Di- and Triimido Osmium(VIII) Complexes. The *tert*-butylimido complex **4** was first prepared from osmium tetroxide and *tert*-butylamine.[5] However, this procedure cannot be used to make the di-, tri-, and tetraimido compounds. The monoimido complex **4** is recovered unchanged after several days of exposure to neat *tert*-butylamine. It was then found that both the diimido complex **5** and the triimido complex **6** can be prepared directly from less substituted members of the oxoimido series by treatment with the appropriate number of equivalents of *N*-*tert*-butylphosphinimine (Scheme I). Although *N*-*tert*-butyltriphenylphosphinimine was satisfactory for preparing

Table I. Preparation of Di- and Triimido Osmium(VIII) Complexes[a]

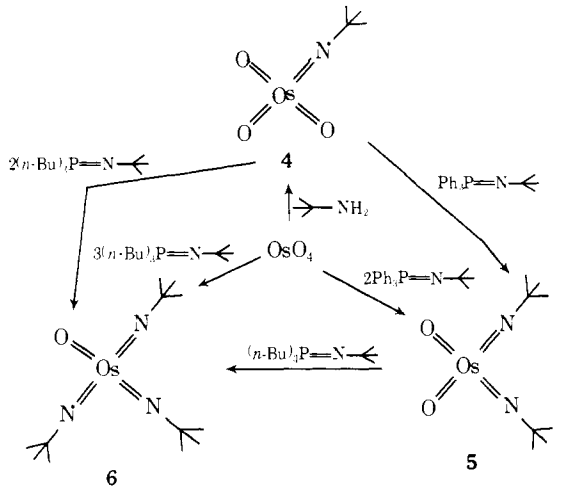
Starting compd	Phosphinimine	Equiv of phosphinimine	Product[b]	% yield[c]	Mp, °C[d]
OsO_4	$Ph_3P{=}N$-*t*-Bu	2.0	$OsO_2(N\text{-}t\text{-}Bu)_2$ (**5**)	63	119–120 dec
$OsO_3(N\text{-}t\text{-}Bu)$	$Ph_3P{=}N$-*t*-Bu	1.1	$OsO_2(N\text{-}t\text{-}Bu)_2$ (**5**)	82	119–120 dec
$OsO_3(N\text{-Ad})$	$Ph_3P{=}N$-Ad	1.2	$OsO_2(N\text{-Ad})_2$ (**8**)	73	209–211.5
$OsO_3(N\text{-}t\text{-Am})$	$Ph_3P{=}N$-Ad	1.2	$OsO_2(N\text{-Ad})(N\text{-}t\text{-Am})$ (**9**)	42	72–74
OsO_4	$(n\text{-Bu})_3P{=}N$-*t*-Bu	4.0	$OsO(N\text{-}t\text{-Bu})_3$ (**6**)	45	114–116 dec
$OsO_3(N\text{-}t\text{-Bu})$	$(n\text{-Bu})_3P{=}N$-*t*-Bu	2.5	$OsO(N\text{-}t\text{-Bu})_3$ (**6**)	45	114–116 dec
$OsO_2(N\text{-}t\text{-Bu})_2$	$(n\text{-Bu})_3P{=}N$-*t*-Bu	1.0	$OsO(N\text{-}t\text{-Bu})_3$ (**6**)	30	114–116 dec
$OsO_2(N\text{-Ad})_2$	$(n\text{-Bu})_3P{=}N$-*t*-Bu	1.4	$OsO(N\text{-Ad})_2(N\text{-}t\text{-Bu})$ (**10**)	45	146 dec

[a] Reactions were performed in refluxing methylene chloride. Cf. Experimental Section for procedures. [b] All new compounds were characterized by spectral and analytical data. [c] Isolated yields after dry column chromatography or preparative thin layer chromatography. [d] Compounds which decomposed on melting gave black liquids with gas evolution.

Table II. Analytical Data for Di- and Triimido Osmium(VIII) Complexes

Compd	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
$OsO_2(N\text{-}t\text{-Bu})_2$	26.37	26.35	4.98	5.06	7.69	7.62
$OsO_2(N\text{-Ad})_2$	46.14	46.41	5.81	5.78	5.38	5.32
$OsO_2(N\text{-Ad})(N\text{-}t\text{-Am})$	39.46	39.67	5.70	5.80	6.14	6.15
$OsO(N\text{-}t\text{-Bu})_3$	34.35	34.34	6.49	6.48	10.02	9.82
$OsO(N\text{-Ad})_2(N\text{-}t\text{-Bu})$	50.06	50.35	6.83	6.80	7.30	7.07

Scheme I



the diimido complex **5**, the more reactive *N-tert*-butyltri-*n*-butylphosphinimine was necessary to prepare the triimido complex **6**. Attempts to synthesize the tetraimido complex **7** from the triimido complex **6** and *N-tert*-butyltri-*n*-butylphosphinimine have failed thus far.

Other *tert*-alkyl derivatives of the di- and triimido compounds were also prepared by the above method. For instance, we prepared the diimido complexes dioxobis(1-adamantylimido)osmium(VIII) (**8**), and dioxo-1-adamantylimido-*tert*-amylimidoosmium(VIII) (**9**), and the triimido complex oxobis(1-adamantylimido)-*tert*-butylimodoosmium(VIII) (**10**) (Table I). Analytical data for the di- and triimido complexes synthesized are provided in Table II.

The diimido osmium(VIII) complexes **5**, **8**, and **9** are nonvolatile, yellow, crystalline solids which appear to be stable to air and moisture when stored in the dark at 0 °C. The triimido complexes **6** and **10** were generally obtained analytically pure after column chromatography as crystalline solids in various shades of orange to red. As with the diimido complexes, the triimido complexes are stable to air and moisture when kept in the dark at 0 °C. Osmometric molecular weight determinations on the diimido complexes **5** and **8** and the triimido complex **6** indicated monomeric species.

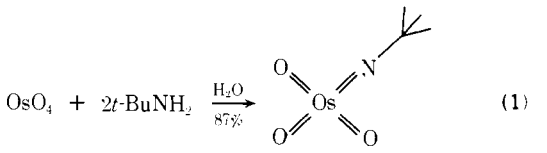
Table III. Infrared Absorptions of Osmium Imido Complexes

Complex	ν(Os=N), cm^{-1}	ν(Os=O), cm^{-1}	Ref
OsO_4		955	6
$OsO_3(N\text{-}t\text{-Bu})$	1184	925, 912	5
$OsO_2(N\text{-}t\text{-Bu})_2$	1200	888, 878	
$OsO_2(N\text{-Ad})_2$	1175, (1100)	880, 865	
$OsO_2(N\text{-Ad})(N\text{-}t\text{-Am})$	1180, (1100)	885, 875	
$OsO(N\text{-}t\text{-Bu})_3$	1190, (1100)	838	
$OsO(N\text{-Ad})_2(N\text{-}t\text{-Bu})$	1160, (1100)	838	

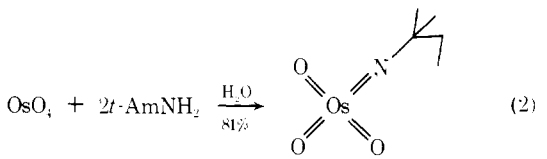
Infrared absorptions in the osmium-oxygen and osmium-nitrogen stretching regions for the various imido complexes are given in Table III. A comparison of ν(Os=O) for osmium tetroxide and the imido complexes indicates that, as each oxo group of osmium tetroxide is replaced by an imido group, the stretching frequencies of the remaining oxo groups decrease by an average of 40 cm^{-1}. The shift of ν(Os=O) to lower wavenumbers is in accord with the expected decrease in the multiple bond character of the Os-O links caused by efficient donation of electron density from nitrogen to osmium. The osmium-nitrogen stretching modes in potassium osmiamate, $K[OsO_3N]$, and potassium nitrilopentachloroosmate, $K_2[OsCl_5N]$, have been assigned to bands at 1023 and 1073 cm^{-1}, respectively.[7] Although the osmium-nitrogen stretching modes for osmium imido complexes have not been positively assigned, Clifford and Kobayashi[5] have attributed the absorption at 1184 cm^{-1} in the IR spectrum of the monoimido complex **4** to the osmium-nitrogen stretching mode. The IR spectra of the di- and triimido complexes exhibited very strong, broad absorption bands centered in the region of 1200–1160 cm^{-1}, and we have tentatively assigned these bands to the osmium-nitrogen stretching mode. The diimido complexes **8** and **9** and the triimido complexes **6** and **10** also exhibited a strong, sharp band at 1100 cm^{-1}. This absorption occurs in the Os-N stretching region but is not observed in the IR spectrum of the

bis(*tert*-butylimido) compound **5**. It is interesting to note that the bands attributed to Os–N stretching modes in the imido complexes are of higher frequency than the bands assigned to the Os–N stretching modes in nitrido complexes. This phenomenon, in which formal metal–nitrogen double bonds absorb at higher frequencies than formal metal–nitrogen triple bonds, has also been noted by Chatt[8] and co-workers in the case of rhenium.

Preparations of Monoimido Osmium(VIII) Complexes. Earlier reported[2,5] preparations of the monoimido complex **4** involve sublimations and are time consuming. We have developed a new procedure for making the monoimido complex which is quick and efficient, and therefore superior to the previous methods. The addition of 2 equiv of *tert*-butylamine to an aqueous solution of osmium tetroxide immediately gave the monoimido complex **4**, as a yellow, curdy precipitate, in excellent yield (eq 1). The complex was collected by filtration



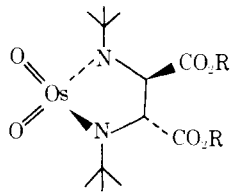
4 (1)



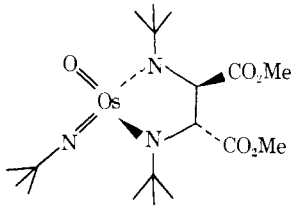
(2)

and dried to give a yellow powder. We have found that further purification of the complex obtained in this manner was unnecessary for most purposes. The *tert*-amylimido derivative was also prepared by the above method in very good yield (eq 2). Attempts to prepare other than *tert*-alkylimido derivatives by this method led to rapid formation of uncharacterized black osmium species. Amines which were investigated included methylamine, isopropylamine, *o*-methylhydroxylamine, 2-amino-2-methylpropionitrile, and *N*-aminophthalimide.

Reaction of Diimido Complex 5 and Triimido Complex 6 with Olefins. Both the diimido complex **5** and the triimido complex **6** reacted with a variety of monosubstituted and trans-disubstituted olefins in a manner analogous to that of osmium tetroxide and the monoimido complex **4**. The major products appeared to be osmium(VI) diamido complexes (i.e., **5a** and **6a**), which on reductive cleavage gave vicinal diamines (Scheme II). This is one[9] of the first reported instances of direct vicinal diamination of olefins. In the case of dimethyl and diethyl fumarate, the diamido complexes **11** and **12** were actually



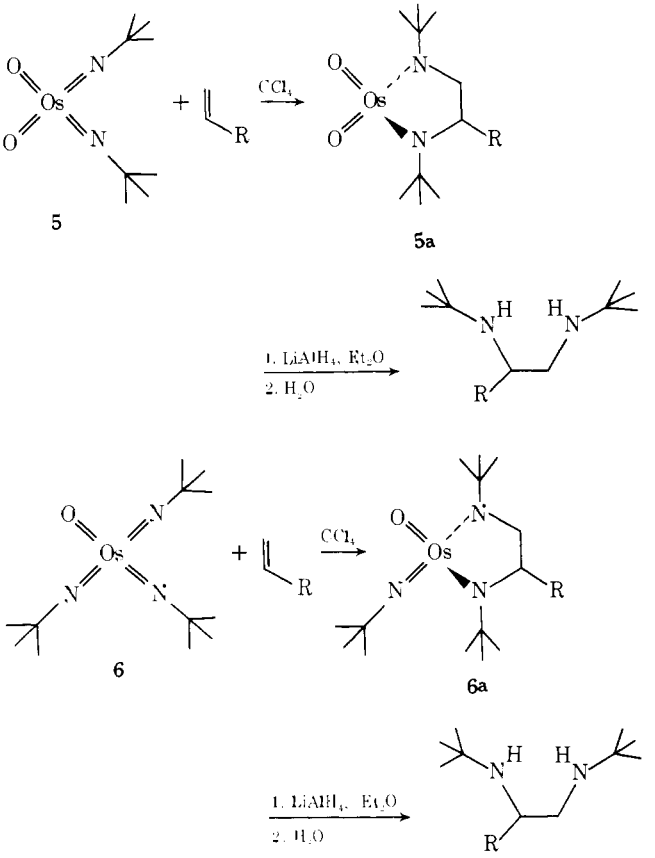
11a, R = Me
b, R = Et



12

isolated.[10] The spectral and analytical data for these surprisingly stable[11] diamido complexes were consonant with the structures shown. Molecular weight determinations on the diamido complex **11b** derived from **5** and diethyl fumarate indicated that these species were monomeric. This is in contrast with osmate(VI) monoesters, the oxygen analogues of the diamido complexes, which are known to exist only as dimers in the absence of coordinating ligands.[12]

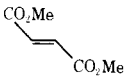
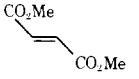
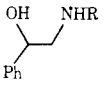
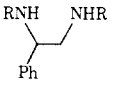
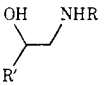
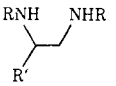
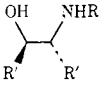
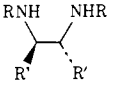
Scheme II



The diimido complex **5** is capable of adding to olefins in any of three ways to give either diol, hydroxyamine, or diamine. Similarly, the triimido complex **6** can add to olefins to give either hydroxyamine or diamine. As the results listed in Table IV clearly show, there is a greater tendency for the nitrogen atoms rather than the oxygen atoms of the imido complexes to add across the olefinic bond. Hence, diamines are the major products in these reactions. In the case of the diimido complex **5**, diol products were never observed. We had earlier reported[2] that, in the reaction of the monoimido complex **4** with olefins, the ratio of hydroxyamine to diol increased as more coordinating solvents were used. By contrast, the product ratios in these reactions of the di- and triimido complexes with olefins were insensitive to the type of solvent employed. Thus, the same product ratios were obtained when pyridine and carbon tetrachloride were used as solvents.

Evidence for the cis stereochemistry of these diamination processes was provided by reaction of **5** with (*E*)- and (*Z*)-1-deuterio-1-decene, and by the ^{1}H NMR spectrum of the diamido complex **11a** in the presence of a chiral shift reagent. Reaction of **5** with the two specifically deuterated[2b,13] 1-decenes gave in each case a different diastereomer of the expected 1-deuterio-1,2-bis(*tert*-butylamino)decane as indicated by their ^{1}H NMR spectra. However, positive threo and erythro assignments could not be made owing to the similarity in chemical shifts of the two protons on the carbons bearing the nitrogens. The ^{1}H NMR spectrum of the diamido complex **11a** in the presence of tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) showed two sharp singlets (half-width = 1.0 Hz) for the methine protons indicating the presence of *d* and *l* enantiomers. Using an analysis similar to that used by Pirkle et al.[14] to distinguish between *meso*- and *dl*-2,3-butylene oxide, one would expect a more complicated pattern for these protons if **11a** consisted of the meso or a mixture of meso and *dl* isomers. This evidence is not conclusive, however, because a specimen of *meso*-**11a** was not available[15] for comparison. Nonetheless, considering the proven stereo-

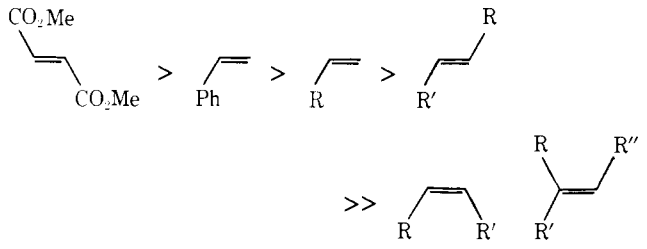
Table IV. Reaction of Di- and Triimido Osmium (VIII) Complexes with Olefins[a]

Olefin	Imido complex	Temp, °C	Products[b] (% yield)
	5	25	11a [60][c]
	6	25	12 [72]
Styrene	5	25	 (10)[d]  (73)
Styrene	6	25	(3) (89)
1-Decene	5	25	 (25)  (41)
1-Decene	6	40	(11) (63)
(*E*)-5-Decene	5	40	 (20)  (76)
(*E*)-5-Decene	6	40	(3) (69)

[a] Reactions were performed in carbon tetrachloride at 25 or 40 °C. [b] All new compounds were characterized by spectral and analytical data. [c] Yields given in brackets are isolated yields after preparative thin layer chromatography. [d] Yields given in parentheses were determined by GLC.

specific cis addition of osmium tetroxide and the monomimido complex **4**[2] to the olefins, the above evidence strongly suggests that stereospecific cis addition is also the rule in these analogous vicinal diamination processes.

The relative reactivities of **5** and **6** toward differently substituted olefins varied as follows:



This order of reactivity indicates that both electronic and steric factors play significant roles in determining the reactivity of the imido complexes with olefins. A most interesting fact about the oxidation of olefins by the di- and triimido complexes[16] is that the oxidations are accelerated by electron-withdrawing substituents. This peculiar reactivity is also exhibited by $KMnO_4$,[17] but is in contrast to the increased reactivity of OsO_4[17,18] with electron-rich olefins. Both the di- and triimido complexes were remarkably unreactive toward cis-disubstituted olefins. The triimido complex **6** did not react with cis olefins, whereas the diimido complex **5** reacted extremely slowly with cyclohexene to give only hydroxyamine in poor yield. The curious preference for trans double bonds over cis double bonds is also exhibited, albeit less dramatically, by the monoimido complex **4**,[2b,c] OsO_4,[18] RuO_4,[18] $KMnO_4$,[18] and Pd(II).[19] In comparing the relative reactivity of **5** to **6**, qualitative observations indicate that the triimido complex **6** is more reactive toward very electron-deficient olefins, such as dimethyl fumarate, whereas the diimido complex **5** is more reactive toward alkyl and aryl substituted olefins.

The realization that olefins underwent cis-vicinal hydroxyamination upon reaction with stoichiometric quantities of monoimido osmium species such as **4**[2] led us to discover much more useful catalytic versions of this transformation.[4,20] Similarly, it is hoped that the stoichiometric cis-vicinal diamination reactions described here bode well for the discovery of catalytic methods for effecting this new synthetic transformation.

Experimental Section

General. Melting points were taken on a Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 567 grating infrared spectrophotometer and are reported in reciprocal centimeters. NMR spectra were recorded on a 60-MHz Varian T-60 spectrometer or a 90-MHz Hitachi Perkin-Elmer R22 spectrometer. $CDCl_3$ was used exclusively as NMR solvent. Microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind., and by Robertson Laboratory, Florham Park, N.J.

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. All fragments containing osmium showed a typical osmium natural abundance isotope pattern, i.e., 41% ^{192}Os, 26% ^{190}Os, 16% ^{189}Os, 13% ^{188}Os, 1.6% ^{187}Os, and 1.6% ^{186}Os. Fragments which show the osmium isotope pattern are starred (*). The *m/e* reported for an isotope cluster is for the highest intensity ion which contains the most abundant osmium isotope, ^{192}Os.

Analytical gas–liquid partition chromatography (GLC) was performed on a Perkin-Elmer flame ionization Model 3920 gas chromatograph using a 6-ft, 5% UCW-98 on Gas Chrom Q, 2 mm i.d. glass column. Preparative GLC separations were performed on a Varian Aerograph Model 920 gas chromatograph using an 8 ft × 0.375 in. column packed with 10% SE-30 on 45/60 mesh Chromosorb W.

The internal standard method was used for quantitative GLC analyses, with response factors determined separately under the analysis conditions by means of a standard solution. Response factors (RF) are defined as

$$RF = \frac{\text{mole of product}}{\text{mole of standard}} \times \frac{\text{area of standard}}{\text{area of product}}$$

Peak areas were measured by electronic integration with either Hewlett-Packard Models 3373B or 3380A electronic integrators.

The dry column technique[21] was used in isolating many of the osmium complexes. Silica gel for dry column chromatography was prepared by adding 3% by weight of water to the silica gel normally used in wet column chromatography. The mixture was shaken until no lumps remained; it was then allowed to sit for at least 24 h before use. The silica gel was used without further treatment if the eluent was a single solvent. If, however, the eluent was a solvent mixture, then the deactivated silica gel was further treated with 10% by weight of the solvent mixture. The silica gel was shaken until no lumps remained and was allowed to sit for 1 h before use.

In general, the specially treated silica gel (100–150 times by weight of the mixture to be chromatographed) was packed dry in a Nylon sleeve of appropriate diameter to give a diameter to length ratio of about 1:20. The mixture to be chromatographed was preabsorbed onto seven times its own weight of silica gel and was applied to the top of the column, followed by sand. The eluting solvent was allowed to flow down the column under a constant head of 2–3 in. of solvent. After the solvent front reached the bottom of the column, the desired bands were collected by laying the column on its side and slicing it into segments. The compounds were extracted from the silica gel with methylene chloride, ethyl acetate, or mixtures thereof.

Hexane was made olefin free by stirring with portions of concentrated sulfuric acid until the sulfuric acid remained colorless. The hexane was then washed with 10% aqueous sodium hydroxide followed by water and it was dried over calcium chloride. The dried hexane was distilled from calcium hydride and stored over 4A molecular sieves. Reagent grade methylene chloride and carbon tetrachloride were dried by passage through a column of neutral alumina (activity 1) and were stored over 4A molecular sieves. Reagent grade ethyl acetate was dried by storage over anhydrous calcium chloride for 24 h followed by passage through a column of neutral alumina (activity 1), and was stored over 4A molecular sieves.

Most reagent grade chemicals were used without purification unless otherwise specified. Osmium tetroxide was purchased from Matthey

Bishop Inc., packaged in 1-g quantities. *N-tert*-Butyltriphenylphosphinimine was prepared by the method of Zimmer and Singh.[22] (*E*)-1-Deuterio-1-decene was prepared via hydroalumination of 1-decyne with diisobutylaluminum hydride followed by quenching with D_2O. (*Z*)-1-Deuterio-1-decene was prepared via hydroalumination of 1-deuterio-1-decyne with diisobutylaluminum hydride followed by quenching with H_2O.[2b,13]

***N*-1-Adamantyltriphenylphosphinimine.** A three-necked 1-L round-bottom flask, fitted with a mechanical stirrer and a nitrogen inlet, was flamed out under a flow of nitrogen. The flask was charged with 6.55 g (25.0 mmol) of triphenylphosphine and 400 mL of anhydrous benzene. The resultant solution was cooled with an ice bath and 1.4 mL (4.0 g, 25 mmol) of bromine was added dropwise, via syringe, with vigorous stirring. The yellow, heterogeneous mixture was stirred for an additional 20 min at 0 °C after all the bromine was added. A solution of 3.78 g (25.0 mmol) of 1-adamantylamine and 2.53 g (3.50 mL, 25.0 mmol) of triethylamine in 100 mL of benzene was then added slowly to the ice-cooled reaction mixture over a period of 30 min. Following the addition of the amines, the reaction mixture was stirred at 25 °C for 2 h, during which time a large amount of precipitate was formed. The precipitate was collected by vacuum filtration, washed with ether (3 × 200 mL), then dissolved in 100 mL of chloroform. The resultant solution was washed with water (1 × 50 mL), dried ($MgSO_4$), and concentrated to give 5.42 g of a pale yellow oil, which solidified on stirring with ethyl acetate. The solid was recrystallized from ethyl acetate to give 4.85 g (40%) of the crystalline 1-adamantylaminotriphenylphosphonium bromide. This phosphonium salt was used in the next step to prepare *N*-1-adamantyltriphenylphosphinimine.

Sodium amide was generated in situ as described by Fieser and Fieser.[23] To a stirred suspension of 0.43 g (11.0 mmol) of sodium amide in 200 mL of liquid ammonia was added 4.85 g (9.8 mmol) of 1-adamantylaminotriphenylphosphonium bromide in small portions. The resulting mixture was stirred at reflux for 30 min, then the ammonia was allowed to boil off. The residue was extracted with 100 mL of methylene chloride and the extract was filtered. The methylene chloride was removed from the filtrate in vacuo to give a white solid which was recrystallized from chloroform–hexane to give 2.9 g (72%) of the *N*-1-adamantyltriphenylphosphinimine: mp 142–146 °C; IR ($CHCl_3$) 2920, 1440, 1350, 1310, 1180, 1130, 1100 cm^{-1}; NMR ($CDCl_3$) δ 1.53 (m, 6), 1.70 (m, 6), 1.92 (br s, 3), 7.20–8.15 (m, 15).

Anal. Calcd for $C_{28}H_{30}NP$: C, 81.72; H, 7.35; N, 3.40. Found: C, 81.66; H, 7.54; N, 3.32.

***tert*-Butylaminotri-*n*-butylphosphonium Chloride.** To a 500-mL round-bottom flask containing a solution of 5.8 g (8.4 mL, 80 mmol) of *tert*-butylamine in 250 mL of anhydrous ether under nitrogen atmosphere was added 9.54 mL (8.68 g, 80 mmol) of *tert*-butyl hypochlorite at 0 °C over a period of 10 min. To the resultant solution was added 16.2 g (19.9 mL, 80 mmol) of tri-*n*-butylphosphine at 0 °C over a period of 10 min. The reaction mixture was stirred for an additional 10 min at 0 °C, then stored in a refrigerator (0 °C) for 12 h. After warming to room temperature, 100 mL of anhydrous ether was added to the reaction mixture (followed by scratching with a glass rod if necessary) to initiate precipitation of the *tert*-butylaminotri-*n*-butylphosphonium chloride. The mixture was filtered under nitrogen and the white solid was washed with anhydrous ether (2 × 50 mL). The hygroscopic white solid was dried at 35 °C (0.01 Torr) for 24 h to give 12.38 g (40%) of *tert*-butylaminotri-*n*-butylphosphonium chloride: mp 80–92 °C; IR (CCl_4) 2960, 1465, 1395, 1370, 1230, 1200 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 9), 1.20–2.50 (m, 28).

Anal. Calcd for $C_{16}H_{37}ClNP$: C, 62.01; H, 12.03; N, 4.52. Found: C, 61.62; H, 12.13; N, 4.92.

The hexafluorophosphate salt was prepared by combining equimolar aqueous solutions of the phosphonium chloride and potassium hexafluorophosphate. The phosphonium hexafluorophosphate salt was collected by filtration and recrystallized from ethanol–water to give white needles, mp 124.5–126 °C.

Anal. Calcd for $C_{16}H_{37}F_6NP_2$: C, 45.82; H, 8.89; N, 3.34; P, 14.77. Found: C, 46.01; H, 8.98; N, 3.46; P, 14.54.

***N*-*tert*-Butyltri-*n*-butylphosphinimine.** Sodium amide was generated in situ as described by Fieser and Fieser.[23] To a stirred suspension of 2.04 g (52.2 mmol) of sodium amide in 250 mL of liquid ammonia was added 13.7 g (44.2 mmol) of *tert*-butylaminotri-*n*-butylphosphonium chloride in small portions. The resulting mixture was stirred at reflux for 30 min before the ammonia was allowed to boil off. The residue was extracted with 150 mL of methylene chloride. The extract was filtered and concentrated to give 10.72 g of a light yellow, water-sensitive liquid. This liquid was distilled to give 10.2 g (84%) of the colorless phosphinimine: bp 100 °C (0.03 Torr); IR (thin film–KCl plate) 2960, 1460, 1350, 1300, 1210, 1095, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.0 (m, 9), 1.28 (s, 9), 1.20–2.10 (m, 18).

Anal. Calcd for $C_{16}H_{36}NP$: C, 70.28; H, 13.27; N, 5.12. Found: C, 70.57; H, 13.31; N, 5.14.

Trioxo-*tert*-butylimidoosmium(VIII) (4). To a 50-mL round-bottom flask containing a stirring magnet and a solution of 1.0 g (3.9 mmol) of osmium tetroxide in 30 mL of water was added slowly 0.66 mL (0.46 g, 7.8 mmol) of *tert*-butylamine at 0 °C. As the first few drops of amine were added, the pale yellow solution quickly became bright yellow. As more amine was added a lemon-yellow precipitate was formed. The mixture was stirred for 30 min after addition of the amine, then the yellow solid was collected by filtration and washed with cold water (3 × 15 mL). The yellow solid was dried in vacuo over phosphorus pentoxide at 25 °C to give 1.05 g (87%) of the monoimido complex **4**, mp 110.5–111.5 °C (lit.[2,5] mp 112 °C). Care must be taken not to maintain the vacuum longer than necessary as the monoimido complex **4** is somewhat volatile. The IR and NMR spectra were identical with those of the complex prepared by the method of Clifford and Kobayashi.[5]

Trioxo-*tert*-amylimidoosmium(VIII). To a 25-mL round-bottom flask containing a stirring magnet and a solution of 0.50 g (2.0 mmol) of osmium tetroxide in 12.5 mL of water cooled in an ice bath was slowly added 0.47 mL (0.35 g, 4.0 mmol) of *tert*-amylamine. A bright yellow precipitate quickly appeared even before all the amine was added. The mixture was stirred vigorously at 0 °C for 1 h. A portion of the precipitate had agglomerated into lumps and these were crushed with a stirring rod before filtering. The yellow precipitate, collected by filtration, was washed with cold water (3 × 10 mL) and dried in vacuo at 25 °C over phosphorus pentoxide to give 0.52 g (81%) of the *tert*-amylimido complex, mp 57–59 °C (lit.[2b,c] mp 60–61 °C). The IR and NMR spectra were identical with those of the authentic compound.[2b,c]

Dioxobis(*tert*-butylimido)osmium(VIII) (5) from Osmium Tetroxide. A three-necked 50-mL round-bottom flask containing a stirring magnet and fitted with a reflux condenser was charged with 2.0 g (7.87 mmol) of osmium tetroxide and 30 mL of methylene chloride. To the pale yellow solution was added 5.24 g (15.74 mmol) of *N*-*tert*-butyltriphenylphosphinimine. The solution immediately became burgundy red in color. After refluxing for 48 h, the black reaction mixture was applied to a silica gel dry column (500 g, CH_2Cl_2) and the diimido complex **5**, R_f 0.5, was isolated as 1.95 g of a yellow-brown solid. Recrystallization from methylene chloride–hexane gave 1.81 g (63%) of yellow, crystalline dioxobis(*tert*-butylimido)osmium(VIII): mp 119–120 °C dec; IR (CCl_4) 2980, 1452, 1362 (CMe_3), 1200 (Os=N), 888 (Os=O), 878 cm^{-1} (Os=O); NMR ($CDCl_3$) δ 1.58 (s); mass spectrum (70 eV) *m/e* (rel intensity) 366*, M^+ (3), 351* (2), 350* (1), 295* (16), 279* (13), 71 (22), 57 (100); mol wt, 365 (calcd for $C_8H_{18}N_2O_2Os$, 364).

Anal. Calcd for $C_8H_{18}N_2O_2Os$: C, 26.37; H, 4.98; N, 7.69. Found: C, 26.35; H, 5.06; N, 7.62.

Dioxobis(*tert*-butylimido)osmium(VIII) (5) from the Monoimido Complex 4. To a 25-mL round-bottom flask fitted with a stirring magnet and a reflux condenser were added 0.618 g (2.0 mmol) of trioxo-*tert*-butylimidoosmium(VIII) (**4**), 10 mL of methylene chloride, and 0.733 g (2.2 mmol) of *N*-*tert*-butyltriphenylphosphinimine. After the burgundy red solution was refluxed for 24 h, the reaction mixture was divided into two equal portions. The diimido complex **5** was isolated via preparative thin layer chromatography of each portion (silica gel, 2000 μ, CH_2Cl_2, R_f 0.5) to give a total of 0.60 g (82%) of yellow crystals, mp 119–120 °C dec.

Dioxobis(1-adamantylimido)osmium(VIII). The preparation of trioxo-1-adamantylimidoosmium(VIII) was reported previously.[2] To a 25-mL round-bottom flask fitted with a stirring magnet and a reflux condenser were added 0.58 g (1.5 mmol) of trioxo-1-adamantylimidoosmium(VIII), 10 mL of chloroform, and 0.76 g (1.85 mmol) of *N*-1-adamantyltriphenylphosphinimine. After the resulting orange-red solution was refluxed for 15 h, it was divided into two equal portions and the diimido complex was isolated via preparative thin layer chromatography of each portion (silica gel, 2000 μ, CH_2Cl_2, R_f 0.5) to give a total of 0.57 g (73%) of a yellow solid. The solid was recrystallized from chloroform–carbon tetrachloride: mp 209–211.5 °C; IR ($CHCl_3$) 3000, 2940, 2920, 2860, 1452, 1345, 1300, 1260, 1230,

1175 (Os=N), 1100, 880 (Os=O), 865 cm^{-1} (Os=O); NMR ($CDCl_3$) δ 1.75 (m, 12, $CCCH_2$), 2.04 (m, 12, $NCCH_2$), 2.32 (m, 6, CCH); mol wt, 534 (calcd for $C_{20}H_{30}N_2O_2Os$, 521).

Anal. Calcd for $C_{20}H_{30}N_2O_2Os$: C, 46.14; H, 5.81; N, 5.38. Found: C, 46.41; H, 5.78; N, 5.32.

Dioxo-1-adamantylimido-*tert*-amylimidoosmium(VIII). To a 25-mL round-bottom flask fitted with a stirring magnet and a reflux condenser were added 0.64 g (2.0 mmol) of trioxo-*tert*-amylimidoosmium(VIII), 15 mL of methylene chloride, and 1.00 g (2.43 mmol) of *N*-1-adamantyltriphenylphosphinimine. After refluxing for 48 h, the reaction mixture was divided into two equal portions, and the diimido complex was isolated via preparative thin layer chromatography of each portion (silica gel, 2000 μ, CH_2Cl_2, R_f 0.4) to give a total of 0.38 g (42%) of a yellow solid: mp 72–74 °C; IR (CCl_4) 2980, 2935, 2910, 2860, 1452, 1180, 1100, 885 (Os=O), 875 cm^{-1} (Os=O); NMR ($CDCl_3$) δ 1.05 (t, 3, J = 7 Hz, CH_2CH_3), 1.50 (s, 6, CCH_3), 1.75 (m, 6), 2.05 (m, 6), 2.30 (m, 3).

Anal. Calcd for $C_{15}H_{26}N_2O_2Os$: C, 39.46; H, 5.70; N, 6.14. Found: C, 39.67; H, 5.80; N, 6.15.

Oxotris(*tert*-butylimido)osmium(VIII) (6) from Osmium Tetroxide. A three-necked 50-mL round-bottom flask fitted with a stirring magnet, a condenser, and a nitrogen inlet was flamed out under a flow of nitrogen. To this flask was added 4.4 g (16.0 mmol) of *N*-*tert*-butyltri-*n*-butylphosphinimine followed by a solution of 1.0 g (3.93 mmol) of osmium tetroxide in 25 mL of methylene chloride. The reaction was slightly exothermic. After the dark red solution was refluxed for 60 h under nitrogen, the crude reaction mixture was applied to a silica gel dry column (800 g of silica gel; ethyl acetate–methylene chloride, 1:4; R_f 0.6) and the triimido complex **6** was isolated as 0.74 g (45%) of an orange-red solid, mp 114–116 °C dec. An analytical sample was prepared by recrystallization by slow evaporation from olefin-free hexane at 0 °C: mp 115.5–116.5 °C dec; IR (CCl_4) 2975, 1451, 1360 (CMe_3), 1190, 1100, 838 cm^{-1} (Os=O); NMR ($CDCl_3$) δ 1.47 (s); mass spectrum (70 eV) *m/e* (rel intensity) 421*, M^+ (11), 405* (24), 390* (65), 350* (25), 334* (23), 282* (28), 279* (43), 71 (55), 57 (100); mol wt, 427 (calcd for $C_{12}H_{27}N_3OOs$, 419.6).

Anal. Calcd for $C_{12}H_{27}N_3OOs$: C, 34.35; H, 6.49; N, 10.02. Found: C, 34.34; H, 6.48; N, 9.82.

Oxotris(*tert*-butylimido)osmium(VIII) (6) from Monoimido Complex 4. A three-necked 100-mL round-bottom flask fitted with a stirring magnet, a condenser, and a nitrogen inlet was flamed out under a flow of nitrogen. To this flask were added 6.84 g (25.0 mmol) of *N*-*tert*-butyltri-*n*-butylphosphinimine and 10 mL of methylene chloride followed by a solution of 3.07 g (10.0 mmol) of the monoimido complex 4 in 40 mL of methylene chloride. The resulting red solution was refluxed under nitrogen for 48 h. The reaction mixture was absorbed onto 50 g of dry column grade silica gel and the triimido complex **6** was isolated by dry column chromatography (900 g of silica gel; ethyl acetate–methylene chloride, 1:4; R_f 0.6) to give 1.89 g (45%) of red crystals, mp 114.5–115.5 °C dec.

Oxotris(*tert*-butylimido)osmium(VIII) (6) from Diimido Complex 5. Comparable treatment of 237 mg (0.65 mmol) of the diimido complex **5** with 184 mg (0.67 mmol) of *N*-*tert*-butyltri-*n*-butylphosphinimine in 5 mL of methylene chloride, followed by preparative thin layer chromatography (silica gel; 2000 μ; ethyl acetate–methylene chloride, 1:4; R_f 0.5), gave the triimido complex **6** as 84 mg (30%) of red crystals, mp 114–115 °C dec.

Oxobis(1-adamantylimido)-*tert*-butylimidoosmium(VIII). To a 10-mL round-bottom flask, which had been flamed out under nitrogen, were added 220 mg (0.80 mmol) of *N*-*tert*-butyltri-*n*-butylphosphinimine, 4 mL of methylene chloride, and 300 mg (0.58 mmol) of dioxobis(1-adamantylimido)osmium(VIII). The red solution was refluxed under nitrogen for 5 days. Preparative thin layer chromatography (silica gel; ethyl acetate–methylene chloride, 1:4; R_f 0.6) gave 150 mg (45%) of the triimido complex as an orange powder: mp 146 °C dec; IR (CCl_4) 2930, 2910, 2850, 1452, 1360, 1300, 1160, 1100, 838 cm^{-1} (Os=O); NMR ($CDCl_3$) δ 1.46 (s, 9, CMe_3), 1.70 (m, 12, $CCCH_2$), 1.94 (m, 12, $NCCH_2$), 2.25 (m, 6, CCH).

Anal. Calcd for $C_{24}H_{39}N_3OOs$: C, 50.06; H, 6.83; N, 7.30. Found: C, 50.35; H, 6.80; N, 7.07.

Reaction of Diimido Complex 5 with Dimethyl Fumarate. To a 10-mL round-bottom flask containing a solution of 364 mg (1.0 mmol) of dioxobis(*tert*-butylimido)osmium (**5**) in 5 mL of methylene chloride was added 159 mg (1.1 mmol) of dimethyl fumarate. The red solution slowly darkened in color as the mixture was stirred at room temperature for 7 h. The diamido osmium(VI) complex **11a** was isolated by preparative thin layer chromatography (silica gel; 2000 μ; CH_2Cl_2; R_f 0.2) to give 302 mg (60%) of a red-brown solid. An analytical sample was prepared by recrystallization from methylene chloride–hexane: mp 114.8–115.3 °C; IR ($CHCl_3$) 2980, 1760, 1735, 1465, 1435, 1395, 1370, 1285, 1250, 1190, 1100, 1010, 910 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s, 18, CMe_3), 3.72 (s, 6, OCH_3), 4.55 (s, 2, NCH).

Anal. Calcd for $C_{14}H_{26}N_2O_6Os$: C, 33.06; H, 5.15; N, 5.51. Found: C, 33.07; H, 5.14; N, 5.51.

Reaction of Diimido Complex 5 with Diethyl Fumarate. To a 10-mL round-bottom flask containing a solution of 36.4 mg (0.1 mmol) of the diimido compound **5** in 5 mL of methylene chloride was added 26 mg (0.15 mmol) of diethyl fumarate. The red solution was refluxed for 5 h. The solvent was evaporated to give a reddish residue which was submitted to preparative thin layer chromatography using hexane–ethyl acetate (3:1) as eluent. The red band at R_f 0.3–0.4 afforded 45 mg (84%) of the diamido complex **11b** as red-brown crystals: mp 97–99 °C; IR (CCl_4) 2970, 1750, 1725, 1460, 1390, 1365, 1275, 1225, 1190, 1095, 1020, 905 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (t, 6, J = 7 Hz, CH_2CH_3), 1.40 (s, 18, *t*-Bu), 4.19 (qr, 4, J = 7 Hz, CH_2CH_3), 4.50 (s, 2, NCH); mol wt by osmometry (in benzene), 500 (calcd, 536.6).

Reaction of Triimido Complex 6 with Dimethyl Fumarate. To a 10-mL round-bottom flask containing a solution of 105 mg (0.25 mmol) of oxotris(*tert*-butylimido)osmium(VIII) (**6**) in 2.5 mL of methylene chloride was added 38 mg (0.27 mmol) of dimethyl fumarate. The resultant solution was stirred at room temperature for 4 h. The diamido osmium(VI) complex **12** was isolated by preparative thin layer chromatography (silica gel; 2000 μ; ethyl acetate–methylene chloride, 1:9; R_f 0.4) to give 103 mg (72%) of a red-brown, crystalline solid. An analytical sample was prepared by recrystallization from methylene chloride–hexane: mp 159.5–160.5 °C; IR (CCl_4) 2980, 1758, 1730, 1370 (CMe_3), 1235, 1200, 1110, 1010, 890 cm^{-1} (Os=O); NMR ($CDCl_3$) δ 1.35 (s, 18, CMe_3), 1.50 (s, 9, CMe_3), 3.67 (s, 3, OCH_3), 3.70 (s, 3, OCH_3), 4.50 (s, 2, NCH).

Anal. Calcd for $C_{18}H_{35}N_3O_5Os$: C, 38.35; H, 6.26; N, 7.45. Found: C, 38.58; H, 6.24; N, 7.35.

General Procedure for Reaction of Osmium(VIII) Imido Compounds with Olefins. To a 10-mL round-bottom flask, containing a solution of 0.10 mmol of the osmium(VIII) imido complex in 1.5 mL of carbon tetrachloride, were added 0.20 mmol of olefin and 100 μL (0.01 mmol) of a 0.1 M solution of tetradecane (internal standard) in carbon tetrachloride. The resulting solution was stirred at 25 or 40 °C until all osmium(VIII) imido compound had disappeared (TLC; silica gel; ethyl acetate–methylene chloride, 1:4). The solvent was then removed in vacuo from the black reaction mixture. The black residue was dissolved in 5 mL of anhydrous ether, and the solution was cooled to 0 °C. To the cooled solution was added 38 mg (1.0 mmol) of lithium aluminum hydride. The reaction mixture was then stirred at 25 °C for 8 h. The mixture was again cooled to 0 °C and water (38 μL), 15% aqueous sodium hydroxide (38 μL), and again water (114 μL) were added dropwise to the vigorously stirred mixture. The reaction mixture was stirred until the precipitate was of a grainy character before it was filtered. The filtrate was analyzed by GLC and the yields of hydroxyamines and diamines were determined by the internal standard method. Yields of hydroxyamines and diamines are given in Table IV.

For each olefin, the corresponding hydroxyamine and diamine were collected via preparative GLC (10% SE-30; 8 ft; 170 °C) from the reaction mixture for the purpose of characterization and as authentic samples for the determination of response factors (RF). Each hydroxyamine was shown to be identical with an authentic sample prepared from the corresponding olefin and the monoimido complex **4**.[2] Spectroscopic and elemental analysis data for the diamines are reported below.

1-Phenyl-1,2-bis(*tert*-butylamino)ethane: IR ($CHCl_3$) 3300 (NH), 2960, 1480, 1450, 1390, 1365, 1225, 1100 cm^{-1}; NMR ($CDCl_3$) δ 1.02 (s, 9, CMe_3), 1.06 (s, 9, CMe_3), 1.42 (br s, 2, NH), 2.60 (m, 2, CCH_2N), 3.70 (m, 1, $ArCHN$), 7.32 (m, 5, ArH); *m/e* 248 (M^+).

Anal. Calcd for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. Found: C, 77.64; H, 11.14; N, 10.99.

1,2-Bis(*tert*-butylamino)decane: IR (CCl_4) 3300 (NH), 2950, 1460, 1390, 1360, 1230, 1100, 1020 cm^{-1}; NMR ($CDCl_3$) δ 0.85–1.50 (m, 35), 2.50 (m, 3, NCH).

Anal. Calcd for $C_{18}H_{40}N_2$: C, 75.98; H, 14.17; N, 9.85. Found: C, 76.25; H, 14.45; N, 9.83.

threo-5,6-Bis(*tert*-butylamino)decane: IR ($CHCl_3$) 3350 (NH), 2950, 1585, 1470, 1400, 1380, 1240, 1190 cm^{-1}; NMR ($CDCl_3$) δ 0.70–1.90 (m, 36), 2.55 (m, 2, NCH), 4.18 (br s, 2, NH).

Anal. Calcd for $C_{18}H_{40}N_2$: C, 75.98; H, 14.17; N, 9.85. Found: C, 76.20; H, 14.39; N, 9.92.

Reaction of Osmium(VIII) Imido Complexes with Cis-Disubstituted and Trisubstituted Olefins. The reaction of diimido complex **5** and triimido complex **6** with (*Z*)-5-decene, cyclohexene, and 3-methyl-2-hexene were investigated. All reactions were monitored by TLC (silica gel; ethyl acetate–methylene chloride, 1:9). Thin layer chromatography of the reaction mixtures indicated that there was no reaction between the triimido complex **6** and the above olefins. Similarly, the diimido complex **5** did not react with (*Z*)-5-decene and 3-methyl-2-hexene. All reactions were performed in a manner similar to that described below for the reaction of cyclohexene with **5**.

To 10 mL of methylene chloride were added 290 mg (0.8 mmol) of diimido complex **5** and 123 mg (1.6 mmol) of cyclohexene. The reaction mixture was stirred at 25 °C for 1 day, after which time no reaction was observed by TLC. The reaction mixture was then heated to 40 °C for 2 days. A black spot at the origin of the TLC plate indicated that some reaction had taken place. Lithium aluminum hydride workup as described in the previous general procedure, using 0.31 g (8 mmol) of $LiAlH_4$, gave 37 mg (20% based on imido complex) of a brown solid. This solid was shown by GLC and NMR to be identical with the hydroxyamine prepared from the monoimido complex **4** and cyclohexene.[2] No diamine was detected.

Reaction of Diimido Complex 5 with (*E*)- and (*Z*)-1-Deuterio-1-decene. To a 25-mL round-bottom flask, fitted with a stirring magnet and a condenser, were added 0.50 g (1.37 mmol) of diimido complex **5**, 10 mL of pyridine, and 0.37 g (0.50 mL, 2.61 mmol) of (*E*)- or (*Z*)-1-deuterio-1-decene. After stirring at 45 °C for 84 h, $LiAlH_4$ workup as described in the general procedure above, using 0.53 g (14.0 mmol) of lithium aluminum hydride, gave a brown oil which was bulb to bulb distilled (70 °C, 0.05 Torr). Pure samples of the diamines from (*E*)- and (*Z*)-1-deuterio-1-decene were obtained by preparative GLC (10% SE-30, 8 ft, 170 °C). The diamine obtained from (*E*)-1-deuterio-1-decene was shown to be different from the diamine obtained from (*Z*)-1-deuterio-1-decene by ^1H NMR. The NMR spectra were obtained after deuterium exchange of the amine protons. The protons on the carbons bearing the nitrogens of the diamine obtained from the *E* olefin appeared as a multiplet extending over the range δ 2.20–2.65. By contrast, the corresponding protons of the diamine obtained from the *Z* olefin appeared as a multiplet in a narrow band centered at δ 2.52. Deuterium decoupling experiments failed to simplify the spectra of the diamines.

threo-1,2-Bis(*tert*-butylamino)-1-deuteriodecane (from *E* olefin): NMR ($CDCl_3$) δ 0.75–1.50 (m, 35), 2.20–2.65 (m, 2).

erythro-1,2-Bis(*tert*-butylamino)-1-deuteriodecane (from *Z* olefin): NMR ($CDCl_3$) δ 0.75–1.50 (m, 35), 2.52 (m, 2).

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References and Notes

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