# Diastereoselectivity in Chiral Osmium Complexes of a Bidentate Bisphosphine Monoxide Ligand

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The chelation of [($\eta^6$-Cy)OsL] fragments (Cy = cymene; L = monodentate ligand) by bisphosphine monoxide ligands generates chiral-at-metal complexes. If the bisphosphine monoxide backbone contains a chiral center, diastereomeric products are formed. Osmium complexes of this type prepared using *rac*-$Ph_2PCH(Me)P(O)Ph_2$ epimerize to form a preferred isomer in which the methyl group is distal to L. This has been observed for the analogous ruthenium complexes, but the interconversion of diastereomers occurs at a greatly reduced rate. The slower interconversion allows spectroscopic characterization of the thermodynamically less favored isomers, as the corresponding ruthenium species are too short-lived for such investigations.

## Introduction

We have recently reported on the utility of bisphosphine monoxide (BPMO) complexes of ruthenium in asymmetric catalysis[1] and on their diastereoselective isomerization behavior.[2] To investigate the behavior of analogous osmium complexes of BPMOs, we have prepared a series of compounds using the ligand *rac*-($Ph_2PCH(Me)P(O)Ph_2$). Although a number of groups have prepared complexes with this[3] and other BPMO ligands,[4] we believe this to be the first report of fully characterized osmium(II) BPMO complexes.

## Results

**Synthesis of [($\eta^6$-Cy)$OsCl_2$($\eta^1$-$Ph_2PCH(Me)P(O)Ph_2$-*P*)] (1).** The interaction of $[CyOsCl_2]_2$ with *rac*-($Ph_2PCH(Me)P(O)Ph_2$) in a mole ratio of 1:2 yields [($\eta^6$-Cy)$OsCl_2$($\eta^1$-$Ph_2PCH(Me)P(O)Ph_2$-*P*)], **1**, Scheme 1. The complex exhibits characteristic NMR behavior, the $^{31}P$ spectrum showing a distinct downfield coordination shift for the resonance of the coordinated P(III) of 4.74 ppm and a reduction in the coupling between the phosphorus nuclei of 43 Hz. The molecular structure was determined by single-crystal X-ray diffraction, and the results are shown in Figure 1, with data collection parameters given in Table 1 and metrical parameters in Table 2. Unlike the previously reported ruthenium analogue,[2] compound **1** in solution shows no propensity to dissociate one of the chloro ligands with concomitant chelation of the phosphine oxide terminus of the ligand, even after prolonged storage as a solution in a polar solvent.

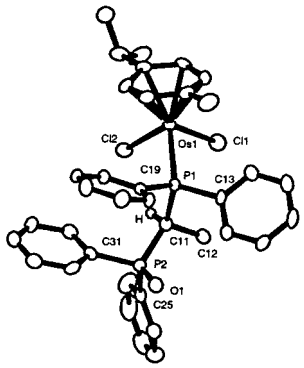


**Figure 1.** ORTEP diagram of **1** showing 50% probability ellipsoids. The compound is racemic, and the ($S_C$)-enantiomer is shown. Note that the chirality descriptor at carbon changes upon binding of the ligand; hence the ($R_C$)-BPMO free ligand becomes ($S_C$) when the phosphine binds to a transition metal.

**Synthesis of [($\eta^6$-Cy)OsCl($\eta^2$-$Ph_2PCH(Me)P(O)Ph_2$-*P,O*)][$SbF_6$] (2).** Treatment of **1** with 1 equiv of $AgSbF_6$ in dichloromethane solution leads to chloride abstraction and chelation of the BPMO by coordination of the phosphine oxide terminus at the vacant site generated forming [($\eta^6$-Cy)OsCl($\eta^2$-$Ph_2PCH(Me)P(O)Ph_2$-*P,O*)][$SbF_6$], Scheme 1. The chelation creates a chiral center at the osmium and, in conjunction with the chirality of the ligand, the possibility of diastereo-

† Yale University.
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(2) Faller, J. W.; Patel, B.; Albrizzio, M. A.; Curtis, M. *Organometallics* **1999**, *18*, 3096. This paper gave the configuration of the BPMO ligand as that of the free phosphine and did not follow the strict chirality descriptor conventions. Note that the chirality descriptor at carbon changes upon binding of the ligand; hence the ($R_C$)-BPMO free ligand becomes ($S_C$) when the phosphine binds to a transition metal.
(3) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656.
(4) (a) Coyle, R. J.; Slovokhotov, Y. L.; Grushin, V. *Polyhedron* **1998**, *17*, 3059. (b) Brassat, I.; Englert, U.; Keim, W.; Keitel, D. P.; Killat, S.; Suranna, G. P.; Wang, R. *Inorg. Chim. Acta* **1998**, *280*, 150. (c) Blagborough, T. C.; Davis, R.; Ivison, P. *J. Organomet. Chem.* **1994**, *467*, 85. (d) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1993**, *212*, 23. (e) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1993**, *204*, 63. (f) Katti, K. V.; Barnes, C. L. *Inorg. Chem* **1992**, *31*, 4231. (g) Fontaine, X. L. R.; Fowles, E. H.; Layzell, T. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 1519. (h) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727. (i) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *325*, 285.

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**Scheme 1. Preparation of 1−6**[a]

$^1/_2$ [CyOsCl$_2$]$_2$ + *rac*-Ph$_2$PCH(Me)P(O)Ph$_2$ ⟶ [(Cy)OsCl$_2$(η$^1$Ph$_2$PCH(Me)P(O)Ph$_2$-*P*)] **1**

**1** $\xrightarrow[-\ AgCl]{+\ AgSbF_6}$ [(Cy)OsCl(η$^2$Ph$_2$PCH(Me)P(O)Ph$_2$-*P*,O)][SbF$_6$] **2**

**1** $\xrightarrow[-\ 2\ AgCl]{+\ 2\ AgSbF_6}$ [(Cy)Os(solv)(η$^2$Ph$_2$PCH(Me)P(O)Ph$_2$-*P*,O)][SbF$_6$]$_2$ **3**

**3** + aldehyde ⟶ [(Cy)Os(aldehyde)(η$^2$Ph$_2$PCH(Me)P(O)Ph$_2$-*P*,O)][SbF$_6$]$_2$ **4-6**

[a] All reactions performed in dichoromethane at ambient temperature

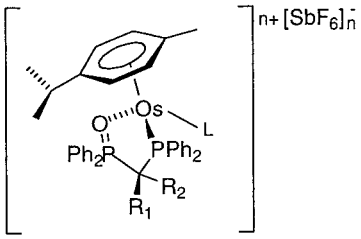
**Table 1. Crystallographic Data for X-ray Diffraction Studies of CyOsCl$_2$(Ph$_2$PCH(Me)Ph$_2$PO), 1, [CyOsCl(Ph$_2$PCH(Me)Ph$_2$PO)]SbF$_6$·CH$_2$Cl$_2$, 2a, and [CyOs(Ph$_2$PCH(Me)Ph$_2$PO)(PhCH=CHCHO)](SbF$_6$)$_2$·CH$_2$Cl$_2$, 4a**

| | 1 | 2a | 4a |
|---|---|---|---|
| formula | Os $Cl_2P_2OC_{36}H_{38}$ | $OsSbCl_3P_2F_6OC_{37}H_{40}$ | $OsSb_2Cl_2P_2F_{12}O_2C_{46}H_{48}$ |
| cryst system | monoclinic | orthorhombic | monoclinic |
| space group | *C*2/*c* (No. 15) | *Pca*2$_1$ (No. 29) | *C*2/*c* (No. 15) |
| *a*, Å | 31.8120(7) | 17.7581(4) | 40.2616(6) |
| *b*, Å | 9.6759(2) | 11.4938(3) | 14.1613(2) |
| *c*, Å | 21.4873(6) | 19.3382(4) | 20.1604(4) |
| *β*, deg | 98.205(1) | 90 | 117.2093(9) |
| *V*, Å$^3$ | 6546.3(2) | 3947.1(3) | 10222.6(3) |
| temp, °C | −90 | −90 | −90 |
| fw | 809.75 | 1094.97 | 1427.42 |
| $\rho_{calcd}$, g/cm$^3$ | 1.643 ($Z$ = 8) | 1.842 ($Z$ = 4) | 1.855 ($Z$ = 8) |
| abs coeff (cm$^{-1}$) | 41.83 | 42.39 | 37.73 |
| cryst size, mm | 0.12 × 0.17× 0.24 | 0.24 × 0.24 × 0.35 | 0.48 × 0.19 × 0.07 |
| diffractometer | | Nonius KappaCCD | |
| monochromator | | graphite | |
| radiatn | | Mo Kα (0.71073 Å) | |
| max 2*θ*, deg | 54.9 | 55.0 | 55.0 |
| refl measrd (unique) | 28608 (7956) | 19973 (5025) | 55894(12169) |
| data used, $F^2 > 3\sigma(F^2)$ | 5077 | 4029 | 6625 ($>5\sigma$) |
| no. of params refined | 379 | 459 | 600 |
| *p* factor | 0.01 | 0.01 | 0.01 |
| final residuals $R$, $R_w$ | 0.032, 0.029 | 0.042, 0.041 | 0.037, 0.046 |
| convergence, largest shift/error | 0.00 | 0.00 | 0.00 |
| GOF | 1.19 | 1.89 | 1.42 |
| largest Δ(*ρ*), e$^-$ Å$^{-3}$ | 0.85 | 2.97 | 1.93 |

**Table 2. Selected Bond Distances (Å) and Angles (deg) for 1, 2a, and 4a**

| | 1 | 2a | 4a |
|---|---|---|---|
| Os(1)−Cl(1) | 2.408(1) | 2.382(3) | |
| Os(1)−Cl(2) | 2.423(1) | | |
| Os(1)−P(1) | 2.372(1) | 2.344(2) | 2.362(2) |
| Os(1)−O(1) | | 2.136(6) | 2.115(4) |
| Os(1)−O(2) | | | 2.125(4) |
| P(2)−O(1) | 1.486(3) | 1.529(7) | 1.530(5) |
| Cl(1)−Os(1)−Cl(2) | 86.44(4) | | |
| Cl(1)−Os(1)−P(1) | 87.26(4) | 85.75(10) | |
| Cl(2)−Os(1)−P(1) | 87.34(4) | | |
| Cl(1)−Os(1)−O(1) | | 86.3(2) | |
| P(1)−Os(1)−O(1) | | 81.2(2) | 82.6(1) |
| P(1)−Os(1)−O(2) | | | 80.8(1) |
| O(1)−Os(1)−O(2) | | | 81.9(1) |
| Os(1)−O(1)−P(2) | | 124.7(4) | 124.2(2) |

mers. In fact, the product exists as two sets of enantiomeric diastereomers, **2a** and **2b** (Figure 2). The two sets of diastereomers have distinct NMR spectra, and so an accurate ratio of **2a**:**2b** of 3.8:1 is readily obtained. This value remains constant over extended periods of time (>72 h), indicating that the rate of epimerization is slow with respect to that seen for the corresponding ruthenium complexes where one set of enantiomers is seen to form exclusively. The $^{31}$P NMR spectra of **2a** and **2b** show characteristic downfield shifts of 23.9 and 28.9 ppm for the P(III) resonances compared to compound **1**




$R_1$ = Me, $R_2$ = H: L = Cl, **2a**; (solv.), **3a**; *trans*-cinnamaldehyde, **4a**; methacrolein, **5a**; crotonaldehyde, **6a**.
$R_1$ = H, $R_2$ = Me: L = Cl, **2b**; (solv.), **3b**; *trans*-cinnamaldehyde, **4b**; methacrolein, **5b**; crotonaldehyde, **6b**.

**Figure 2.** Complexes **2**−**6**. Only one diastereomer of each enantiomeric pair is shown.

and 36.5 and 52.8 ppm for the P(V) resonances, respectively. In the $^1$H NMR, there is a distinct upfield shift of the resonance of the methine proton on the backbone of the ligand from $\delta$ 5.30 in **1** of 0.86 ppm in **2a** and 1.54 ppm in **2b**, entirely consistent with chelation. Crystallization of pure **2a**, vida infra, provided a definitive structure correlation with NMR, since the diastereomer interconversion is slow. The structure of **2a** is shown in Figure 3. The methyl groups of the isopropyl substituent of the cymene ring are diastereotopic in **1**, and the differences in chemical shifts become even more pronounced in both isomers of **2**.

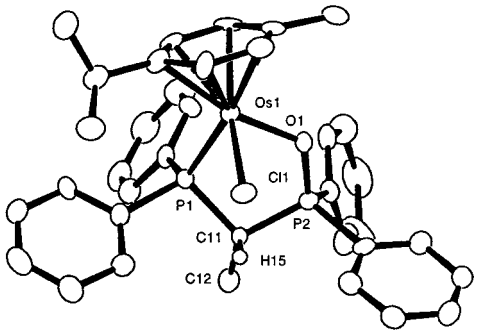



**Figure 3.** ORTEP diagram of cation **2a** showing 50% probability ellipsoids. The compound is racemic, and the ($R_{Os}$,$S_C$)-enantiomer is shown.

**Synthesis of [($\eta^6$-Cy)Os($\eta^2$-$Ph_2$PCH(Me)P(O)$Ph_2$-*P,O*)][$SbF_6$]$_2$ (3).** Treatment of **1** with 2 equiv of $AgSbF_6$ leads to removal of both chloro ligands and the chelation of the BPMO, forming **3a** and **3b**, Scheme 1 and Figure 2. The complexes are formally coordinatively unsaturated doubly charged 16-electron Lewis acids, but since again two sets of resonances are seen in the NMR spectra, it can reasonably be inferred that the cations are weakly coordinated to either a molecule of solvent or a counterion or involve a weak agostic interaction. If this were not the case, the cation would be effectively "square planar" (or possibly rapidly equilibrating between two configurations), and therefore there would only be a single isomer seen.[5] The ratio of **3a**:**3b** of 1.4:1 reflects the lower barrier to epimerization accessible via a "swing" mechanism in the 16-electron intermediate when the ligand L in Figure 2 is a weakly coordinated solvent molecule. This contrasts with the case where L is a nonlabile group, such as the chloro ligand in **2a** and **2b**.

The doubly charged Lewis acids **3** react with aldehydes in solution to form complexes of the general formula [($\eta^6$-Cy)Os($\eta^2$-$Ph_2$PCH(Me)P(O)$Ph_2$-*P,O*)(aldehyde)][$SbF_6$]$_2$ (aldehyde = *trans*-cinnamaldehyde, **4**, methacrolein, **5**, and crotonaldehyde, **6**). The aldehydes used here all have the potential to act as ligands coordinating to the osmium through either $\pi$-bonding interactions, via the carbon−carbon double bond, or $\sigma$-bonding, through the carbonyl oxygen. Simple hard−soft arguments might predict that in such circumstances an osmium(II) would preferentially bind an olefinic double bond, but in fact in all cases the aldehyde coordinates exclusively through the carbonyl oxygen. This is established by comparison of the $^1$H NMR spectra of **4**−**6** with those of the corresponding ruthenium complexes and the crystal structure of the *trans*-cinnamaldehyde complex **4a**, Figure 4 and Tables 1 and 2.

The relative configurations are found to be ($R_{Os}$, $S_C$) and ($S_{Os}$, $R_C$) or ($R^*_{Os}$, $S^*_C$) for **4a**. This configuration allows the methyl group on the backbone of the ligand to be oriented away from the coordinated aldehyde to minimize steric conflict. Structural studies on ruthenium complexes of this and other similarly substituted BPMOs show similar preferences for orienting the largest group on the backbone of the ligand away from the monodentate ligand.[2]

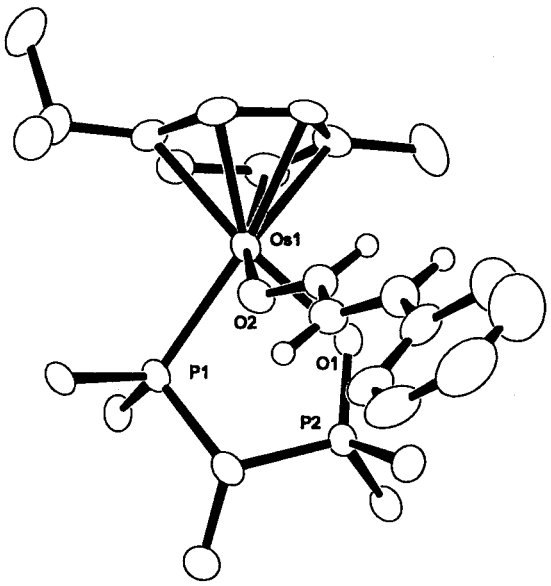



**Figure 4.** ORTEP diagram of **4a** showing 50% probability ellipsoids. The phenyl groups of the phosphines are omitted for clarity. The compound is racemic, and the ($R_{Os}$,$S_C$)-enantiomer is shown.

The orientation of the coordinated cinnamaldehyde is controlled by both steric and electronic considerations. The difference between the P and O donors of the chelating ligand influences which of the metals d-orbitals interact with the p-orbitals of the carbonyl function of the aldehyde. This confers a preferential alignment of the carbonyl group with respect to the metal (torsion angle P1−Os−O2−C = 153.2(5)°), and the proximity of the phenyl rings on the P(III) force the phenyl substituent on the aldehyde to adopt a transoid disposition in order to minimize steric conflict. The only arrangement that meets these criteria is that seen in the structure of **4a**, Figure 4.

The metrical data shown in Table 2 allow comparison of the compounds. As might be expected, the P−O bond lengthens upon coordination. The bite angle of the BPMO is rather small, 81.2° and 82.6° for **2a** and **4a**, respectively. All of the angles involving the legs of the "three-legged piano stool" structure are less than 90°. The angles for P(1)−Os(1)−O(2) of 80.8° and O(1)−Os(1)−O(2) of 81.9° found in **4a** are relatively small for donors not constrained by a chelate.

## Discussion

Coordinatively unsaturated 16-electron organometallic complexes are not ordinarily expected to be stereochemically rigid,[6] although there are examples in the literature of chiral species of this type that do not undergo such racemizations.[7,8] Complexes **3** have, if taken as being only coordinated weakly by a solvent molecule, the lowest energy pathway to interconversion amongst the complexes reported here. This could involve either a dissociation of the solvent to form a [($\eta^6$-

(5) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278. For amine coordinated examples, see: (a) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601. (b) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956.

(6) (a) Ward, T. R.; Schafer, O.; Daul, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207. (b) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488. (c) Hoffman, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

Cy)Os($\eta^2$-$Ph_2PCH(Me)P(O)Ph_2$-*P,O*)]$^{2+}$ ion with a plane of symmetry, precedent for which in the case of related ruthenium complexes can be found in the literature,[6] or an $\eta^2$-$\eta^1$-$\eta^2$ process of hemidissociation of the BPMO followed by rechelation in the opposite sense. While it is difficult to be certain, it seems from the observations made here that the former mechanism is more likely because of the relatively rapid rate of epimerization of the aldehyde complex **4** (half-life 3 h.) compared to the chloro complex **2** (half-life ≫72 h.). Coupled with this, there is no spectroscopic evidence for the formation of a cationic $\eta^1$-BPMO complex, even in the presence of a large excess of aldehydes (>10-fold). It is also more reasonable to envisage a neutral monodentate ligand dissociating more readily than one-half of a chelating ligand.

The low rate of interconversion allows observation, at least in solution state, of the isomers not seen for the corresponding ruthenium complexes. The $^{31}P$ NMR data for these reveal distinct differences in chemical shift on changing the relative configuration. In the $^1H$ NMR spectra, the difference between the two types of unique proton on the ligand is the most pronounced. The chemical shifts differ by some 0.8 ppm and exhibit distinct couplings, indicative of the different spatial relationships of the spin-active nuclei.

All of the products reported here with the BPMO chelated are a mixture of the two types of diastereomer, the thermodynamically favored **a** and the less favored **b**. For the latter group of products, the methyl group is oriented toward the monodentate ligand L and so creates steric conflict. This set of products was not observed for the corresponding ruthenium species and indicates the relative kinetic stability of the Os−L bond compared to the Ru−L system, where dissociation of L must be more readily achieved in order to allow the faster epimerization. This is also seen in the absence of the ionization of a chloro ligand from **1** to give the osmium analogue of [($\eta^6$-Cy)RuCl($\eta^2$-$Ph_2PCH(Me)P(O)Ph_2$-*P,O*)]Cl.

The aldehyde complex **4a** can be converted to the chloro complexes **2** by dissolving it in a methanolic solution of potassium chloride. The replacement of the aldehyde is too rapid to follow by NMR, and the formation of the chloro complex is complete within minutes at room temperature. The ratio of **2a**:**2b** in a solution prepared in this way is 7.2:1, substantially displaced from the 3.8:1 found for the chloro complex prepared from **1**. This suggests that the replacement of the aldehyde by a chloro ligand occurs largely with retention of configuration at the metal, since the proportion of the thermodynamically preferred isomer is enhanced. With the high concentration of **2a** obtained from this reaction, it is possible to obtain pure **2a** by recrystallization. This allowed the preparation of crystals suitable for X-ray diffraction determination.

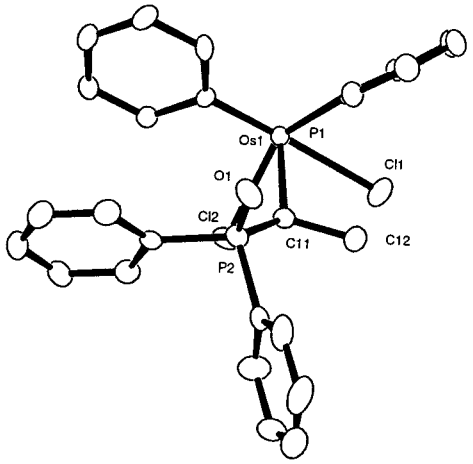



**Figure 5.** ORTEP diagram of **1** showing 50% probability ellipsoids illustrating the conformation of the phenyl rings. The compound is racemic, and the ($S_C$)-enantiomer is shown. The cymene group has been omitted for clarity.

The question of the selectivity in the formation of the original chelated complex of **2a** over **2b** arises in a way which it does not for the ruthenium analogue. In that case, the fast rate of epimerization does not allow the opportunity to determine whether the initial chelation occurs with any preference, but for osmium a definite preference for the loss of one of the two chloro ligands and subsequent chelation is observed. The activation of one of these two seemingly equivalent ligands with respect to the other may be linked to the preferred disposition of the phenyl groups on the P(III) seen in the $\eta^1$ complex **1**, which is in turn controlled by the methyl group on the backbone of the ligand. Comparison of the structure of **1** with that of the ruthenium analogue and the hitherto unreported $Cp^*Rh(Cl)_2$ complex of the same ligand reveals a definite and coherent preference for the arrangement of the phenyl groups. This carries the chiral information on the backbone of the ligand into the inner coordination sphere of the complex and may serve to activate one chloro over the other. Figure 5 shows a view down the P−Os axis in the structure of ($S_C$)-**1**. One should note that one phenyl is nearly parallel to the P−Os vector and the helicity of the other phenyl is *M*, and this would appear to be controlled by the stereochemistry at the bridging carbon. The Os−Cl distances are significantly different, Os−Cl1 = 2.408(1) Å and Os−Cl2 = 2.423(1) Å, and suggest that one might be removed more readily than the other. Some type of anchiomeric assistance could also be involved from the tethered PO as a silver removes the chloride. Regardless, the chlorides are diastereotopic and would be expected to have different chemical behavior. One might also note that the $CyRuCl_2(Ph_2PCH_2Ph_2PO)$ crystallizes as a racemate considering the configuration of the phenyls (which in the absence of a backbone substituent would not have a preference for *P* or *M* helicity). In this case the Ru−Cl distances are 2.403(1) and 2.423(2) Å.[2]

A further comment on the helicity of the phenyl groups is in order. When the P,O chelate is formed, it forces a different orientation of the methyl owing to the constraints of formation of the five-membered ring. In this case the methyl group is synclinal to both phenyls, whereas in the $\eta^1$-complex the methyl is synclinal to one

(7) (a) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798. (b) Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(8) Faller, J. W.; Chase, K. J.; Mazzieri, M. R. *Inorg. Chim. Acta* **1995**, *229*, 39.

(9) (a) Bye, E.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 5893. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (c) Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Top. Curr. Chem.* **1974**, *47*, 1. (d) Faller J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *90*, 99.

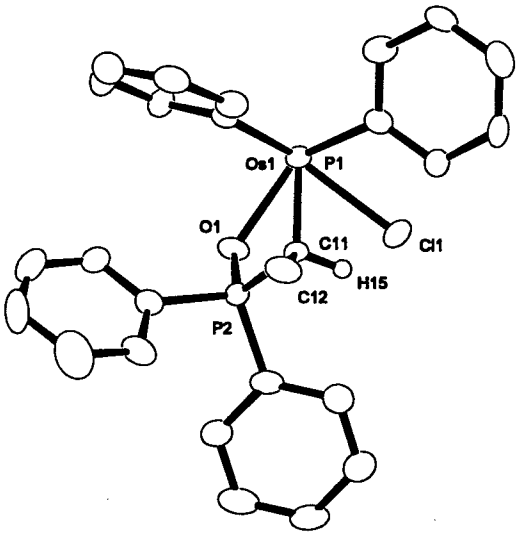



**Figure 6.** ORTEP view of **2a** showing 50% probability ellipsoids illustrating the conformation of the phenyl rings. The compound is racemic, and the ($S_C$)-enantiomer is shown. The cymene group has been omitted for clarity.

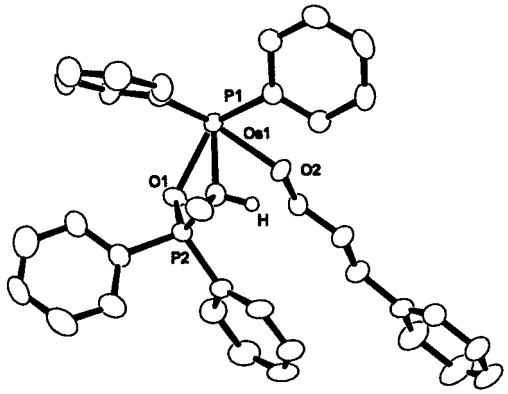



**Figure 7.** ORTEP view of **4a** showing 50% probability ellipsoids illustrating the conformation of the phenyl rings. The compound is racemic, and the ($S_C$)-enantiomer is shown. The cymene group has been omitted for clarity.

and anticlinal to the other. This induces a different phenyl to be parallel to the P−Os vector and the other to assume a *P* helicity. The orientations in the chloride, **2a**, and cinnamaldehyde complex, **4a**, are similar as shown in Figures 6 and 7. The chirality imposed by phenyl group orientation has been investigated previously[9] and has been found important in explanations of chiral induction with CHIRAPHOS.[10] We anticipate that it will play an important role in asymmetric catalysis with BMPO ligands.

## Conclusion

We have shown that the osmium BPMO complexes [($\eta^6$-Cy)Os($\eta^2$-$Ph_2$PCH(Me)P(O)$Ph_2$-*P*,*O*)(L)][$SbF_6$]$_2$ exhibit a greatly reduced rate of epimerization compared to those seen for the corresponding ruthenium complexes. Further, although the rate is reduced, the thermodynamically preferred isomer is that in which the largest group on the backbone of the ligand is oriented away from the monodentate ligand, the same as that preferred in the ruthenium complexes. The Lewis acidity of the osmium(II) center is sufficient to force preferential coordination of carbonyl oxygen over an olefinic double bond, a result unexpected for a third-row transition metal in a low oxidation state.

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## Experimental Section

**General Procedures**. All synthetic manipulations were carried out under an atmosphere of oxygen-free nitrogen using standard Schlenk and glovebox techniques. Diethyl ether and dichloromethane were distilled over sodium benzophenone ketyl and calcium hydride, respectively. Ethyl acetate, absolute methanol, and hexanes were reagent grade and used without further purification. The ligand $Ph_2$PCH(Me)P(O)$Ph_2$[3] and [CyOs$Cl_2$]$_2$[11] were prepared by modifications of published procedures. *trans*-Cinnamaldehyde, methacrolein, crotonaldehyde, and silver hexafluoroantimonate were commercial (Aldrich) and used as received. The NMR spectra were recorded on a GE Omega 500 spectrometer (202.43 MHz for $^{31}$P), and chemical shifts are reported in ppm relative to residual protio solvent ($^1$H) or external 85% $H_3PO_4$ ($^{31}$P). Elemental analyses were performed by Atlantic Microlabs.

**Preparation of [($\eta^6$-Cy)OsCl$_2$($\eta^1$-$Ph_2$PCH(Me)P(O)$Ph_2$-*P*)] (1)**. To a solution of [($\eta^6$-Cy)Os$Cl_2$]$_2$ (50 mg, 0.063 mmol) in 10 mL of dichloromethane was added $Ph_2$PCH(Me)P(O)$Ph_2$ (52 mg, 0.126 mmol) as a solid. The resultant clear orange-yellow solution was stirred at room temperature for 2 h before removal of the solvent under reduced pressure. The pale yellow solid residue was chromatographed over silica gel using 10% ethyl acetate in hexanes as eluent. A yellow orange band was collected and the solvent removed under reduced pressure to yield a yellow solid, which was recrystallized from dichloromethane/diethyl ether to give 82 mg of microcrystalline **1**. Yield: 80.4%. $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): 8.80−7.02 (20H, m, arom), 5.72 (1H, d, $J$ = 6.7 Hz, Cy-H), 5.32 (1H, d, $J$ = 6.7 Hz, Cy-H), 5.30, (1H, qdd, obsc, $HCP_2$) 5.29 (1H, d, $J$ = 6.7 Hz, Cy-H), 4.32 (1H, d, $J$ = 6.7 Hz, Cy-H), 2.92 (1H, hept., $J$ = 7.0 Hz, $HC(CH_3)_2$), 1.68 (3H, s, Cy-$CH_3$), 1.31 (3H, d, $J$ = 7.0 Hz, HC($CH_3$)($CH_3$)), 1.28 (3H, d, $J$ = 7.0 Hz, HC($CH_3$)($CH_3$)), 0.96 (3H, ddd, $J$ = 7.5, $^2J_{H-P}$ = 13.2, $^2J_{H-P}$ = 18.0 Hz, $HCP_2(CH_3)$). $^{31}$P{$^1$H} NMR: 33.29 (d, $J$ = 22 Hz, P(V)), −7.86 (d, $J$ = 22 Hz, P(III)). IR (KBr disk) $\nu_{(P=O)}$: 1194 cm$^{-1}$. Anal. Calcd for $C_{36}H_{38}OP_2Cl_2Os$: C, 53.40; H, 4.73. Found: C, 52.94; H, 4.81.

**Preparation of [($\eta^6$-Cy)OsCl($\eta^2$-$Ph_2$PCH(Me)P(O)$Ph_2$-*P*,*O*)][$SbF_6$] (2)**. To a solution of **1** (25 mg, 0.031 mmol) in 3 mL of dichloromethane was added $AgSbF_6$ (11 mg, 0.031 mmol) in 2 mL of dichloromethane. A white precipitate of AgCl formed, and after 30 min the mixture was centrifuged. The supernatant was collected by syringe and the solvent removed under reduced pressure. The solid yellow residue was recrystallized from dichloromethane/diethyl ether to give 26 mg of microcrystalline **2**. Yield: 83.0%. $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): **2a** 8.00−6.92 (20H, m, arom), 5.96 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.94 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.90 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.82 (1H, d, $J$ = 5.5 Hz, Cy-H), 4.44 (1H, qdd, $J$ = 5.3 Hz, $^2J_{H-P}$ = 10.0 Hz, $^2J_{H-P}$ = 7.5 Hz, $HC(CH_3)P_2$), 2.38 (1H, hept., $J$ = 7.0 Hz, $HC(CH_3)_2$), 2.21 (3H, s, Cy-$CH_3$), 1.24 (3H, ddd, obsc, $HCP_2(CH_3)$), 1.09 (3H, d, $J$ = 7.0 Hz, HC($CH_3$)($CH_3$)), 0.81 (3H, d, $J$ = 7.0 Hz, HC($CH_3$)($CH_3$)). $^{31}$P{$^1$H} NMR: 72.65 (d, $J$ = 21 Hz, P(V)), 16.00 (d, $J$ = 21 Hz, P(III)); **2b** 8.05−6.92 (20H, m, arom), 5.60 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.56 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.42 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.39 (1H, d, $J$ = 5.5 Hz, Cy-H), 3.76 (1H, qdd, $J$ = 5.5 Hz, $^2J_{H-P}$ = 9.5 Hz, $^2J_{H-P}$ = 4.6 Hz, $H(CH_3)CP_2$), 2.54 (1H, hept., $J$ = 7.0 Hz, $HC(CH_3)_2$), 2.24 (3H, s, Cy-$CH_3$), 1.27 (3H, ddd, obsc, $HCP_2(CH_3)$), 1.02 (3H, d, $J$ = 7.0 Hz, HC($CH_3$)($CH_3$)), 0.90 (3H, d, $J$ = 7.0 Hz, HC($CH_3$)($CH_3$)). $^{31}$P{$^1$H} NMR: 88.93 (d, $J$ = 20.5 Hz, P(V)), 22.38 (d, $J$ = 20.5 Hz, P(III)). IR (KBr disk) $\nu_{(P=O)}$: 1120 cm$^{-1}$ Anal. Calcd for $C_{36}H_{38}OF_6P_2ClSbOs$: C, 42.81; H, 3.79. Found: C, 43.26; H, 3.81.

**Preparation of [($\eta^6$-Cy)Os($\eta^2$-$Ph_2PCH(Me)P(O)Ph_2$-*P,O*)(SLV)][$SbF_6$]$_2$ (3).** To a solution of **1** (25 mg, 0.031 mmol) in 3 mL of dichloromethane was added $AgSbF_6$ (22 mg, 0.031 mmol) in 2 mL of dichloromethane. A white precipitate of AgCl formed and after 30 min, and the mixture was centrifuged. The supernatant was collected by syringe and the solvent removed under reduced pressure. The yellow product proved difficult to recrystallize and so was characterized by spectroscopy and used for further reactions in situ. $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): **3a** 8.10−7.22 (20H, m, arom), 6.32 (1H, d, $J$ = 6.5 Hz, Cy-H), 6.14 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.96 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.84 (1H, d, $J$ = 6.5 Hz, Cy-H), 3.57 (1H, qdd, $J$ = 5.8 Hz, $^2J_{H-P}$ = 9.6 Hz, $^2J_{H-P}$ = 4.6 Hz, *H*C(CH$_3$)P$_2$), 2.39 (1H, hept., $J$ = 7.2 Hz, *H*C(CH$_3$)$_2$), 2.09 (3H, s, Cy-CH$_3$), 1.21 (3H, ddd, obsc, HCP$_2$(C*H*$_3$)), 1.18 (3H, d, $J$ = 7.2 Hz, HC(C*H*$_3$)(CH$_3$)), 0.86 (3H, d, $J$ = 7.2 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 79.68 (s, P(V)), 23.53 (s, P(III)); **3b** 8.10−7.22 (20H, m, arom), 6.39 (1H, d, $J$ = 6.5 Hz, Cy-H), 6.04 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.94 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.88 (1H, d, $J$ = 6.5 Hz, Cy-H), 4.41 (1H, qdd, $J$ = 5.4 Hz, $^2J_{H-P}$ = 11.0 Hz, $^2J_{H-P}$ = 7.2 Hz, *H*C(CH$_3$)P$_2$), 2.68 (1H, hept., $J$ = 7.0 Hz, *H*C(CH$_3$)$_2$), 2.11 (3H, s, Cy-CH$_3$), 1.38 (3H, ddd, obsc, HCP$_2$(C*H*$_3$)), 1.15 (3H, d, $J$ = 7.0 Hz, HC(C*H*$_3$)(CH$_3$)), 0.91 (3H, d, $J$ = 7.0 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 74.06 (s, P(V)), 18.14 (s, P(III)).

**Preparation of [($\eta^6$-Cy)Os($\eta^2$-$Ph_2PCH(Me)P(O)Ph_2$-*P,O*)(aldehyde)][$SbF_6$]$_2$ (4−6).** These complexes were prepared in situ by the addition of the appropriate aldehyde to a solution of **3** prepared as given above and were characterized by NMR. Crystals of **4a** were obtained by the vapor diffusion of diethyl ether into a methanolic solution of **4a** using a closed concentric vial arrangement. $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): **4a** 9.46 (1H, d, $J$ = 9.0 Hz, CHO) 7.90−7.18 (25H, m, arom), 6.54 (1H, d, $J$ = 9.0 Hz, C*H*(CHO)), 6.51 (1H, d, $J$ = 9.0 Hz, C*H*(Ph)) 6.41 (1H, d, $J$ = 5.5 Hz, Cy-H), 6.24 (1H, d, $J$ = 5.5 Hz, Cy-H), 6.14 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.92 (1H, d, $J$ = 5.5 Hz, Cy-H), 3.77 (1H, qdd, $J$ = 5.5, $^2J_{H-P}$ = 9.5, $^2J_{H-P}$ = 4.5 Hz, *H*C(CH$_3$)P$_2$), 2.45 (3H, s, Cy-CH$_3$), 2.32 (1H, hept., $J$ = 6.5 Hz, *H*C(CH$_3$)$_2$), 1.27 (3H, ddd, $J$ = 5.5, $^2J_{H-P}$ = 11.1, $^2J_{H-P}$ =12.8 Hz, HCP$_2$(C*H*$_3$)), 1.06 (3H, d, $J$ = 6.5 Hz, HC(C*H*$_3$)(CH$_3$)), 0.78 (3H, d, $J$ = 6.5 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 78.65 (s, P(V)), 25.89 (s, P(III)); **4b** 9.46 (1H, d, $J$ = 9.0 Hz, CHO) 7.90−7.18 (25H, m, arom), 6.54 (1H, d, $J$ = 9.0 Hz, C*H*(CHO)), 6.51 (1H, d, $J$ = 9.0 Hz, C*H*(Ph)) 6.20 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.98 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.88 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.80 (1H, d, $J$ = 5.5 Hz, Cy-H), 4.45 (1H, qdd, $J$ = 5.8, $^2J_{H-P}$ = 9.7, $^2J_{H-P}$ = 7.6 Hz, HCP$_2$), 2.20 (3H, s, Cy-CH$_3$), 2.44 (1H, hept., $J$ = 6.5 Hz, *H*C(CH$_3$)$_2$), 1.23 (3H, ddd, $J$ = 5.8, $^2J_{H-P}$ = 11.2, $^2J_{H-P}$ =13.0 Hz, HCP$_2$(C*H*$_3$)), 1.09 (3H, d, $J$ = 6.5 Hz, HC(C*H*$_3$)(CH$_3$)), 0.82 (3H, d, $J$ = 6.5 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 73.95 (s, P(V)), 18.34 (s, P(III)). The crystal lattice contained methylene chloride, which was slowly lost on standing. The sample for elemental analysis was dried overnight under vacuum, and the solvent was completely removed in the process. Anal. Calcd for $C_{45}H_{46}O_2F_{12}P_2Sb_2Os$: C, 40.26; H, 3.45. Found: C, 40.11; H, 3.43.

**5a:** 9.46 (1H, s, CHO) 7.95−7.12 (20H, m, arom), 6.35 (1H, s, C*H*=C(CH$_3$)(CHO)), 6.06 (1H, d, $J$ = 6.5 Hz, Cy-H), 6.00 (1H, s, C*H*=C(CH$_3$)(CHO)), 5.91 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.86 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.75 (1H, d, $J$ = 6.5 Hz, Cy-H), 3.68 (1H, qdd, $J$ = 5.2, $^2J_{H-P}$ = 9.2, $^2J_{H-P}$ = 4.4 Hz, *H*C(CH$_3$)P$_2$), 2.61 (1H, hept., $J$ = 7.2 Hz, *H*C(CH$_3$)$_2$), 2.21 (3H, s, Cy-CH$_3$), 1.86 (3H, s, CH=C(C*H*$_3$)(CHO)), 1.24 (3H, ddd, obsc, HCP$_2$(C*H*$_3$)), 1.28 (3H, d, $J$ = 7.2 Hz, HC(C*H*$_3$)(CH$_3$)), 0.94 (3H, d, $J$ = 7.2 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 80.95 (s, P(V)), 29.43 (s, P(III)); **5b** 9.46 (1H, s, CHO) 7.95−7.12 (20H, m, arom), 6.35 (1H, s, C*H*=C(CH$_3$)(CHO)), 6.00 (1H, s, C*H*=C(CH$_3$)(CHO)), 5.96 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.94 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.89 (1H, d, $J$ = 6.5 Hz, Cy-H), 5.81 (1H, d, $J$ = 6.5 Hz, Cy-H), 4.44 (1H, qdd, $J$ = 5.4, $^2J_{H-P}$ = 10.0, $^2J_{H-P}$ = 7.5 Hz, *H*C(CH$_3$)P$_2$), 2.38 (1H, hept., $J$ = 6.8 Hz, *H*C(CH$_3$)$_2$), 2.34 (3H, s, Cy-CH$_3$), 1.84 (3H, s, CH=C(C*H*$_3$)(CHO)), 1.24 (3H, ddd, obsc, HCP$_2$(C*H*$_3$)), 1.08 (3H, d, $J$ = 6.8 Hz, HC(C*H*$_3$)(CH$_3$)), 0.86 (3H, d, $J$ = 6.8 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 73.60 (s, P(V)), 17.63 (s, P(III)). Anal. Calcd for $C_{40}H_{44}O_2F_{12}P_2Sb_2Os$: C, 37.52; H, 3.46. Found: C, 37.42; H, 3.63.

**6a:** 9.27 (1H, d, $J$ = 8.8 Hz, CHO) 7.95−7.08 (20H, m, arom), 7.06 (1H, m, (CH$_3$)CHC*H*(CHO), 6.10 (1H, m, (CH$_3$)C*H*CH-(CHO), 5.96 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.94 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.88 (1H, d, $J$ = 5.5 Hz, Cy-H), 5.81 (1H, d, $J$ = 5.5 Hz, Cy-H), 3.64 (1H, qdd, $J$ = 5.5, $^2J_{H-P}$ = 9.5, $^2J_{H-P}$ = 4.5 Hz, *H*C(CH$_3$)P$_2$), 2.38 (1H, hept., $J$ = 7.0 Hz, *H*C(CH$_3$)$_2$), 2.26 (3H, s, Cy-CH$_3$), 2.05 (3H, dd, $J$ = 5.0, 1.6 Hz, (C*H*$_3$)CHCH(CHO)) 1.27 (3H, ddd, obsc, HCP$_2$(C*H*$_3$)), 1.16 (3H, d, $J$ = 7.0 Hz, HC-(C*H*$_3$)(CH$_3$)), 0.84 (3H, d, $J$ = 7.0 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 73.65 (s, P(V)), 17.48 (s, P(III)); **6b** 9.27 (1H, d, $J$ = 8.8 Hz, CHO) 7.95−7.08 (20H, m, arom), 7.10 (1H, m, (CH$_3$)-CHC*H*(CHO), 6.32 (1H, d, $J$ = 5.5 Hz, Cy-H), 6.20 (1H, d, $J$ = 5.5 Hz, Cy-H), 6.15 (1H, d, $J$ = 5.5 Hz, Cy-H), 6.10 (1H, m, (CH$_3$)C*H*CH(CHO), 6.08 (1H, d, $J$ = 5.5 Hz, Cy-H), 4.46 (1H, qdd, $J$ = 5.3, $^2J_{H-P}$ = 10.0, $^2J_{H-P}$ = 7.5 Hz, *H*C(CH$_3$)P$_2$), 2.38 (1H, hept., $J$ = 6.8 Hz, *H*C(CH$_3$)$_2$), 2.26 (3H, s, Cy-CH$_3$), 2.02 (3H, dd, $J$ = 5.0, 1.6 Hz, (C*H*$_3$)CHCH(CHO)) 1.27 (3H, ddd, obsc, HCP$_2$(C*H*$_3$)), 1.16 (3H, d, $J$ = 6.8 Hz, HC(C*H*$_3$)(CH$_3$)), 0.84 (3H, d, $J$ = 6.8 Hz, HC(C*H*$_3$)(CH$_3$)). $^{31}$P{$^1$H} NMR: 78.79 (s, P(V)), 26.29 (s, P(III)). The sample for analysis was recrystallized from methylene chloride/diethyl ether. Anal. Calcd for $C_{40}H_{44}O_2F_{12}P_2Sb_2Os$. $C_2H_5O_{0.5}$: C, 38.29; H, 3.75. Found: C, 38.48; H, 3.76.

**X-ray Crystallography.** Single crystals suitable for X-ray analysis were formed by vapor diffusion of diethyl ether into a chloroform solution of **1** or diethyl ether and methylene chloride for **2a** and **4a**. Crystallographic data are summarized in Table 1. The structures were determined from data collected with a Nonius KappaCCD at −90 °C. Lorentz and polarization corrections were applied to all data. An empirical absorption correction was applied using SORTAV.[12] Intensities of equivalent reflections were averaged. The structures were solved by direct methods (SIR92[13]) using the teXan crystal structure analysis package, and the function minimized was $\sum w(|F_o| - |F_c|)^2$ in all cases. Hydrogen atoms were placed at calculated positions before each refinement and were included in the refinement, but were not refined.

The correct polarity for **2a** was determined by refining the inverted structure, which gave $R$ = 0.050 and $R_w$ = 0.050, whereas the reported coordinates gave $R$ = 0.042 and $R_w$ = 0.041.

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**Supporting Information Available:** Tables of crystal data, positional and thermal parameters, and bond lengths and angles for **1**, **2a**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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