Chiral-at-Metal Osmium(VI) Phosphine Complexes

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Received November 26, 2003

The chiral-at-metal osmium complex $[N(n\text{-}Bu)_4][cis\text{-}Os(N)(CH_2SiMe_3)PhCl_2]$ results from series of alkylation and protonation reactions from $[N(n\text{-}Bu)_4][Os(N)Cl_4]$. (*S,S*)-Chiraphos displaces a chloride from this complex to produce two isomers of $Os(N)(CH_2SiMe_3)PhCl$-((*S,S*)-chiraphos) with different configurations at osmium. ^{31}P NMR spectroscopy indicates that one isomer has a phosphorus donor from the chiraphos ligand *trans* to the nitride, while the other has chloride in this position. Molecular mechanics calculations suggest that the axial phosphine isomer has an *S* configuration at osmium. This isomer reversibly loses an additional chloride ion and can be separated from the isomer with the opposite configuration by the careful addition of $AgSbF_6$. The diastereomers $[SbF_6][(S)\text{-}Os(N)(CH_2SiMe_3)Ph((S,S)$-chiraphos)] and $[SbF_6][(R)\text{-}Os(N)(CH_2SiMe_3)Ph((S,S)$-chiraphos)] can be isolated separately. The two isomers of $[SbF_6][Os(N)(CH_2SiMe_3)Ph((R,R)$-chiraphos)] are enantiomers to those of $[SbF_6][Os(N)(CH_2SiMe_3)Ph((S,S)$-chiraphos)]. The molecular structures of acetonitrile adducts $[SbF_6][(S)\text{-}Os(N)(CH_2SiMe_3)Ph((S,S)$-chiraphos)(NCMe)] and $[SbF_6][(R)\text{-}Os(N)(CH_2SiMe_3)Ph((S,S)$-chiraphos)(NCMe)], from a crystal containing both isomers, show equatorial, chelating (*S,S*)-chiraphos ligands with acetonitrile *trans* to the nitride in each.

Introduction

Asymmetric catalysts are a key to the selective synthesis of fine chemicals and pharmaceuticals.[1] Hydrogenation catalyzed by rhodium or iridium complexes with chiral phosphines is a step in the synthesis of commercially important molecules such as aspartame, naproxen, and levodopa. Asymmetric hydrogenation of carbonyl compounds by (binap)ruthenium(II) complexes is one step in the commercial production of carbapenem antibiotics.[2] The epoxidation of allylic alcohols catalyzed by titanium(IV) tartrate complexes provides epoxides in high enantiomeric excess,[3] and manganese complexes with chiral salen ligands epoxidize simple alkenes with good stereoselectivity.[4]

Most chiral metal complexes derive their asymmetry from chiral ligands.[5] Among the most common of these chiral ligands are bidentate phosphine ligands such as (*S,S*)-chiraphos and (*S*)-binap.[6] Other asymmetric catalysts are metal complexes with chiral, chelating nitrogen ligands such as amines, pyridines, azoxalines, and salen derivatives.[7] Chiral-at-metal complexes derive their asymmetry from the arrangement of ligands around the metal center.[8] Recent examples of chiral-at-metal organometallic complexes include half-sandwich complexes with a pseudo-tetrahedral geometry around the metal similar to carbon.[9]

The investigation of chiral-at-metal complexes is important because these complexes could provide more steric interaction with substrates and improve stereocontrol in catalytic reactions. Here we report the synthesis of a chiral osmium(VI) complex, $[N(n\text{-}Bu)_4][cis\text{-}Os(N)(CH_2SiMe_3)PhCl_2]$, and its substitution reactions with (*S,S*)-chiraphos and (*R,R*)-chiraphos.

Results

We can prepare $[N(n\text{-}Bu)_4][cis\text{-}Os(N)(CH_2SiMe_3)PhCl_2]$ through a series of alkylation and protonation steps starting from $[N(n\text{-}Bu)_4][Os(N)Cl_4]$ (Scheme 1). A

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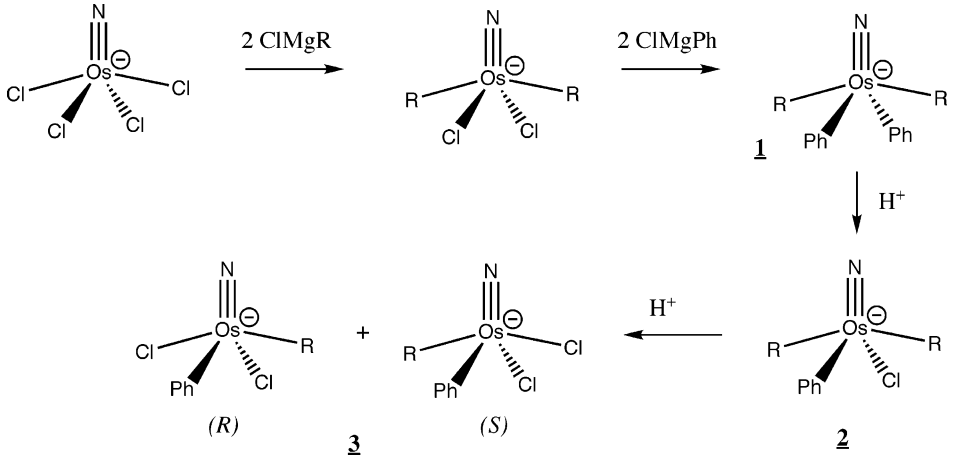
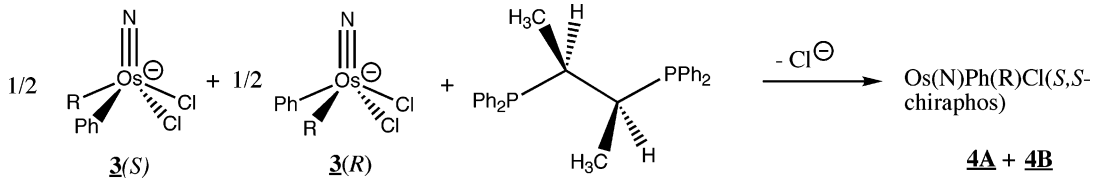
10.1021/om034329f CCC: $27.50
Publication on Web 03/30/2004

Scheme 1



Scheme 2



suspension of $[N(n\text{-}Bu)_4][Os(N)Cl_4]$ in diethyl ether reacts with 2 equiv of $Mg(CH_2SiMe_3)Cl$ to give $[N(n\text{-}Bu)_4][trans\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$. The product crystallizes from cold ether in 70% yield. It must be isolated quickly from the reaction mixture to prevent *cis*−*trans* isomerization that is mediated by $MgCl_2$ in solution. The red-orange complex $[N(n\text{-}Bu)_4][trans\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$ reacts with 2 equiv of MgPhCl in diethyl ether to produce a yellow solution of $[N(n\text{-}Bu)_4][trans\text{-}Os(N)(CH_2SiMe_3)_2Ph_2]$, **1**. Yellow crystals of analytically pure **1** form from dichloromethane/diethyl ether solution in 62% yield. Metathesis of the cation with $[PPh_4]Br$ in CH_2Cl_2 gives a tetraphenylphosphonium salt, $[PPh_4][trans\text{-}Os(N)(CH_2SiMe_3)_2Ph_2]$. The ^1H NMR spectrum of **1** shows a single resonance line for the four equivalent methylene protons of the two (trimethylsilyl)methyl groups, confirming the *trans* geometry of these ligands.

The osmium-alkyl carbon bonds in **1** should be more electron rich than the osmium-phenyl carbon bonds, but 1 equiv of HCl or pyridinium chloride cleanly protonates the bond to the phenyl group. Red crystals of $[N(n\text{-}Bu)_4][trans\text{-}Os(N)(CH_2SiMe_3)_2PhCl]$, **2**, form from diethyl ether solution in 47% yield. The ^1H NMR spectrum of the product contains resonances for the tetra-*n*-butylammonium cation and the phenyl group along with two doublets at 1.94 and 1.29 ppm for the diastereotopic methylene protons and a singlet at 0.05 ppm for the trimethylsilyl group of the equivalent (trimethylsilyl)methyl ligands. Integration shows that there are two (trimethylsilyl)methyl groups per phenyl group.

The next equivalent of HCl cleaves one or the other of the equivalent alkyl ligands and produces a racemic mixture of $[N(n\text{-}Bu)_4][(S)\text{-}Os(N)(CH_2SiMe_3)PhCl_2]$ and $[N(n\text{-}Bu)_4][(R)\text{-}Os(N)(CH_2SiMe_3)PhCl_2]$, **3**. The reaction between **1** and 2 equiv of HCl in dichloromethane/diethyl ether gives a red product. The crude material crystallizes in 74% yield from THF/hexane at −30 °C. The ^1H NMR spectrum includes two doublets for the diastereotopic methylene protons of the (trimethylsilyl)-methyl ligand, showing that this complex has a *cis* geometry. Excess HCl reacts with **3** to cleave the remaining Os−Ph bond and produce $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)Cl_3]$.

We can assign the configuration of the osmium(VI) center in the enantiomers of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)PhCl_2]$ by analogy with an asymmetric carbon if we consider the *cis*-Cl_2 ligands to be one group, L (Figure 1).

Complex **3** reacts with the chiral diphosphine (*S*,*S*)-chiraphos in dichloromethane to generate $Os(N)(CH_2SiMe_3)PhCl$((*S*,*S*)-chiraphos), **4**, and $[N(n\text{-}Bu)_4]Cl$ (Scheme 2). The slow addition of 1 equiv of $AgSbF_6$ facilitates removal of the free chloride as AgCl. The remaining salt, $[N(n\text{-}Bu)_4][SbF_6]$, precipitates when diethyl ether is added to the solution. The product is a hexane-soluble oil that was characterized by field desorption mass spectrometry and by spectroscopic techniques. The ^1H, ^{13}C, and ^{31}P NMR spectra clearly show that **4** is a mixture of two isomers, **4A** and **4B**. The ^{31}P NMR signals of one isomer are at 41.5 and 23.3 ppm, while those for the other isomer are at 31.9 and 31.8 ppm.

In the ^1H and ^{31}P NMR spectra of $Os(N)(CH_2SiMe_3)PhCl$((*S*,*S*)-chiraphos) at room temperature, the signals for one of the diastereomers, **4A**, are broad, while the signals for the other, **4B**, are sharp. The signals for **4A** become sharper as the temperature is reduced or when $[N(n\text{-}Bu)_4]Cl$ is added to the solution. Figure 2 shows

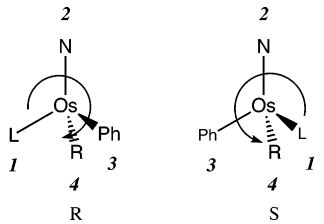
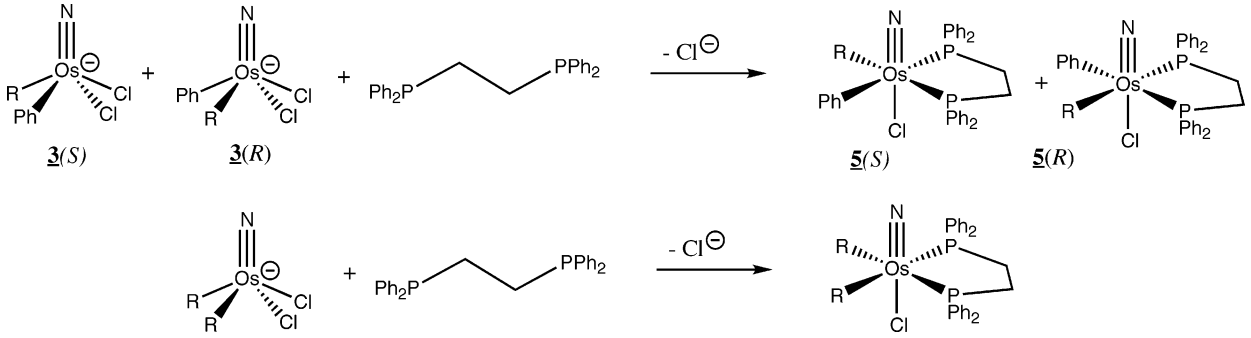
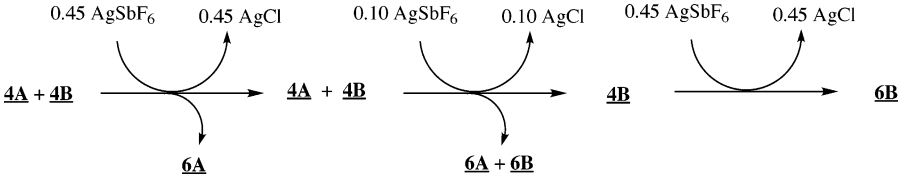


Figure 1. Stereochemistry about Os(VI) in Os(N)R(Ph)L complexes.

Scheme 3



Scheme 4



the signals corresponding to the $SiMe_3$ groups of **4A** (right) and **4B** (left) in the ^1H NMR spectrum from 26 to −50 °C. The two signals have areas equal to one another at all temperatures. The line width of the signal for **4A** is equal to that of **4B** at −40 °C and below. The diastereomers **4A** and **4B** do not interconvert in solution.

We previously reported the synthesis of $Os(N)(CH_2SiMe_3)_2Cl(dppe)$ from $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and dppe.[10] The ^1H and ^{31}P NMR spectra of this complex clearly show that the chloride is axial and the two alkyl ligands are *cis* to one another and *trans* to the dppe ligand. There is a single peak at 29.8 ppm for the equivalent phosphorus atoms of the dppe ligand in the ^{31}P NMR spectrum. The reaction between racemic $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)PhCl_2]$, **3**, and dppe produces a racemic mixture of $Os(N)(CH_2SiMe_3)PhCl(dppe)$, **5** (Scheme 3). The ^{31}P NMR spectrum of this complex includes two doublets at 27.7 and 24.2 ppm for inequivalent phosphorus atoms in similar chemical environments.

Cationic isomers with the formula $[Os(N)(CH_2SiMe_3)Ph((S,S)\text{-chiraphos})][SbF_6]$, **6**, result from abstraction of the remaining chloride ligand of $Os(N)(CH_2SiMe_3)PhCl((S,S)\text{-chiraphos})$, **4**, by $AgSbF_6$ in dichloromethane solution. The product crystallizes from dichloromethane/diethyl ether solution at −30 °C. The NMR spectra show that two isomers of the product, **6A** and **6B**, are formed.

The isomers of $Os(N)(CH_2SiMe_3)PhCl((S,S)\text{-chiraphos})$, **4**, vary in their reactivity with Ag(I). When slightly less than 0.5 equiv of $AgSbF_6$ is added slowly to a solution of **4** in CD_2Cl_2, ^1H and ^{31}P NMR spectroscopy show that **4A** is cleanly converted to one isomer of $[Os(N)(CH_2SiMe_3)Ph((S,S)\text{-chiraphos})][SbF_6]$, **6A**, while **4B** remains unreacted. We can separately isolate the isomers of **6** by combining **4** and 0.45 equiv of $AgSbF_6$ in CH_2Cl_2, filtering the mixture to remove AgCl, adding hexane, and filtering to collect the precipitated **6A**. We then recover the unreacted **4** from the filtrate and combine this with 0.10 equiv of $AgSbF_6$ in CH_2Cl_2. After adding hexane to the solution and filtering, we can isolate **4B** from the filtrate. We cannot isolate the more reactive isomer **4A** from mixtures of **4A** and **4B**. A solution of **4B** reacts with $AgSbF_6$ in CH_2Cl_2 to produce **6B** (Scheme 4).

The halide abstraction is most selective in CH_2Cl_2 at room temperature. At −30 °C, the reaction between **4** and 0.45 equiv of $AgSbF_6$ in CH_2Cl_2 produces both **6A** and **6B** in a 6:1 ratio. The same reaction in acetonitrile solution produces nearly equal amounts of the two isomers of **6**. The isomers **6A** and **6B** do not interconvert in solution at room temperature. These complexes readily add acetonitrile in the sixth coordination position to form stable adducts $[Os(N)(CH_2SiMe_3)Ph((S,S)\text{-chiraphos})(NCMe)][SbF_6]$, **7A** and **7B**.

The alkyl and aryl resonances in the ^1H NMR spectra of **6A** and **6B** show coupling to each of the inequivalent phosphorus atoms of the (*S,S*)-chiraphos ligand. The ^1H NMR spectra of **7A** and **7B** are very similar to **6A** and **6B** except that the alkyl resonances are shifted to higher field. The ^{31}P NMR spectrum of **6A** includes two signals at 59.2 and 49.8 ppm for the diphosphine ligand. The

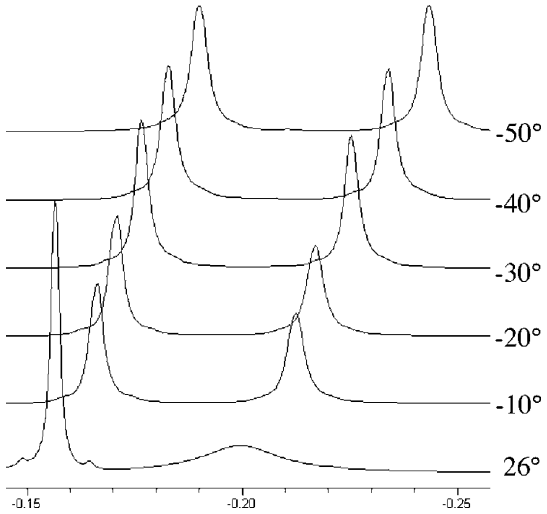


Figure 2. Variable-temperature ^1H NMR spectrum of **4**, $SiMe_3$ Region in CD_2Cl_2.

(10) Shapley, P. A.; Marshman, R. R.; Shusta, J. M.; Gebeyehu, Z.; Wilson, S. R. *Inorg. Chem.* **1994**, *33*, 498−502.

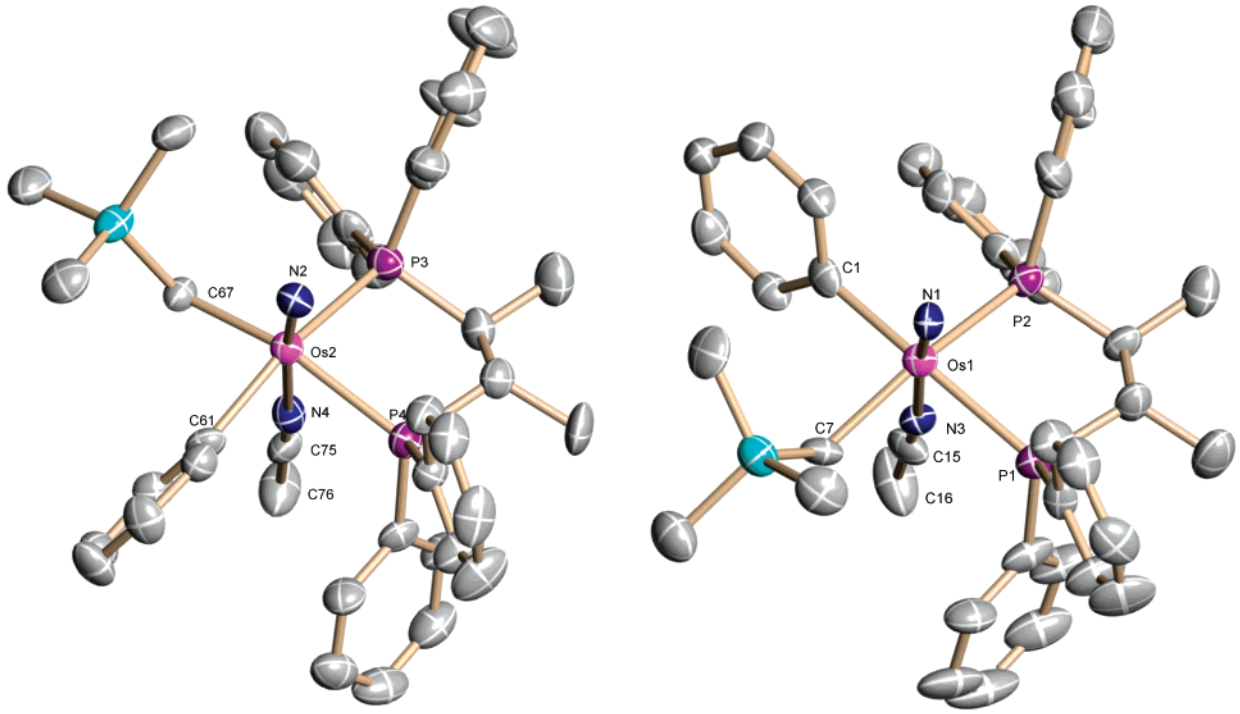
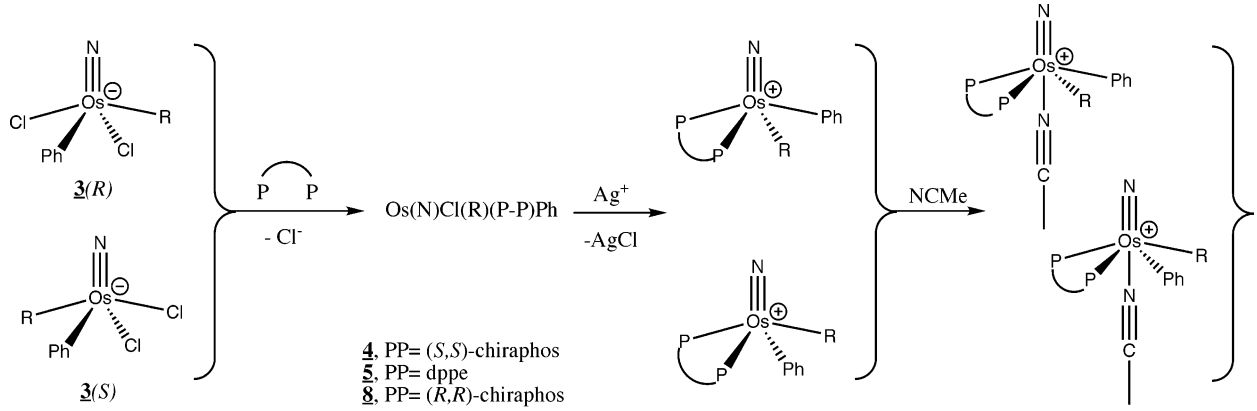


Figure 3. Molecular structures of (*S*)-**7** and (*R*)-**7**.

Scheme 5



chemical shift of these signals for **6B** are very similar at 56.1 and 47.1 ppm. For **7A** and **7B**, the phosphorus signals are at 51.4, 37.9 and 40.0, 39.7, respectively.

We also prepared the related complexes [Os(N)(CH_2-$SiMe_3$)Ph((*R*,*R*)-chiraphos)][SbF_6], **9**, and [Os(N)(CH_2-$SiMe_3$)Ph(dppe)][SbF_6], **10**, from **3** and either (*R*,*R*)-chiraphos or dppe, followed by the addition of 2 equiv of $AgSbF_6$. Like **6**, [Os(N)(CH_2SiMe_3)Ph((*R*,*R*)-chiraphos)][SbF_6] is a mixture of two isomers, **9A** and **9B**. The chemical shifts of the resonances of these cationic complexes shift with concentration, but the ^{1}H NMR spectrum of a mixture of **9A** and **9B** is superimposable on a spectrum of a mixture of **6A** and **6B** at the same concentration. We obtained the molecular structures of both **7A** and **7B** from a single-crystal X-ray diffraction. Unfortunately, we were not able to obtain good quality X-ray data from either of the separated isomers. In each of the isomers, the acetonitrile ligand is *trans* to the nitrido group. The (*S*,*S*)-chiraphos, (trimethylsilyl)-methyl, and phenyl ligands are in the equatorial plane. The two complexes are diastereomers with an opposite configuration at the osmium centers. The molecular structures of the isomers shown below (Figure 3) are very similar to that of [Os(N)(CH_2SiMe_3)$_2$(NCMe)(dppe)]-[BF_4], **13**.[10]

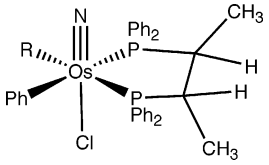
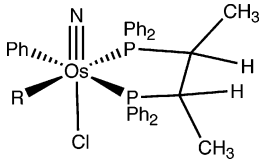
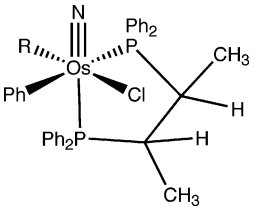
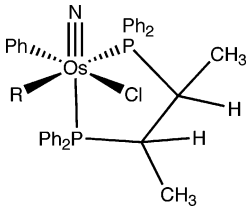
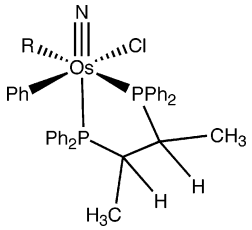
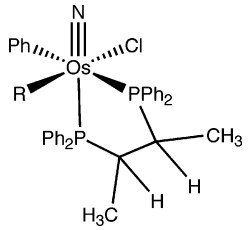
Selected bond distances and angles of (*S*)-**7**, (*R*)-**7**, and **13** are listed in Table 1. The Os−N bond distances for (*S*)-**7** and (*R*)-**7** vary slightly from each other at 1.642-(5) and 1.624(6) Å, respectively. The bond between the osmium and the phenyl carbon, 2.113(7) Å, for (*R*)-**7** is shorter than the corresponding Os−C bond in the other diastereomer, 2.128(7) Å. These distances are marginally longer than those found in structures of CpOs(N)-Ph_2, InOs(N)Ph_2, and Tp*Os(N)Ph_2, which range from 2.088(4) to 2.119(3) Å.[11] The bond angles around the N≡

(11) Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071−4076.

Table 1. Selected Bond Distances (Å) and Angles (deg)

	(*S*)-**7**	(*R*)-**7**	**13**
Os≡N	1.642(5)	1.624(6)	1.638(5)
Os−C (CH_2SiMe_3)	2.138(7)	2.130(6)	2.147(6), 2.142(6)
Os−C (Ph)	2.128(7)	2.113(7)	
Os−P *cis* to (CH_2SiMe_3)	2.465(2)	2.4616(19)	2.455(2), 2.451(2)
Os−P *cis* to (Ph)	2.4392(19)	2.4318(19)	
Os−**N**≡CMe	2.370(6)	2.366(6)	2.399(6)
N≡**Os**−**N**CMe	175.8(2)	174.3(2)	178.2(2)
Os−**N**≡**C**Me	172.9(6)	175.8(6)	168.2(6)
N≡Os−C (CH_2SiMe_3)	104.3(3)	104.5(3)	103.4(3), 100.5(3)
N≡Os−C (Ph)	97.4(3)	98.0(3)	
N≡Os−P *cis* to (CH_2SiMe_3)	93.4(2)	98.3(2)	98.9(2), 101.7
N≡Os−P *cis* to (Ph)	101.85(19)	97.7(2)	
P−Os−P	83.66(7)	83.47(7)	81.67(6)

Table 2. Possible Isomers of 4 and the Calculated Relative Energies for Each Equilibrium Geometry

Energy	*S* isomers	Energy	*R* isomers
(a) 157 kcal/mol)		(d) 155 kcal/mol)	
(b) 167 kcal/mol)		(e) 178 kcal/mol)	
(c) 175 kcal/mol)		(f) 178 kcal/mol)	

Os are smaller for the Ph group and the P *trans* to it than the (trimethylsilyl)methyl group and the P *trans* to it, creating a puckered or buckled square for the equatorial ligands.

Discussion

The selective electrophilic attack on the aryl group over the aliphatic group does not follow the expected M−C strength trend. A bond between a metal and an sp^2-hybridized carbon of a phenyl group is typically stronger and shorter than a bond between that metal and an sp^3-hybridized alkyl carbon.[12] The osmium−carbon bonds to the phenyl ligand in the isomers of ***7*** are shorter than the corresponding bonds to the alkyl ligands.

The chelating diphosphine ligand (*S*,*S*)-chiraphos displaces chloride from the racemic mixture of the osmium(VI) anions [*cis*-Os(N)(CH_2SiMe_3)$PhCl_2$]$^-$ to produce two isomers of **4**. The displacement reaction is analogous to the reaction of dppe with [Os(N)(CH_2SiMe_3)$_2Cl_2$]$^-$ that produces Os(N)(CH_2SiMe_3)$_2$Cl(dppe).[10] There are six possible isomers of complex **4**, but the ^1H and ^{31}P NMR spectra show that only two of these form.

(12) (a) Bennet, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100.

Molecular mechanics calculations can provide information about the steric interactions leading to the relative stability of these isomers. We calculated the energies of the equilibrium geometries of the six possible isomers of **4** with the SPARTAN '02 mechanics program (MMFF94) using as constraints the Os−ligand bond lengths and angles from the X-ray crystal structure of [Os(N)(CH_2SiMe_3)Ph(NCMe)((*S*,*S*)-chiraphos)][SbF_6] and related molecules (Table 2). Axial Os−P and Os−Cl distances are greater than the equatorial distances due to the strong *trans* effect of the nitrido ligand. The *R* and *S* isomers with axial chloride ligands are most stable. Of the four isomers with equatorial chloride ligands, three have nearly equivalent energies, but one *S* isomer is more stable.

Although the two isomers with equatorial diphosphine ligands are most stable, the mechanism of substitution reactions at five-coordinate nitrido osmium complexes promotes formation of an isomer with one axial phosphine donor (Scheme 6). Donors coordinate weakly and reversibly to the open coordination position *trans* to the nitrido group. Coordination of one phosphorus atom of (*S*,*S*)-chiraphos to [N(*n*-Bu)$_4$][(*S*)-Os(N)(CH_2SiMe_3)-$PhCl_2$], **3**, followed by intramolecular displacement of chloride *trans* to the phenyl group leads to the low-energy *S* isomer (b). Coordination of a phosphorus atom

Scheme 6

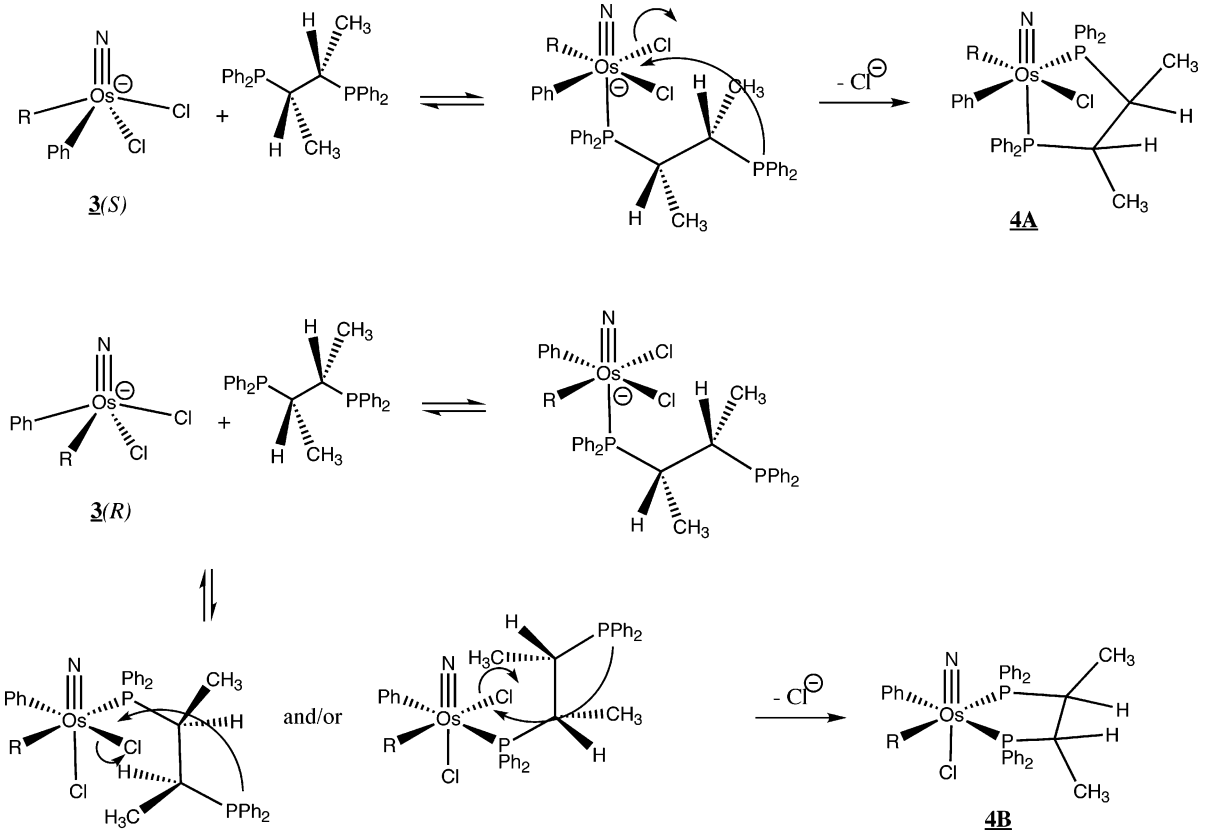


Table 3. Summary of Crystal Data for 7A and 7B

empirical formula	$C_{44}H_{57}F_6N_2OOsP_2SbSi$
space group	$P2_12_12_1$
cryst syst	orthorhombic
unit cell dimens	$a = 15.287(5)$ Å, $\alpha = 90°$
	$b = 18.889(7)$ Å, $\beta = 90°$
	$c = 33.168(11)$ Å, $\gamma = 90°$
volume	9577(6) Å^3
Z	8
density(calcd)	1.589 Mg/m^3
temperature	193(2) K
wavelength	0.71073 Å
abs coeff	3.364 mm^{-1}
θ range for data collection	1.47−25.37°
no. of indep reflns	17 526 [R(int) = 0.0812]
final R indices [$I>2\sigma(I)$]	R1 = 0.0378, wR2 = 0.0576
R indices (all data)	R1 = 0.0629, wR2 = 0.0616

to the open coordination site of [N(*n*-Bu)$_4$][(*R*)-Os(N)-(CH$_2$SiMe$_3$)PhCl$_2$] followed by intramolecular substitution of chloride does not lead to a low-energy structure. Instead, the phosphorus ligand dissociates. A slower equatorial displacement of an axial chloride by the nucleophilic phosphorus atom followed by intramolecular displacement of another equatorial chloride leads to the low-energy *R* isomer (d).

Evidence for these assignments comes from the ^{31}P NMR spectra of the isomers of **4**. The spectrum of **4A** shows two resonances separated by over 18 ppm. The chemical shifts should not vary by this degree due to the differences in the *trans*-alkyl or aryl ligand. The other isomer, **4B**, has two ^{31}P NMR resonances for P *trans* to phenyl and P *trans* to (trimethylsilyl)methyl with very similar chemical shifts. The racemic dppe analogue also has two phosphorus resonances with very similar chemical shifts. It is likely that one phosphorus atom of the (*S*,*S*)-chiraphos ligand in **4A** is axial, *trans* to the nitrido ligand. The only low-energy isomer of **4** with an axial phosphorus ligand has the *S* configuration about the osmium center and is labeled (b) in Table 2. The other isomer, **4B**, must have the opposite configuration about osmium and has only equatorial phosphorus ligands, consistent with isomer (d).

In the polar, noncoordinating solvents dichloromethane or chloroform, **4A**, but not **4B**, is in equilibrium with an isomer of [Os(N)Ph(CH$_2$SiMe$_3$)(*S*,*S*-chiraphos)]Cl. The ^{1}H NMR spectrum is broad at room temperature but becomes sharp when [N(*n*-Bu)$_4$]Cl is added to the solution. The excess chloride drives the equilibrium toward the neutral chloride adduct. The equilibrium is temperature dependent. Below −40 °C, the resonances of **4A** are as sharp as those for **4B**, indicating that chloride loss is no longer rapid. Because **4A** does not isomerize in solution, rearrangement of [Os(N)Ph(CH$_2$-SiMe$_3$)(*S*,*S*-chiraphos)]Cl must be slow relative to re-addition of Cl$^-$ to the metal center. The isomer with the equatorial diphosphine **4B** has lower steric strain than **4A** and is more stable with respect to chloride dissociation. Isomer **4A** dissociates chloride more readily, and this isomer selectively reacts with silver(I) salts to form **6A**. When the chloride is removed, the trigonal bipyridamidal intermediate rearranges to the more stable square pyramidal geometry (Scheme 7). ^{31}P NMR spectroscopy shows that the phosphine ligands in **6A** and **6B** have similar environments.

The cationic (*R*,*R*)-chiraphos complexes [Os(N)(CH$_2$-SiMe$_3$)Ph((*R*,*R*)-chiraphos)][SbF$_6$], **9A** and **9B**, are diastereomers. These are enantiomers of the (*S*,*S*)-chiraphos complexes (Figure 5).

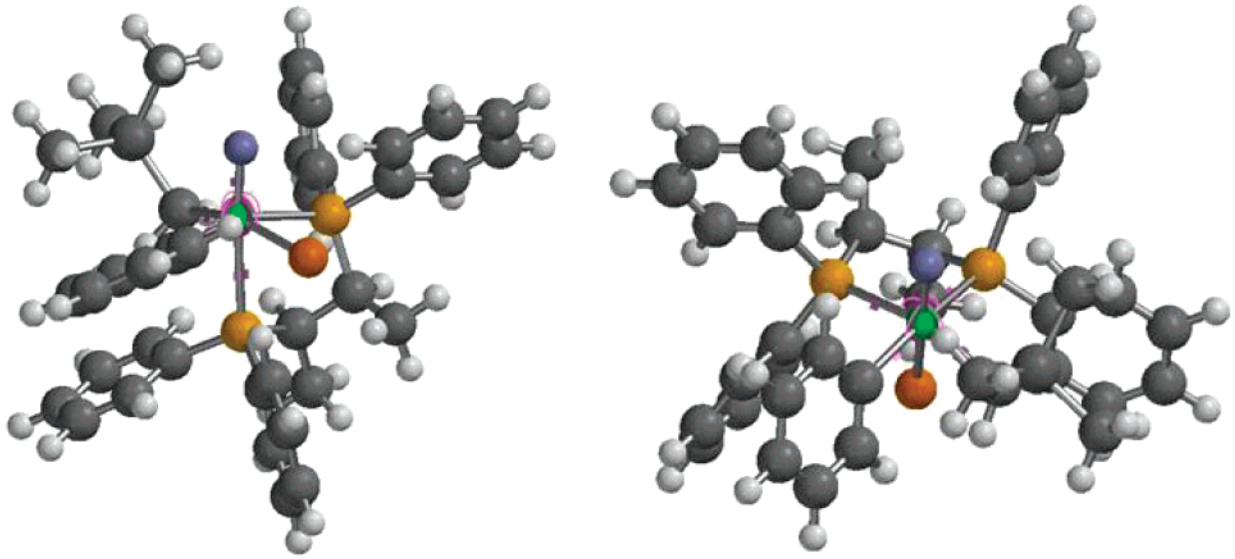


Figure 4. Proposed low-energy geometry of **4A** and **4B**.

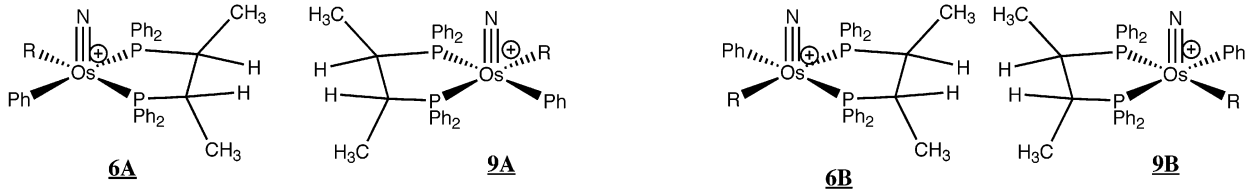
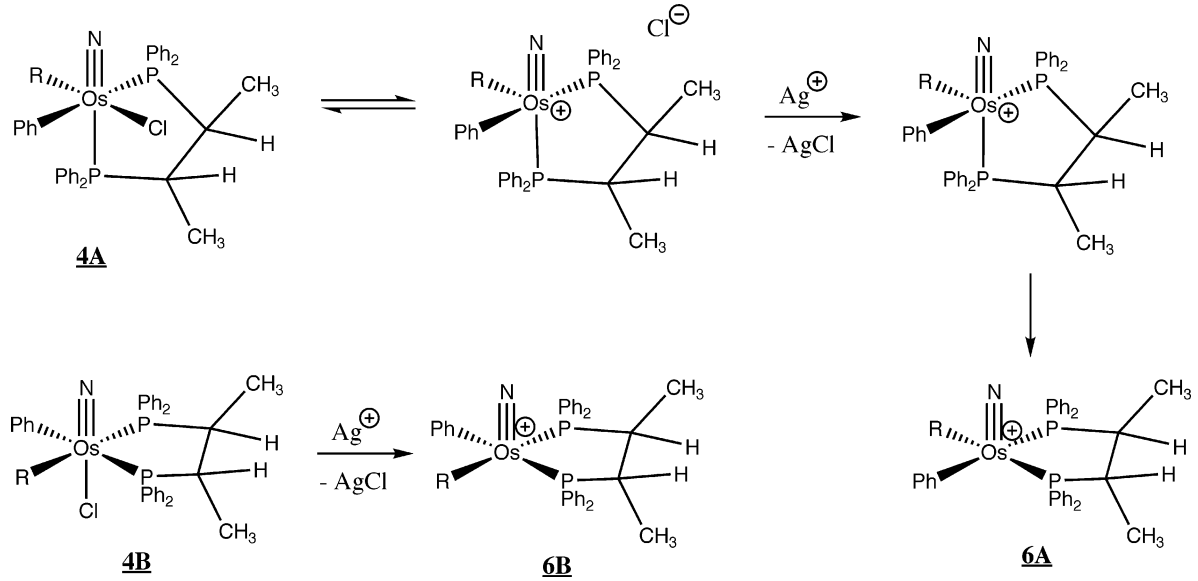


Figure 5. Proposed configuration of the isomers of **6** and **9**.

Scheme 7



We have prepared the chiral-at-metal oxidation catalysts $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)(CH_3)(\mu\text{-}O)_2CrO_2]$[13] and $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)Ph(\mu\text{-}O)_2CrO_2]$ as racemic mixtures, but their resolution into separated enantiomers is difficult.[14] Because of the thermal and configurational stability of the chiral-at-metal osmium(VI) complexes **6A** and **6B**, they may be useful precursors to asymmetric, bimetallic oxidation catalysts. We are currently examining the reactivity of these phosphine complexes and related chiral amino complexes with oxometalates.

Conclusion

Diphosphines displace chloride from the chiral-at-osmium complexes $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)PhCl_2]$ to produce neutral complexes $[Os(N)(CH_2SiMe_3)PhCl(\text{diphosphine})]$. With the chiral diphosphine (*S*,*S*)-chiraphos, there are six possible isomers of $[Os(N)(CH_2SiMe_3)PhCl((S,S)\text{-chiraphos})]$, but only two of these are formed. NMR spectroscopy and molecular mechanics calculations allow us to propose likely structures for these two isomers. The less stable isomer is formed under kinetic

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(14) Pool, D. H. Ph.D. Thesis, University of Illinois, Urbana, IL, 2003.

control from an intermediate with a monodentate chiraphos ligand *trans* to the nitrido group of one enantiomer of the osmium complex. The more stable isomer forms as a result of a slower equatorial coordination of the phosphine and displacement of chloride from the other enantiomer of the osmium precursor. Because the two isomers of [Os(N)(CH_2SiMe_3)PhCl((*S*,*S*)-chiraphos)] have different stabilities with respect to chloride loss, we can separately prepare and isolate the two diastereomers [(*S*)-Os(N)(CH_2SiMe_3)Ph((*S*,*S*)-chiraphos)]$^+$ and [(*R*)-Os(N)(CH_2SiMe_3)Ph((*S*,*S*)-chiraphos)]$^+$.

Experimental Section

All reactions were conducted under N_2 using standard air-sensitive techniques unless otherwise indicated. Anhydrous $(C_2H_5)_2O$, THF, and C_6H_{14} were distilled from Na/benzophenone; $C_6H_5CH_3$ was distilled from Na; and CH_2Cl_2 and CH_3CN were distilled from CaH_2. Deuterated solvents were stored over 4 Å molecular sieves. The compounds [PPh_4][Os(N)Cl_4], [N(*n*-Bu)$_4$][Os(N)Cl_4][15] and *trans*-[N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$-Cl_2][16] were prepared according to literature methods. (*S*,*S*)-Chiraphos and (*R*,*R*)-chiraphos were purchased from Aldrich and Across and used without further purification.

NMR spectra were recorded on one of the following spectrometers in the University of Illinois School of Chemical Sciences VOICE NMR Laboratory: Varian Unity 400 MHz, Varian Unity 500 MHz, or Varian Unity Inova 500NB MHz. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. Electronic spectra were recorded on a Hewlett-Packard 8452A diode array UV−visible spectrophotometer. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Mass spectra were recorded by the University of Illinois School of Chemical Sciences Mass Spectrometry Laboratory. X-ray diffraction data were obtained by the University of Illinois School of Chemical Sciences George L. Clark X-ray Facility and 3M Materials Laboratory.

***trans*-[N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$$Ph_2$], 1.** A solution of MgPhBr (0.940 mL, 2.36 M in THF, 2.22 mmol) was added to a solution of *trans*-[N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$$Cl_2$] (0.510 g, 0.737 mmol) in 10 mL of Et_2O. Initially upon addition the solution becomes clear and precipitate begins forming quickly. After stirring the mixture for 30 min, 30 mL of Et_2O was added and the mixture was cooled to −30 °C for 24 h. The crude product was collected by filtration and crystallized from CH_2Cl_2 and Et_2O at −30 °C. Yellow crystals of **1** (0.433 g, 0.558 mmol, 62%) were collected and dried under vacuum. IR (KBr, cm^{-1}): 3044, 2964, 2878 (ν_{CH}), 1567 (m, $\nu_{C=C}$), 1470 (s), 1455 (s), 1236 (s), 1107 (s, ν_{OsN}), 1022 (m), 862 (s), 826 (s), 733 (s), 700 (s). ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 7.0 (m, 8 H, *Ph*), 6.7 (m, 2 H, *Ph*), 3.0 (m, 8 H, NCH_2), 1.6 (m, 8 H, NCH_2CH_2), 1.4 (m, 8 H, $NCH_2CH_2CH_2$), 1.3 (s, 4 H, CH_2Si), 1.0 (t, J = 7 Hz, 12 H, $NCH_2CH_2CH_2CH_3$), 0.0 (s, 18 H, Si(CH_3)$_3$). ^{13}C{^{1}H} (125 MHz, $CDCl_3$, 295 K): δ 179.9 (s, *Ph*), 138.1 (s, *Ph*), 126.2 (s, *Ph*), 119.4 (s, *Ph*), 58.9 (s, NCH_2), 23.9 (s, NCH_2CH_2), 19.7 (s, $NCH_2CH_2CH_2$), 17.4 (s, CH_2Si), 13.6 (s, $NCH_2CH_2CH_2CH_3$), 2.0 (s, SiMe_3). Anal. Calcd for $C_{36}H_{68}N_2$-$OsSi_2$: C, 55.77; H, 8.84; N, 3.61. Found: C, 55.84; H, 8.65; N, 3.75.

***trans*-[PPh_4][Os(N)(CH_2SiMe_3)$_2$$Ph_2$].** Crystals of *trans*-[N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$$Ph_2$] (0.403 g, 0.520 mmol) and [PPh_4]Br (0.218 g, 0.520 mmol) were combined in CH_2Cl_2, and the solution was filtered through Celite. The solution was concentrated and cooled to −30 °C until yellow crystals formed. The product was washed three times with Et_2O, then dried under vacuum to give 0.342 g (0.392 mmol, 75%) of the tetraphenylphosphonium salt. ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): δ 7.9 (m, 4 H, P*Ph*), 7.7 (m, 8 H, P*Ph*), 7.6 (m, 8 H, P*Ph*), 6.9 (m, 8 H, *Ph*), 6.6 (m, 2 H, *Ph*), 1.2 (s, 4 H, CH_2Si), −0.1 (s, 18 H, Si(CH_3)$_3$). Anal. Calcd for $C_{44}H_{52}NOsPSi_2$: C, 60.59; H, 6.01; N, 1.61. Found: C, 60.36; H, 5.90; N, 1.79.

***trans*-[N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$PhCl], 2.** Solid pyridinium chloride (0.041 g, 0.359 mmol) was added to a 30 mL CH_2Cl_2 solution of **1** (0.139 g, 0.179 mmol) and stirred for 30 min. The reaction mixture quickly became orange. The solvent was removed under vacuum, and the residue was extracted with Et_2O. Hexane was added to the extract, and it was cooled to −30 °C. Red crystals formed and were collected by filtration (0.062 g, 0.085 mmol, 47%). IR (KBr, cm^{-1}): 3054 (w, phenyl ν_{CH}), 2960 (s, ν_{CH}), 2901 (m, ν_{CH}), 2876 (s, ν_{CH}), 2856 (s, ν_{CH}), 1574 (m, $\nu_{C=C}$), 1482 (s), 1474 (s), 1459 (s), 1381 (m), 1237 (s), 1108 (s, ν_{OsN}), 856 (s), 832 (s), 733 (s). ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 7.0 (m, 2 H, *Ph*), 6.7 (m, 1 H, *Ph*), 6.6 (m, 2 H, *Ph*), 3.2 (m, 8 H, NCH_2), 1.9 (d, J = 8 Hz, 2 H, CH^aH^{b}Si), 1.6 (m, 8 H, NCH_2CH_2), 1.5 (m, 8 H, $NCH_2CH_2CH_2$), 1.3 (d, J = 8 Hz, 2 H, CH^aH^bSi), 1.0 (t, J = 7 Hz, 12 H, $NCH_2CH_2CH_2CH_3$), 0.1 (s, 18 H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 295 K): δ 162.3 (s, *Ph*), 136.8 (s, *Ph*), 126.4 (s, *Ph*), 120.7 (s, *Ph*), 59.0 (s, NCH_2), 25.1 (s, CH_2Si), 24.0 (s, NCH_2CH_2), 19.7 (s, $NCH_2CH_2CH_2$), 13.7 (s, $NCH_2CH_2CH_2CH_3$), 1.7 (s, SiMe_3). Anal. Calcd for $C_{30}H_{63}ClN_2OsSi_2$: C, 49.11; H, 8.66; N, 3.82. Found: C, 49.21; H, 8.68; N, 3.89.

[N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)PhCl$_2$], 3. A diethyl ether solution of HCl (0.480 mL, 0.62 M in Et_2O, 0.298 mmol) was diluted to 15 mL with CH_2Cl_2 and cooled to −30 °C. This was added slowly to a 15 mL CH_2Cl_2 solution of **1** (0.115 g, 0.148 mmol) and stirred at −30 °C for 2 h. The color changed from yellow to orange to red. Solvent was removed under vacuum, and the residue was crystallized from CH_2Cl_2 and Et_2O at −30 °C. Red crystals (0.074 g, 0.109 mmol, 74%) of **3** were collected and dried under vacuum. IR (KBr, cm^{-1}): 3058 (w, phenyl ν_{CH}), 3044 (w, phenyl ν_{CH}), 2960 (s, ν_{CH}), 2874 (s, ν_{CH}), 1478 (s), 1458 (m), 1380 (m), 1242 (m), 1148 (w), 1128 (s, ν_{OsN}), 1022 (m), 876 (sh), 854 (s), 834 (s), 737 (s), 702 (m). ^{1}H NMR ($CDCl_3$, 500 MHz, 297 K): δ 7.1 (m, 2 H, *Ph*), 6.9 (m, 2 H, *Ph*), 6.8 (m, 1 H, *Ph*), 3.2 (m, 8 H, NCH_2), 3.1 (d, J = 8 Hz, 1 H, CH^aH^b-$SiMe_3$), 2.9 (d, J = 8 Hz, 1 H, CH^aH^bSiMe_3), 1.6 (m, 8 H, NCH_2CH_2), 1.4 (m, 8 H, $NCH_2CH_2CH_2$), 1.0 (t, J = 7 Hz, 12 H, $NCH_2CH_2CH_2CH_3$), 0.0 (s, 9 H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 297 K): δ 154.2 (s, *Ph*), 137.2 (s, *Ph*), 127.2 (s, *Ph*), 123.5 (s, *Ph*), 58.9 (s, NCH_2), 24.0 (s, NCH_2CH_2), 19.7 (s, $NCH_2CH_2CH_2$), 14.1 (s, CH_2Si), 13.7 (s, $NCH_2CH_2CH_2CH_3$), 0.2 (s, SiMe_3). Anal. Calcd for $C_{26}H_{52}Cl_2N_2OsSi$: C, 45.80; H, 7.69; N, 4.11; Cl, 10.40. Found: C, 46.08; H, 7.68; N, 4.24; Cl, 10.48.

[PPh_4][Os(N)(CH_2SiMe_3)PhCl$_2$]. $HCl_{(g)}$ (4.8 mL, 0.192 mmol) was added by syringe to a solution of *trans*-[PPh_4][Os-(N)(CH_2SiMe_3)$_2$$Ph_2$] (0.084 g, 0.096 mmol) in 10 mL of CH_2Cl_2 and 2 mL of Et_2O at −78 °C. The solution was maintained at −30 °C for 24 h, then the solvent and excess HCl were removed from the reaction mixture under vacuum. The residue was crystallized from CH_2Cl_2/Et_2O to give red crystals (0.049 g, 0.063 mmol, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): δ 7.8 (m, 4 H, P*Ph*), 7.8 (m, 8 H, P*Ph*), 7.6 (m, 8 H, P*Ph*), 7.0 (m, 2 H, *Ph*), 6.8 (m, 2 H, *Ph*), 6.7 (m, 1 H, *Ph*), 2.9 (d, J = 8 Hz, 1 H, CH^aH^{b}SiMe$_3$), 2.8 (d, J = 8 Hz, 1 H, CH^aH^bSiMe$_3$), −0.0 (s, 9 H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 295 K): δ 154.5 (s, Os*Ph*), 137.1 (s, Os*Ph*), 135.7 (d, J_{PC} = 3 Hz, P*Ph*), 134.4 (d, J_{PC} = 10 Hz, P*Ph*), 130.8 (d, J_{PC} = 13 Hz, P*Ph*), 127.0 (s, Os*Ph*), 122.8 (s, Os*Ph*), 117.3 (d, J_{PC} = 90 Hz, P*Ph*), 13.4 (s, CH_2Si), 0.3 (s, SiMe_3). Anal. Calcd for $C_{34}H_{36}NCl_2OsPSi_2$: C, 52.43; H, 4.66; N, 1.80. Found: C, 52.55; H, 4.57; N, 1.93.

[Os(N)(CH_2SiMe_3)PhCl((*S*,*S*)-chiraphos)], 4. (*S*,*S*)-Chiraphos (0.074 g, 0.174 mmol) was added to a solution of **3** (0.117 g, 0.172 mmol) in 15 mL of CH_2Cl_2. The solution turned from red to orange. A solution of $AgSbF_6$ (0.074 g, 0.174 mmol) in 5

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(16) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493−7496.

mL of CH_2Cl_2 was slowly added with stirring. White solid AgCl formed. The reaction mixture was filtered through Celite, and the filtrate was concentrated under vacuum. Ethyl ether was added until white solid $[N(n\text{-}Bu)_4][SbF_6]$ precipitated. The mixture was filtered again, and solvent was removed from the filtrate under vacuum. The residue was extracted with diethyl ether. The volume of the solution was doubled with hexane, and the solution was filtered through Celite. Solvent was removed under vacuum from a red oil (0.109 g, 0.131 mmol, 76%) consisting of the two diastereomers of **4**. Field desorption MS showed parent ion peaks with the predicted isotope patterns for $C_{38}H_{44}F_6NOsP_2SbSi$.

4A: ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 8.0 (m, 2 H, P*Ph*), 7.9 (m, 2 H, P*Ph*), 7.7 (m, 2 H, P*Ph*), 7.6−7.3 (m, 9 H, P*Ph*), 7.1 (m, 2 H, P*Ph*), 7.2 (m, 1 H, P*Ph*), 6.9−6.8 (m, 3−4 H, Os*Ph*), 4.1 (m, 1 H, PC*H*Me), 2.5 (dd, J_{HH} = 12 Hz, J_{HP} = 12 Hz, 1 H, C*H*^{a}H^{b}SiMe$_3$), 2.1 (m, 1 H, PC*H*Me), 1.8 (dd, J_{HH} = 12 Hz, J_{HP} = 9 Hz, 1 H, CH^a*H*^{b}SiMe$_3$), 1.5 (dd, J_{HH} = 7 Hz, J_{HP} = 12 Hz, 3 H, PCH*Me*), 1.1 (dd, J_{HP} = 12 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*), −0.2 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 295 K): δ 153.7 (dd J_{CP} = 65 Hz, J_{CP} = 7 Hz, Os*Ph*), 135.9 (d, J_{CP} = 8 Hz, P*Ph*), 135.7 (d, J_{CP} = 11 Hz, P*Ph*), 134.1 (d, J_{CP} = 10 Hz, P*Ph*), 134.0 (d, J_{CP} = 8 Hz, P*Ph*), 132.0 (d, J_{CP} = 38 Hz, P*Ph*), 131.5 (s, P*Ph*), 131.3 (d, J_{CP} = 2 Hz, P*Ph*), 131.2 (d, J_{CP} = 40 Hz, P*Ph*), 130.4 (s, P*Ph*), 129.5 (d, J_{CP} = 2 Hz, P*Ph*),-128.7 (d, J_{CP} = 10 Hz, P*Ph*), 128.3 (d, J_{CP} = 10 Hz, P*Ph*), 127.8 (bs, Os*Ph*), 127.1 (d, J_{CP} = 10 Hz, P*Ph*), 126.8 (d, J_{CP} = 10 Hz, P*Ph*), 126.0 (d, J_{CP} = 60 Hz, P*Ph*), 125.4 (d, J_{CP} = 47 Hz, P*Ph*), 123.2 (s, Os*Ph*), 44.7 (dd, J_{CP} = 29 Hz, J_{CP} = 12 Hz, P*C*HMe), 37.6 (dd, J_{CP} = 36 Hz, J_{CP} = 7 Hz, P*C*HMe), 16.3 (d J_{CP} = 42 Hz, *C*H$_2$SiMe$_3$), 14.6 (dd, J_{CP} = 13 Hz, J_{CP} = 5 Hz, PCH*Me*), 13.0 (dd, J_{CP} = 16 Hz, J_{CP} = 6 Hz, PCH*Me*), 1.2 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 295 K): δ 41.5 (s), 23.3 (s).

4B: ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 8.1 (m, 2 H, P*Ph*), 7.8 (m, 2 H, P*Ph*), 7.7 (m, 2 H, P*Ph*), 7.6 (m, 6 H, P*Ph*), 7.5 (m, 1 H, P*Ph*), 7.4 (m, 2 H, P*Ph*), 7.4 (m, 2 H, Os*Ph*), 7.2 (m, 1 H, P*Ph*), 7.1 (m, 2 H, P*Ph*), 6.9 (m, 3 H, Os*Ph*, 1 H, P*Ph*), 4.1 (m, 1 H, PC*H*Me), 2.3 (dd, J_{HH} = 12 Hz, J_{HP} = 12 Hz, 1 H, C*H*^{a}H^b-SiMe$_3$), 2.2 (m, 1 H, PC*H*Me), 1.8 (dd, J_{HH} = 12 Hz, J_{HP} = 9 Hz, 1 H, CH^a*H*^{b}SiMe$_3$), 1.4 (dd, J_{HH} = J_{HP} = 12 Hz, 7 Hz, 3 H, PCH*Me*), 1.1 (dd, J_{HH} = 7 Hz, J_{HP} = 12 Hz, 3 H, PCH*Me*), −0.2 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 295 K): δ 152.0 (dd J_{CP} = 62 Hz, J_{CP} = 8 Hz, Os*Ph*), 141.7 (s, Os*Ph*), 135.8 (d, J_{CP} = 10 Hz, P*Ph*), 135.1 (d, J_{CP} = 12 Hz, P*Ph*), 135.1 (d, J_{CP} = 12 Hz, P*Ph*), 131.4 (s, P*Ph*), 131.3 (s, P*Ph*), 130.75 (d, J_{CP} = 43 Hz, P*Ph*), 130.67 (d, J_{CP} = 2 Hz, P*Ph*), 129.8 (d, J_{CP} = 2 Hz, P*Ph*), 128.9 (d, J_{CP} = 10 Hz, P*Ph*), 128.2 (d, J_{CP} = 9 Hz, P*Ph*), 127.7 (d, J_{CP} = 10 Hz, P*Ph*), 127.6 (s, Os*Ph*), 126.8 (d, J_{CP} = 30 Hz, P*Ph*),126.7 (d, J_{CP} = 53 Hz, P*Ph*), 126.5 (d, J_{CP} = 10 Hz, P*Ph*), 124.9 (d, J_{CP} = 53 Hz, P*Ph*), 123.2 (s, Os*Ph*), 44.2 (dd, J_{CP} = 29 Hz, J_{CP} = 13 Hz, P*C*HMe), 37.8 (dd, J_{CP} = 35 Hz, J_{CP} = 6 Hz, P*C*HMe), 18.1 (dd J_{CP} = 42 Hz, J_{CP} = 3 Hz, *C*H$_2$SiMe$_3$), 14.5 (dd, J_{CP} = 13 Hz, J_{CP} = 5 Hz, PCH*Me*), 12.6 (dd, J_{CP} = 16 Hz, J_{CP} = 6 Hz, PCH*Me*), 1.2 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 295 K): δ 31.9 (s), 31.8 (s).

[Os(N)(CH$_2$SiMe$_3$)PhCl((*S*,*S*)-chiraphos)], 4B. The unreacted **4A** and **4B** from the preparation of **6A** (above) were dissolved in 15 mL of CH_2Cl_2. To this was added a solution of $AgSbF_6$ (0.005 g, 0.014 mmol) in CH_2Cl_2 over a 10 min period. The solution was filtered and concentrated. Hexane was added to precipitate the **6** produced in the reaction. The mixture was filtered and the solvent was removed from the solution to give **4B** (0.038 g, 0.046 mmol, 35%), which was pure by NMR spectroscopy. This sample was used to assign the peaks due to **4B** in the NMR spectra of the mixture of diastereomers.

[Os(N)(CH$_2$SiMe$_3$)PhCl(dppe)], 5. This was prepared in the same manner as **4** from **3** (0.055 g, 0.081 mmol), dppe (0.033 g, 0.083 mmol), and $AgSbF_6$ (0.029 g, 0.082 mmol). The product was an orange oil (0.055 g). ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 7.9 (m, 2 H, P*Ph*), 7.7 (m, 2 H, P*Ph*), 7.6 (m, 2 H, P*Ph*), 7.6−7.3 (m, 11 H, P*Ph*), 7.3 (m, 1 H Os*Ph*), 7.1 (m, 2 H, Os*Ph*), 7.0−6.9 (m, 5 H, P*Ph*, Os*Ph*), 3.7 (m, 1 H, PC*H*$_2$), 3.4 (m, 1 H, PC*H*$_2$), 2.6 (m, 1 H, PC*H*$_2$), 2.5 (dd, J_{HP} = 13 Hz, J_{HH} = 12 Hz 1 H, C*H*^{a}H^{b}SiMe$_3$), 2.1 (m, 1 H, PC*H*$_2$), 1.8 (dd, J_{HH} = 12 Hz, J_{HP} = 9 Hz, 1 H, CH^a*H*^{b}SiMe$_3$), −0.1 (s, 9 H, Si-(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 295 K): δ 153.7 (dd J_{CP} = 64 Hz, J_{CP} = 8 Hz, Os*Ph*), 142.1 (s, Os*Ph*), 134.4 (d, J_{CP} = 11 Hz, P*Ph*), 134.0 (d, J_{CP} = 8 Hz, P*Ph*), 133.0 (d, J_{CP} = 11 Hz, P*Ph*), 132.8 (d, J_{CP} = 8 Hz, P*Ph*), 131.5 (d, J_{CP} = 2 Hz, P*Ph*), 131.0 (d, J_{CP} = 2 Hz, P*Ph*), 130.7 (d, J_{CP} = 2 Hz, P*Ph*), 130.4 (d, J_{CP} = 35 Hz, P*Ph*), 130.2 (d, J_{CP} = 2 Hz, P*Ph*), 128.82 (d, J_{CP} = 9 Hz, P*Ph*), 128.80 (d, J_{CP} = 10 Hz, P*Ph*), 128.4 (dd, J_{CP} = 51 Hz, J_{CP} = 2 Hz, P*Ph*), 128.0 (d, J_{CP} = 10 Hz, P*Ph*), 127.9 (d, J_{CP} = 3 Hz, Os*Ph*), 127.6 (d, J_{CP} = 11 Hz, P*Ph*), 123.6 (s, Os*Ph*), 31.6 (dd, J_{CP} = 38 Hz, J_{CP} = 6 Hz, PCH$_2$), 29.8 (dd, J_{CP} = 34 Hz, J_{CP} = 9 Hz, PCH$_2$), 17.9 (dd, J_{CP} = 44 Hz, J_{CP} = 3 Hz, *C*H$_2$SiMe$_3$), 1.2 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 295 K): δ 27.7 (d, J_{PP} = 9 Hz), 24.2 (d, J_{PP} = 9 Hz).

[Os(N)(CH$_2$SiMe$_3$)Ph((*S*,*S*)-chiraphos)][SbF$_6$], 6A. A 5 mL CH_2Cl_2 solution of $AgSbF_6$ (0.021 g, 0.059 mmol) was slowly added to a 10 mL CH_2Cl_2 solution containing 2 equiv of **4** (0.109 g, 0.131 mmol). The mixture was filtered through Celite and concentrated under vacuum. Hexane was added to give a total volume of 60 mL, and the solution was cooled to −30 °C. Orange oil formed. The solution was decanted from the oil. The oil was washed three times with hexane. The hexane solutions containing unreacted **4A** and **4B** were combined and concentrated under vacuum and used in the reaction below. The oil was dried under vacuum (0.061 mg, 0.059 mmol, 45%). ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 7.9−7.5 (m, 14 H, P*Ph*), 7.5 (m, 1 H, P*Ph*), 7.5 (m, 1 H, P*Ph*), 7.2 (m, 2 H, P*Ph*), 7.0 (m, 2 H, Os*Ph*), 6.9 (m, 1 H, Os*Ph*), 6.6 (m, 4 H, P*Ph*), 3.3 (m, 1 H, PC*H*Me), 3.1 (dd, J_{HP} = 17 Hz, J_{HH} = 8 Hz, 1 H, C*H*^{a}H^{b}SiMe$_3$), 2.4 (m, 1 H, PC*H*Me), 1.9 (dt, J_{HH} = 8, J_{HP} = 3 Hz Hz, 1 H, CH^a*H*^{b}SiMe$_3$), 1.5 (dd, J_{HP} = 14 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*), 1.1 (dd, J_{HP} = 15 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*), −0.5 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 295 K): δ 158.3 (dd, J_{CP} = 33 Hz, J_{CP} = 8 Hz, Os*Ph*), 141.7 (bs, Os*Ph*), 135.7 (d, J_{CP} = 10 Hz, P*Ph*), 135.2 (d, J_{CP} = 2 Hz, P*Ph*), 134.8 (d, J_{CP} = 14 Hz, P*Ph*), 133.8 (d, J_{CP} = 2 Hz, P*Ph*), 133.4 (d, J_{CP} = 3 Hz, P*Ph*), 132.8 (d, J_{CP} = 8 Hz, P*Ph*), 132.4 (s, P*Ph*), 132.3 (d, J_{CP} = 14 Hz, P*Ph*), 130.30 (d, J_{CP} = 12 Hz, P*Ph*), 130.27 (d, J_{CP} = 11 Hz, P*Ph*), 129.9 (d, J_{CP} = 12 Hz, P*Ph*), 129.4 (d, J_{CP} = 14 Hz, P*Ph*), 129.3 (s, Os*Ph*), 124.7 (s, Os*Ph*), 124.1 (d, J_{CP} = 55 Hz, P*Ph*), 119.8 (d, J_{CP} = 55 Hz, P*Ph*), 119.0 (d, J_{CP} = 54 Hz, P*Ph*), 118.6 (d, J_{CP} = 49 Hz, P*Ph*), 44.7 (dd, J_{CP} = 35 Hz, J_{CP} = 9 Hz, P*C*HMe), 33.1 (dd, J_{CP} = 33 Hz, J_{CP} = 7 Hz, P*C*HMe), 24.0 (dd, J_{CP} = 25 Hz, J_{CP} = 3 Hz, *C*H$_2$SiMe$_3$), 14.3 (dd, J_{CP} = 16 Hz, J_{CP} = 4 Hz, PCH*Me*), 13.9 (dd, J_{CP} = 14 Hz, J_{CP} = 6 Hz, PCH*Me*), −0.4 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 295 K): δ 59.2 (s), 49.8 (s). Electrospray MS shows a parent peak with an isotope pattern identical to that calculated for $C_{38}H_{44}F_6NOsP_2SbSi$.

[Os(N)(CH$_2$SiMe$_3$)Ph((*S*,*S*)-chiraphos)][SbF$_6$], 6B. To a 15 mL CH_2Cl_2 solution of **4B** (0.038 g, 0.046 mmol) was added $AgSbF_6$ (0.017 g, 0.048 mmol). White solid AgCl precipitated. The mixture was filtered, and the solvent was removed under vacuum. The residue was extracted with Et_2O to get a yellow solution. The solvent was removed under vacuum, leaving an oil (0.047 g, 0.046 mmol, 100%). ^{1}H NMR ($CDCl_3$, 500 MHz, 295 K): δ 7.8−7.5 (m, 14 H, P*Ph*), 7.5 (m, 2 H, P*Ph*), 7.3 (m, 2H, P*Ph*), 7.0 (m, 2 H, Os*Ph*), 6.9 (m, 1 H, Os*Ph*), 6.5 (m, 4 H, Os*Ph*, P*Ph*), 3.1 (m, 1 H, PC*H*Me), 2.9 (m, 1 H, PC*H*Me), 2.9 (ddd, J_{HP} = 18 Hz, J_{HH} = 7 Hz, J_{HP} = 2 Hz, 1 H, C*H*^{a}H^{b}SiMe$_3$), 2.1 (dt, J_{HH} = 7 Hz, J_{HP} = 4, 1 H, CH^a*H*^{b}SiMe$_3$), 1.4 (dd, J_{HP} = 15 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*), 1.3 (dd, J_{HP} = 15 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*), −0.3 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 295 K): δ 155.9 (db, J_{CP} = 37 Hz, Os*Ph*), 138.5 (s, Os*Ph*), 134.6 (d, J_{CP} = 13 Hz, P*Ph*), 134.1 (d, J_{CP} = 10 Hz, P*Ph*), 133.8 (d, J_{CP} = 2 Hz, P*Ph*), 133.6 (s, P*Ph*), 133.6 (d, J_{CP} = 11 Hz, P*Ph*), 133.4 (d, J_{CP} = 2 Hz, P*Ph*), 133.3 (d,

J_{CP} = 3 Hz, P*Ph*), 133.0 (d, J_{CP} = 10 Hz, P*Ph*), 130.4 (d, J_{CP} = 11 Hz, P*Ph*), 129.7 (d, J_{CP} = 12 Hz, P*Ph*), 129.4 (d, J_{CP} = 11 Hz, P*Ph*), 128.4 (s, Os*Ph*), 124.1 (s, Os*Ph*), 122.7 (d, J_{CP} = 57 Hz, P*Ph*), 121.1 (d, J_{CP} = 53 Hz, P*Ph*), 120.2 (d, J_{CP} = 47 Hz, P*Ph*), 119.2 (d, J_{CP} = 53 Hz, P*Ph*), 44.4 (dd, J_{CP} = 35 Hz, J_{CP} = 9 Hz, PC*H*Me), 37.0 (dd, J_{CP} = 33 Hz, J_{CP} = 6 Hz, PC*H*Me), 30.8 (d, J_{CP} = 25 Hz, *C*H_2SiMe$_3$), 15.0 (dd, J_{CP} = 14 Hz, J_{CP} = 4 Hz, PCH*Me*), 13.7 (dd, J_{CP} = 14 Hz, J_{CP} = 5 Hz, PCH*Me*), 0.6 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz, 295 K): δ 56.1 (s), 47.1 (d, J = 6 Hz).

[Os(N)(CH$_2$SiMe$_3$)Ph((*S*,*S*)-chiraphos)(NCMe)][SbF$_6$], 7. Acetonitrile (0.034 mL, 0.653 mmol) was added to a 10 mL CH_2Cl_2 solution of either **6A**, **6B**, or a mixture of the two isomers (0.061 mg, 0.059 mmol). In each reaction, the solvent was removed under vacuum and the product was characterized spectroscopically.

7A: ^{1}H NMR (CDCl$_3$, 500 MHz, 295 K): δ 7.8 (m, 4 H, P*Ph*), 7.7−7.5 (m, 10 H, P*Ph*), 7.4 (m, 3 H, P*Ph*, Os*Ph*), 7.2 (m, 2 H, Os*Ph*), 7.0 (m, 4 H, P*Ph*), 6.9 (m, 2 H, Os*Ph*), 3.1 (m, 1 H, PC*H*Me), 2.8 (dd, J_{HP} = 14 Hz, J_{HH} = 10 Hz, 1 H, C*H*^{a}H^{b}SiMe$_3$), 2.6 (m, 1 H, PC*H*Me), 1.9 (s, 3 H, NC*Me*), 1.7 (m, 1 H, CH^a*H*^{b}SiMe$_3$), 1.5 (dd, J_{HP} = 13 Hz, J_{HP} = 7 Hz, 3 H, PCH*Me*), 1.2 (dd, J = 14 Hz, J = 6 Hz, 3 H, PCH*Me*), −0.3 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 295 K): δ 154.0 (bd, J_{CP} = 41 Hz, Os*Ph*), 135.1 (d, J_{CP} = 13 Hz, P*Ph*), 134.7 (d, J_{CP} = 9 Hz, P*Ph*), 133.3 (s, P*Ph*), 133.2 (d, J_{CP} = 10 Hz, P*Ph*), 133.2 (s, P*Ph*), 133.0 (d, J_{CP} = 8 Hz, P*Ph*), 132.9 (s, P*Ph*), 131.7 (s, P*Ph*), 129.72 (d, J_{CP} = 11 Hz, P*Ph*), 129.67 (d, J_{CP} = 10 Hz, P*Ph*), 129.5 (d, J_{CP} = 12 Hz, P*Ph*), 129.1 (bs, Os*Ph*), 128.8 (d, J_{CP} = 11 Hz, P*Ph*), 125.6 (d, J_{CP} = 50 Hz, P*Ph*), 124.6 (s, Os*Ph*), 122.1 (d, J_{CP} = 57 Hz, P*Ph*), 121.5 (d, J_{CP} = 47 Hz, P*Ph*), 120.7 (d, J_{CP} = 48 Hz, P*Ph*), 118.7 (s, N*C*Me), 45.9 (dd, J_{CP} = 32, J_{CP} = 10 Hz, P*C*HMe), 34.6 (dd, J_{CP} = 32, J_{CP} = 6 Hz, P*C*HMe), 18.6 (m, *C*H_2SiMe$_3$), 14.8 (dd, J_{CP} = 14, J_{CP} = 4 Hz, PCH*Me*), 12.4 (dd, J_{CP} = 13, J_{CP} = 5 Hz, PCH*Me*), 2.1 (s, NC*Me*), 0.4 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz, 295 K): δ 51.4 (s), 37.9 (s).

7B: ^{1}H NMR (CDCl$_3$, 500 MHz, 295 K): δ 7.9 (m, 4 H, P*Ph*), 7.8−7.6 (m, 11 H, P*Ph*), 7.5 (m, 2 H, P*Ph*), 7.4 (m, 1 H, Os*Ph*), 7.3 (m, 2 H, Os*Ph*), 7.0−6.8 (m, 7 H, P*Ph*, Os*Ph*), 3.5 (m, 1 H, PC*H*Me), 2.4 (m, 1 H, PC*H*Me), 2.3 (ddd, J_{HP} = 13 Hz, J_{HH} = 10 Hz, J_{HP} = 2 Hz, 1 H, C*H*^{a}H^{b}SiMe$_3$), 1.7 (s, 3 H, NC*Me*), 1.7 (ddd, J_{HH} = 10 Hz, J_{HP} = 8 Hz, J_{HP} = 3 Hz, 1 H, CH^a*H*^{b}SiMe$_3$), 1.5 (dd, J_{HP} = 14 Hz, J_{HP} = 7 Hz, 3 H, PCH*Me*), 1.3 (dd, J = 13 Hz, J = 7 Hz, 3 H, PCH*Me*), −0.2 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 295 K): δ 149.3 (bd, J_{CP} = 45 Hz, Os*Ph*), 140.5 (bs, Os*Ph*), 135.1 (d, J_{CP} = 12 Hz, P*Ph*), 133.92 (d, J_{CP} = 12 Hz, P*Ph*), 133.86 (d, J_{CP} = 14 Hz, P*Ph*), 133.8 (d, J_{CP} = 14 Hz, P*Ph*), 132.9 (d, J_{CP} = 2 Hz, P*Ph*), 132.7 (d, J_{CP} = 3 Hz, P*Ph*), 132.3 (d, J_{CP} = 2 Hz, P*Ph*), 131.8 (d, J_{CP} = 2 Hz, P*Ph*), 129.6 (d, J_{CP} = 12 Hz, P*Ph*), 129.4 (d, J_{CP} = 10 Hz, P*Ph*), 129.1 (d, J_{CP} = 11 Hz, P*Ph*), 128.7 (d, J_{CP} = 11 Hz, P*Ph*), 128.5 (d, J_{CP} = 2 Hz, Os*Ph*), 124.9 (d, J_{CP} = 53 Hz, P*Ph*), 124.6 (s, Os*Ph*), 122.7 (d, J_{CP} = 51 Hz, P*Ph*), 122.6 (s, Os*Ph*), 122.43 (d, J_{CP} = 42 Hz, P*Ph*), (122.4 (d, J_{CP} = 51 Hz, P*Ph*), 45.4 (dd, J_{CP} = 31, J_{CP} = 11 Hz, P*C*HMe), 35.9 (dd, J_{CP} = 31, J_{CP} = 6 Hz, P*C*HMe), 19.9 (m, *C*H_2SiMe$_3$), 14.7 (dd, J_{CP} = 14, J_{CP} = 5 Hz, PCH*Me*), 11.7 (dd, J_{CP} = 14, J_{CP} = 6 Hz, PCH*Me*), 2.5 (s, NC*Me*), 0.9 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz, 295 K): δ 40.0 (s), 39.7 (s).

Structural Determination of 7. Crystals of **7** grew from CH_2Cl_2, Et_2O, and hexane at −30 °C. The data crystal was cut from a larger parent crystal. The data crystal was mounted using oil (Paratone-N, Exxon) to a 0.2 mm cryo-loop (Hampton Research) with the (1 0 0) scattering planes roughly normal to the spindle axis. Four frame series were filtered for statistical outliers, then corrected for absorption by integration using SHELXTL/XPREP before using SAINT/SADABS to sort, merge, and scale the combined data.[17] A series of identical frames was collected twice during the experiment to monitor decay. No decay correction was applied. Systematic conditions suggested the unambiguous space group. The crystal was orthorhombic with the space group $P2_12_12_1$. The structure was solved by Patterson methods (Sheldrick, 2001). Methyl H atom positions, R−CH_3, were optimized by rotation about R−C bonds with idealized C−H, R- -H, and H- -H distances.[18] Remaining H atoms were included as riding idealized contributors. Methyl H atom *U*'s were assigned as 1.5 times U_{eq} of the adjacent atom; remaining H atom *U*'s were assigned as 1.2 times adjacent U_{eq}. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2.[18] The highest peaks in the final difference Fourier map were in the vicinity of Os atoms; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

[Os(N)(CH$_2$SiMe$_3$)Ph((*R*,*R*)-chiraphos)][SbF$_6$], 8. This was prepared in the same manner as **6** from **3** (0.034 g, 0.050 mmol), (*R*,*R*)-chiraphos) (0.021 g, 0.049 mmol), and $AgSbF_6$ (0.035 g, 0.099 mmol). The product was an orange solid (0.022 g, 0.021 mmol, 42%). ^{1}H NMR (CDCl$_3$, 400 MHz, 295 K): δ 7.9−6.4 (m, 25 H, P*Ph*, Os*Ph*), 3.3 (m, 1 H, PC*H*Me, isomer A), 3.1 (m, 3 H, PC*H*Me, isomer B; C*H*^{a}H^{b}SiMe$_3$, isomer A), 2.9 (m, 2 H, PC*H*Me, C*H*^{a}H^{b}SiMe$_3$, isomer B), 2.4 (m, 1 H, PC*H*Me, isomer A), 2.1 (dt, J_{HH} = 7 Hz, J_{HP} = 4 Hz, 1 H, CH^a*H*^{b}SiMe$_3$, isomer B), 1.9 (dt, J_{HH} = 8 Hz, J_{HP} = 4 Hz, 1 H, CH^a*H*^{b}SiMe$_3$, isomer A), 1.5 (dd, J_{HP} = 14 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*, isomer A), 1.4 (dd, J_{HP} = 15 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*, isomer B), 1.3 (dd, J_{HP} = 15 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*, isomer B), 1.1 (dd, J_{HP} = 15 Hz, J_{HH} = 7 Hz, 3 H, PCH*Me*, isomer A), −0.3 (s, 9 H, Si(C*H*$_3$)$_3$, isomer B), −0.5 (s, 9 H, Si(C*H*$_3$)$_3$, isomer A). Anal. Calcd for $C_{38}H_{44}F_6NOsP_2SbSi$: C, 44.18; H, 4.30; N, 1.36. Found: C, 44.00; H, 4.03; N, 1.41.

[Os(N)(CH$_2$SiMe$_3$)Ph(dppe)][SbF$_6$], 10. This was prepared in the same manner as **6** from **3** (0.024 g, 0.035 mmol), dppe (0.015 g, 0.038 mmol), and $AgSbF_6$ (0.025 g, 0.071 mmol). The product was an oil (0.024 g). ^{1}H NMR (CDCl$_3$, 500 MHz, 295 K): δ 7.9 (m, 2 H, *Ph*), 7.8 (m, 1 H, *Ph*), 7.7−7.6 (m, 10 H, *Ph*), 7.3 (m, 3 H, *Ph*), 7.0 (m, 2 H, *Ph*), 6.9 (m, 2 H, *Ph*), 6.8 (m, 1 H, *Ph*), 6.5 (m, 2 H, *Ph*), 6.3 (m, 2 H, *Ph*), 3.8 (m, 1 H, C*H*$_2$P), 3.3 (dd, J_{HP} = 16 Hz, J_{HH} = 8 Hz, 1H, C*H*^{a}H^{b}SiMe$_3$), 3.1−2.9 (m, 3 H, C*H*$_2$P), 2.0 (dt, J_{HH} = 8 Hz, J_{HP} = 4 Hz, 1 H, CH^a*H*^{b}SiMe$_3$), −0.3 (s, 9 H, Si(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz, 295 K): δ 55.9 (bs), 53.2 (d, J_{PP} = 17 Hz).

Acknowledgment. This research has been supported by a grant from the U.S. Environmental Protection Agency's Science to Achieve Results (STAR) program, EPA R 829553. We also gratefully acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society (ACS-PRF 36240-AC). NMR spectra were obtained in the Varian Oxford Instrument Center for Excellence in NMR Laboratory. Funding for this instrumentation was provided in part from the W. M. Keck Foundation, the National Institutes of Health (PHS 1 S10 RR10444-01), and the National Science Foundation (NSF CHE 96-10502). Purchase of the Siemens Platform/CCD diffractometer by the School of Chemical Sciences was supported by National Science Foundation grant CHE 9503145.

Supporting Information Available: For **7**, tables of crystal data collection and refinement parameters, bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034329F

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