Synthesis, Structures, and Solution Behavior of Bis(sulfoxide)-Pincer Complexes of Palladium(II)

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Cyclometalation of bis(sulfoxide)-substituted *m*-xylene derivatives, *rac*/*meso*-1,3-(^{i}PrS(O)CH_2)$_2$$C_6H_4$, occurred readily with Pd(II) using two synthetic routes. The first route utilized [Pd(NCMe)$_4$][(BF_4)$_2$] as starting material and led to the exclusive isolation of the C_2-symmetric diastereomer [*rac*-2,6-(^{i}PrS(O)CH_2)$_2$$C_6H_3$Pd(NCMe)][$BF_4$], *rac*-**3**, even though spectroscopic measurements confirmed the formation of *meso*-**3**. The second palladation pathway used Pd(BF_4)Cl(NCPh)$_2$ and both diastereomers *rac*- and *meso*-2,6-(^{i}PrS(O)CH_2)$_2$$C_6H_3$PdCl, *rac*- and *meso*-**4**, were separable by fractional crystallization. Characterization of the isolated complexes using ^{1}H and ^{13}C NMR, FT-IR, and X-ray crystallography illuminated subtle differences between the two diastereomers of **4** and provided a rationale for the greater solution stability of *rac*-**4** relative to *meso*-**4**. The source of the instability is due to the stereochemical configuration at sulfur. Additional solution studies, examined by variable-temperature ^{1}H NMR (25 to −130 °C), probed the dynamic exchange behavior of the three complexes. In addition, electrospray mass spectrometry experiments of *rac*-**4** in methanol solutions detected the presence of the unsupported μ-chloro-bridged dimer, [2,6-(^{i}PrS(O)CH_2))$_2$$C_6H_3$Pd]$_2$-$\mu^2$-Cl.

Introduction

The construction of C_2-symmetric, multidentate ligands capable of coordinating reactive metals has been the focus of attention for more than a decade, and many C_2-symmetric metal−ligand complexes have been utilized as efficient asymmetric catalysts.[1] A survey of the literature reveals that the primary elements used to chelate the metal are N, O, or P, but with the exception of P any source of chirality is well-removed from the active metal center. An ideally suited chiral ligand for the generation of C_2-symmetric metal−ligand complexes is the sulfoxide. A bidentate bis(sulfoxide) ligand presents many advantages: (i) the source of chirality is at sulfur, (ii) the sulfur is configurationally stable, and (iii) there is a wealth of chemistry associated with the preparation and isolation of optically pure sulfoxides. In light of all these advantages, only eight reports exist in which bidentate sulfoxide metal complexes have been prepared.[2] Only three investigate the catalytic properties of these systems.[2c,f,h]

The first example to test the catalytic potential of a bis(sulfoxide) appeared in 1978.[2c] MacMillan and James reported the preparation of several bis(sulfoxide)−Ru(II) adducts. These species catalyzed the asymmetric hydrogenation of prochiral olefins, albeit with very low enantioselectivity. The second reported example in which a bis(sulfoxide) served as a supporting ligand for homogeneous catalysis appeared in 1993.[2f] The report entailed the preparation of two optically pure bis(sulfoxide) ligands, S_S,S_S-bis(*p*-tolylsulfinyl)methane and S_S,S_S-2-bis(*p*-tolylsulfinyl)propane, and showed that these two ligands supported enantioselective Diels−Alder catalysis using FeI_3 in situ followed by introduction of substrates. The chelated species were not isolated, but the authors suggested that chelation occurred through oxygen to form a six-membered chelate with iron(III). Another report utilized S_S,S_S-1,2-bis(*p*-tolylsulfinyl)benzene and found that this bidentate ligand provided very stable, optically pure, *S*-ligated chelates with Pd(II), Rh(I), and Ru(II).[2h] The bis(sulfoxide)−Pd(II) adduct afforded reasonable asymmetric induction in the asymmetric allylic alkylation reaction. Other reports exist describing the preparation and characterization of bis(sulfoxide)−metal complexes. Cattalini et

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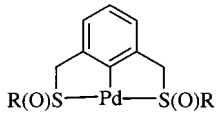
Chart 1. Bis(sulfoxide)-Pincer−Metal Complex



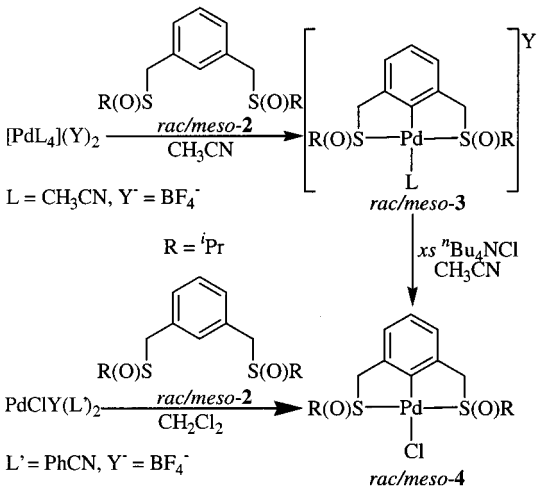
1,3-$(RS(O)CH_2)_2C_6H_3Pd$

R = ^{i}Pr

al. reported the isolation and the molecular structures of both *rac*- and *meso*-diastereomers of bis(phenylsulfinyl)ethane$PtCl_2$, (DPSE)$PtCl_2$.[2d] A later report compared the reactivity of the two diastereomers toward ligand association reactions.[2e] This report is of interest, as it represents the only available study that probes the stability of a bis(sulfoxide) chelate toward substitution reactions. Ruthenium(II)−bis(sulfoxide) complexes containing two bidentate ligands accumulate in Chinese hamster ovary cells and bind to DNA.[2i] The data indicated that the *trans*-complexes were more effective than the *cis*-complexes. The last example to mention is that in which a bis(sulfoxide) ligand, 3,4-bis(*p*-tolylsufinyl)hexane, was found to support chelation to both Pd(II) and Rh(I).[2j] An X-ray crystallographic structure of the C_2-symmetric Pd(II) chelate confirmed that *S*-ligation was present. The authors mentioned the potential of the bis(sulfoxide) as a supporting ligand for asymmetric synthesis, but presented no experiments to support this notion.

Our program of study is directed toward the utilization of chiral bis(sulfoxide) ligands with the aim to understand (i) whether *S*- or *O*-ligation is operative, (ii) relationships between structural and spectroscopic properties, (iii) the stability of metal-chelates, and (iv) the viability of this class of bidentate ligands to support homogeneous catalysis. In this report, sulfoxides were introduced into a pincer framework, and resultant Pd(II) cyclometalation yielded the bis(sulfoxide)-pincer Pd(II) complex, $(RS(O)CH_2)_2C_6H_3Pd$, R(LCL)Pd. The pincer ligand−metal complexes are exceedingly stable due to the formation of the very strong σ M−C bond with additional stabilization resulting from the two pendant ligands. Incorporation of the bis(sulfoxide) within this framework should yield complexes that are very stable, but with the added advantage of introducing a source of chirality that is directly ligated to the metal center. An additional attraction is that a wealth of chemistry exists in which the chelating auxiliaries (L) are either *N*-,[3] *P*-,[4] or *S*-based.[5] These pincer ligands chelate a wide array of transition metals, several of which have been shown to possess a variety of catalytic activities. Herein, we describe the synthesis of a tridentate bis(sulfoxide)-pincer ligand and its ability to chelate palladium(II). In addition, we report the isolation and X-ray crystallographic determination of these chelates, as well as their behavior in solution.

Scheme 1. Palladation Synthetic Route



Results and Discussion

Synthesis of Bis(sulfoxide)−Pincer−Pd(II) Complexes. Formation of pincer-ligated metal species occurred first by chelation of the two pendant arms followed by metalation at the *ipso* carbon.[3h,4l] Reaction of an equimolar mixture of diastereomeric ligand, *rac*/*meso*-$(^iPrS(O)CH_2)_2C_6H_4$, *rac*/*meso*-**2**, prepared using variations of published procedures,[6] and the appropriate palladium starting material[5i] afforded two convenient routes for the preparation of palladated bis(sulfoxide) pincer, Scheme 1. Metalation of *rac*/*meso*-**2** using [Pd(NCMe)$_4$][$(BF_4)_2$] in acetonitrile in the presence, or

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absence, of 2,6-di^{t}Bu-pyridine (DTBP) resulted in the formation of *rac*/*meso*-**3**. In the absence of base, the reaction required longer times (24 h) and higher temperature (60 °C); however, introducing base to the reaction solution afforded the palladated product in less time (<15 min) and at ambient temperature. Thus, the presence of base serves to increase the isolated yield at lower temperatures and diminished reaction times; moreover, the order of addition was very important. The best yields occurred upon mixing ligand and metal precursor before the addition of base. In the absence of added base, periodic sampling of the reaction solution in CD_3CN by ^1H NMR revealed that chelation occurred immediately upon mixing of free ligand with $[Pd(NCCH_3)_4]^{2+}$. The chelated intermediate disappeared with time to yield two sets of resonances of equal integrated intensity attributable to the metalated products, *rac*/*meso*-**3**, as evidenced by a well-resolved AB quartet (5.041, 4.956 ppm ($^2J_{AB}$ = 15.8 Hz)) and a very broad resonance at 4.80 ppm. There was no evidence for palladation at other points in the ring. Regardless of the conditions used, reduction of the solution volume followed by diethyl ether-induced precipitation provided the exclusive isolation of *rac*-**3** with yields (based on Pd(II)) of either 25% (without base) or 35% (with base). X-ray crystallography and other experimental data (see below) revealed that the well-defined AB-quartet was attributable to *rac*-**3**, whereas *meso*-**3** gave broadened resonances.

The isolated yield of *rac*-**3** from reaction solutions in the presence of added base (35%) seems low, but is good when compared to free ligand (70% based on 50:50 mixture of free ligand). In an attempt to improve the overall yield, we sought an alternative route. Palladation of *rac*/*meso*-**2** occurred when treated with $PdCl(BF_4)(NCPh)_2$ in methylene chloride at room temperature in less than 2 h. Interestingly, the exclusive isolation of *rac*-**4** occurred upon repeated trituration of the crude solid in the presence of cold methanol followed by a single recrystallization of the diastereomeric mixture from an ethyl acetate/methylene chloride/methanol (6:3:1) solution. This treatment yielded the exclusive isolation of *rac*-**4** in average isolated yields of 41% (82% based on free *rac*-**2**). Isolation of the other diastereomer, *meso*-**4**, occurred with very poor yields (9%) from the original mother liquor. Interestingly, addition of DTBP did not affect the yield for this reaction. Both *rac*- and *meso*-**4** were indefinitely stable in the solid state. The former complex showed stability in HCl-acidified (50 mM) ethanol/water solution over a 24 h period at room temperature, but the latter decomposed under identical conditions. The general insensitivity of *rac*-**4** to acidic conditions allowed chromatographic purification without any detectable decomposition.

As shown in Scheme 1, conversion of *rac*/*meso*-**3** to *rac*/*meso*-**4** occurred upon addition of an excess of ^{n}Bu$_4$NCl in acetonitrile. The reaction proceeded at room temperature under a nitrogen atmosphere and was essentially quantitative. Despite the inability to isolate *meso*-**3** from original reaction mixtures, confirmation of its identity occurred upon treatment of crude reaction mixtures containing both *rac*/*meso*-**3** with excess ^{n}Bu$_4$NCl, thereby producing *rac*/*meso*-**4**.

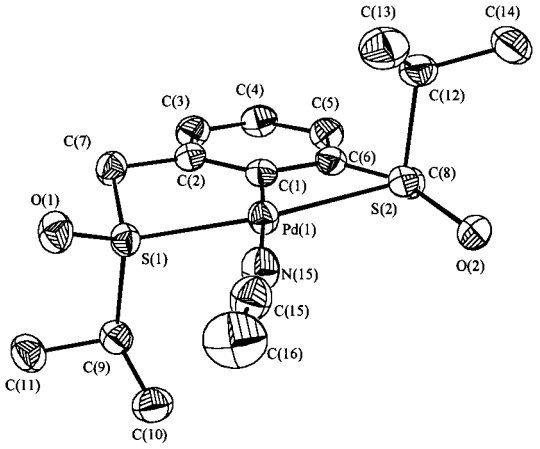

Figure 1. ORTEP plot (50% probability) of the S_S,S_S-enantiomer of $[rac\text{-}2,6\text{-}(^i PrS(O)CH_2)_2C_6H_3PdNCCH_3][BF_4]\cdot CH_3CN$, *rac*-**3**. BF_4^- and CH_3CN and all hydrogen atoms were omitted for clarity.

Molecular Structures of Bis(sulfoxide)-Pincer Pd(II) Complexes. The chemistry of metal−sulfoxide complexation is rich with a variety of bonding modes exhibited by the sulfoxide.[7] The ambidentate nature of the sulfoxide provides the possibility of either *S*- or *O*-ligated complexes; even a few rare reports exist in which both the sulfur and oxygen serve as a bridging ligand between two metal centers.[8] Generally, *S*-ligation is the predominantly observed mode of ligation for the heavier metals of groups 8−10. A survey of the CCDC database revealed that out of the 135 reported group 8−10 transition metal complexes that contain two or more sulfoxide ligands, *S*-ligated sulfoxides dominated 88% of the time. Thus, the working hypothesis was that the bis(sulfoxides) prepared in this study would exhibit *S*-ligation to the Pd(II) center. The observed IR data for all pincer−metal chelates supported this notion, as the observed S=O stretching frequencies, ν_{SO}, are all about 50 cm^{-1} higher in frequency than the free sulfoxide, as consistent with earlier work.[9] Conclusive evidence to validate the initial hypothesis occurred upon the determination of the molecular structures for *rac*-**3**, *rac*-**4**, and *meso*-**4**.

ORTEP representations (50% probability) of *rac*-**3**, *rac*-**4**, and *meso*-**4** together with the adopted numbering schemes are presented in Figures 1−3, respectively. Table 1 provides a listing of the crystal structure and refinement data, while Table 2 contains selected bond distances and bond, torsional, and interplanar angles for these complexes. Inspection of the structures for both *rac*-**3** and *rac*-**4** reveal that both metallocycles are dissymmetric, with the principle symmetry element being a C_2-axis that is collinear with the Pd(1)−C(1) bond. The isopropyl groups are *anti* with respect to the coordination plane and occupy axial positions, whereas the oxygen atoms occupy equatorial positions. The molecular structure of *meso*-**4**, Figure 3, shows that this

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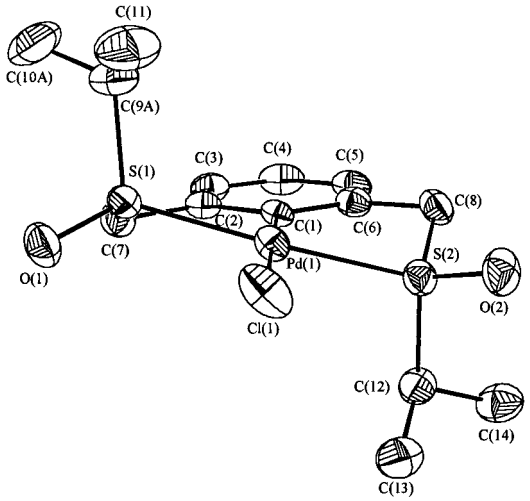

Figure 2. ORTEP plot (50% probability) of the R_S,R_S-enantiomer of *rac*-2,6-(^{i}PrS(O)CH$_2$)$_2$C$_6$H$_3$PdCl, *rac*-**4**. All hydrogen atoms were omitted for clarity.

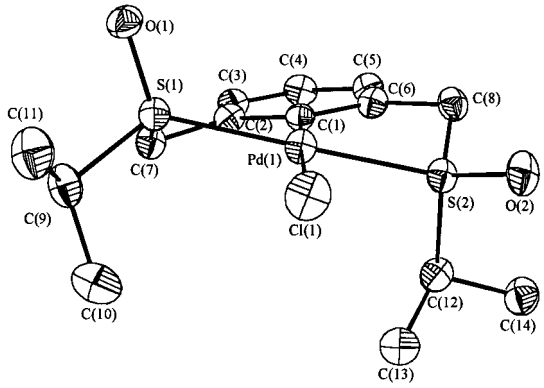

Figure 3. ORTEP plot (50% probability) of the S_S,R_S-enantiomer of *meso*-2,6-(^{i}PrS(O)CH$_2$)$_2$C$_6$H$_3$PdCl, *meso*-**4**. All hydrogen atoms were omitted for clarity.

molecule is asymmetric.[10] Unlike the C_2-symmetric complexes, the isopropyl groups occupy both axial and equatorial positions.

The palladium coordination sphere is approximately square planar for each species. The deviation from ideal square planar geometry is due to the diminished bite angle (C(1)−Pd(1)−S(1) < 90° for all complexes) of the terdentate ligand and its ability to accommodate the relatively long Pd−C$_{ipso}$ bond. The Pd−C$_{ipso}$ bond distances observed here are much longer than that observed in ortho-palladated dibenzyl sulfoxide carboxylates (cf. Pd−C$_{ipso}$ 1.945(22) Å).[11] The coordination planes for all three species are planar, as evidenced by the rms deviations of the calculated least-squares planes, P_{coord}. The Pd−C$_{ipso}$ and Pd−N (or Pd−Cl) distances are within the expected norms for these types of complexes, vide infra. Comparison of the metrical parameters of both *rac*- and *meso*-**4** shows that all observed bond distances for the former are shorter than the latter (cf. Table 2). Thus, chelation to the Pd(II) center is more loosely bound within the *meso*-pincer framework. This is particularly important, as it provides direct evidence to support the observed difference in reactivity between the two species.

Many examples of *trans* sulfoxide coordination to either Ru or Rh are known,[7] but this coordination mode is relatively rare for Pd(II). To date, only one example exists, *trans*-Cl$_2$Pd(DMSO)$_2$,[12] where a comparison is possible. The average Pd−S bond distance observed in this complex (2.296(4) Å) is slightly longer than the average value observed here (2.279(10) Å). This small difference is most likely due to the restriction imposed by the terdentate ligand.

Finally, the S−O bond distances deserve mention, as previous work demonstrated that the S−O bond of sulfoxides decreases in length when metal coordination occurs through the sulfur. Crystalline material *rac*/*meso*-**2** was obtained upon slow evaporation of saturated ethyl acetate solutions, but compositional disorder prohibited an accurate determination of the S−O bond distance in *rac*-**2**. Fortunately, the molecular structures of several benzyl alkyl sulfoxides are available for comparison.[13] The average S−O bond distance for these sulfoxides (N = 4) is 1.507(8) Å. Thus, keeping with expectations, the average S−O bond distance of 1.477(6) Å observed for all three complexes is shorter than the S−O bond distance observed in free sulfoxides.

The inherent instability of the *meso*-diastereomer relative to the *rac*-diastereomer deserves further discussion, as the only apparent difference between the two is the differing stereochemistry of the coordinated sulfoxide moiety. Since *meso*-**3** was not isolated, the discussion will focus on both diastereomers of **4**. Inspection of the bond distances of the Pd(II) coordination sphere, Table 2, reveals that there are some differences between the two, as evidenced by the fact that the Pd−C$_{ipso}$ and Pd−Cl distances for *meso*-**4** are slightly longer than *rac*-**4**. The Pd−S distances observed for *meso*-**4** are significantly larger than those observed in *rac*-**4**. Of particular interest is the rather long elongation of the S(1)−Pd(1) distance of 2.2988(9) Å compared to the S(2)−Pd(1) distance of 2.2750(9) Å in *meso*-**4** (cf. Pd−S$_{av}$ 2.268(3) Å for *rac*-**4**). The stereochemical configuration of the S(1) is reverse that in S(2), and a consequence of this is that the isopropyl group is in an equatorial position. It appears that steric interactions between the isopropyl methyls and the chloride force an elongation of this bond. This elongation results in an additional twist about the Pd−C$_{ipso}$ bond, as evidenced by an increase in the interplanar angle of *meso*-**4** (19.3°) relative to *rac*-**4** (16.1°). It is of interest to examine other complexes of this type to see if steric interactions between the ligand and metal substituents provide a similar degree of contortion about the Pd−C bond.

There exists several analogous Pd(II)−pincer complexes available for comparison to the structures available in this report.[4,5] Table 3 contains a compilation of structural data (d_{M-C}, d_{M-X}, and Ω) for a number of these complexes (entries 1−9, 2,6-(LCH$_2$)$_2$C$_6$H$_3$Pd-X (where L = S(O)R, SR, PR$_2$)). Allowing for variability

(10) Retention of the "*meso*" descriptor, while not strictly correct, is used to denote the stereochemistry of the bis(sulfoxide)-pincer ligand.

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Table 1. Crystal Data and Structure Refinement Parameters for *rac*-3, *rac*-4, and *meso*-4

	rac-**3**	*rac*-**4**	*meso*-**4**
empirical formula	$C_{18}H_{27}BF_4N_2O_2S_2Pd$	$C_{14}H_{21}O_2S_2ClPd$	$C_{14}H_{21}O_2S_2ClPd$
fw	532.76	427.28	427.28
Cryst syst	monoclinic	triclinic	triclinic
space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$
unit cell dimens			
a, Å	11.5230(7)	9.8442(5)	5.7637(4)
b, Å	19.4203(12)	10.1872(5)	8.2709(5)
c, Å	11.6945(7)	10.7321(6)	17.9146(12)
α, deg	90	115.5170(10)	76.8990(10)
β, deg	115.2100(10)	92.0540(10)	82.2520(10)
γ, deg	90	116.1840(10)	89.8400(10)
volume, Å^3	2367.7(2)	837.01(8)	823.84(9)
Z	4	2	2
D_{calcd}, Mg/m^3	1.573	1.695	1.722
abs coeff, mm^{-1}	1.008	1.515	1.539
F(000)	1136	432	432
cryst size, mm^3	0.55 × 0.55 × 0.25	0.43 × 0.31 × 0.27	0.317 × 0.210 × 0.136
θ range, data collection, deg	2.10 to 27.50	2.19 to 27.54	1.18 to 27.50
no. of reflns collected	36 160	7523	8890
no. of ind reflns	5432 [R(int) = 0.0214]	3766 [R(int) = 0.0260]	3735 [R(int) = 0.0311]
completeness to θ	99.9%	97.5%	98.4%
abs corr	empirical, SADABS	empirical, SADABS	empirical, SADABS
refinement method	full-matrix least-squares, F^2	full-matrix least-squares, F^2	full-matrix least-squares, F^2
goodness-of-fit on F^2	1.092	1.048	1.072
final R indices [$I>2\sigma(I)$]	R1 = 0.0257 wR2 = 0.0636	R1 = 0.0342 wR2 = 0.0777	R1 = 0.0502 wR2 = 0.1413

Table 2. Selected Bond Distances and Bond, Torsional (ω), and Interplanar (Ω) Angles for *rac*-3, *rac*-4, and *meso*-4

	rac-**3**	*rac*-**4**	*meso*-**4**
	Bond Distances, Å		
Pd(1)−C(1)	1.9904(19)	2.007(3)	2.012(4)
Pd(1)−X	2.1068(18)[a]	2.3815(9)[b]	2.3832(10)[b]
Pd(1)−S(1)	2.2737(5)	2.2663(9)	2.2988(9)
Pd(1)−S(2)	2.2875(5)	2.2690(8)	2.2750(9)
S(1)−O(1)	1.4716(14)	1.470(2)	1.487(3)
S(2)−O(2)	1.4788(15)	1.475(2)	1.481(3)
	Bond Angles, deg		
C(1)−Pd(1)−X	177.55(7)[a]	178.19(8)[b]	176.85(10)[b]
C(1)−Pd(1)−S(1)	83.28(6)	82.96(9)	81.38(10)
C(1)−Pd(1)−S(2)	82.66(6)	81.92(9)	81.78(10)
S(1)−Pd(1)−X	94.93(5)[a]	97.68(3)[b]	101.09(4)[b]
S(2)−Pd(1)−X	99.12(5)[a]	97.39(3)[b]	95.63(4)[b]
S(1)−Pd(1)−S(2)	165.944(18)	164.85(3)	162.81(4)
	Torsion Angles, ω (deg)[c]		
O(1)−S(1)−Pd(1)−X	33.6[a]	−32.7[b]	93.1[b]
O(2)−S(2)−Pd(1)−X	35.4[a]	−32.1[b]	−29.0[b]
C(9)−S(1)−Pd(1)−X	−92.9[a]	96.1[b]	−39.8[b]
C(12)−S(2)−Pd(1)−X	−93.7[a]	96.1[b]	99.9[b]
C(11)−C(9)−S(1)−O(1)	44.5	68.7	−49.5
C(13)−C(12)−S(2)−O(2)	−80.6	64.7	78.7
	Interplanar Angles, Ω (deg)[d]		
	14.1	16.1	19.3

[a] X = N(15). [b] X = Cl(1). [c] For a torsion angle defined by $i-j-k-l$, sign conventions are (+) if a clockwise and (−) if a counterclockwise rotation of the $i-j$ bond vector is required to bring it in line with the $k-l$ vector as one views along the $j-k$ vector. [d] Angle between the least-squares planes of the arene and the coordination plane.

Table 3. Comparison of Pd−C_{Ipso} and Pd−Cl Bond Lengths with the Interplanar Angle (Ω) for Pincer Complexes 2,6-(LCHR)$_2$C$_6$H$_3$PdCl

entry	L	d_{Pd-C}, Å	d_{Pd-Cl}, Å	Ω (deg)[a]	ref
1	S(O)^{i}Pr (R = H)	2.007	2.382	16.1	*rac*-**4**
2	S(O)^{i}Pr (R = H)	2.012	2.383	19.3	*meso*-**4**
3	SAr[b] (R = H)	1.968	2.396	3.0	5d
4	SEt (R = H)	1.977	2.403	8.0	5d
5	SBn (R = H)	1.983	2.391	6.5	5d
6	S^{t}Bu (R = H)	1.988	2.418	15.1	5a
7	PPh$_2$ (R = H)	1.997	2.368	19.8	4b
8	P^{c}Hex (R = H)	2.012	2.427	5.0	4c
9	PPh$_2$ (R = Me)	2.029	2.377	16.4	4f

[a] Interplanar angle (Ω) defined as the angle between calculated least-squares planes of the arene and coordination plane. [b] Ar = 2-C(O)OMe-C$_6$H$_4$.

in experimental data, the general trend to note is that, with the exception of entry 8, introduction of sterically demanding substituents increases the interplanar angle, Ω, which in turn increases the Pd−C_{ipso} distance. When the Pd−C bond lengths decrease, the Pd−Cl distances increase. This comes as no surprise considering that the arene carbon is a strong σ-donor with a very strong *trans* influence. This is an important observation that may have a bearing on many pincer-based systems that catalyze a number of reactions. For instance, 2,6-(R$_2$PCH$_2$)$_2$C$_6$H$_3$IrH$_2$ (R(PCP)IrH$_2$, R = ^{i}Pr, ^{t}Bu) is capable of catalytic transfer dehyrogenation of alkanes.[5g,h] Interestingly, the system with the ^{i}Pr substituent is a much better catalyst than the Ir complex bearing ^{t}Bu groups. It has been speculated that the steric bulk of the ^{t}Bu group is responsible for the attenuation of the observed reactivity and overall catalytic activity. Coupled with these observations is the fact that ^{i}Pr(PCP)Ir(CO) oxidatively adds H$_2$,[14] but ^{t}Bu(PCP)Ir(CO) does not.[5h] The suggestion that the ^{t}Bu groups inhibit H$_2$ addition may in fact be due to an increase in Ω, and thus a concomitant increase in d_{Ir-C}, which would attenuate the reactivity of the Ir(I) center. It would be interesting to see if a sterically less demanding phosphine substituent would result in a greater catalytic activity.

Comparison to Other *trans*-Ligated Bis(sulfoxides). When *S*-ligation occurs in metal-bound sulfoxide complexes, the sulfur−metal bond is either σ-only or $\sigma-\pi$.[7] In the event that σ-only bonding occurs, the S−O bond order increases in order to compensate the diminishment of the electron density at the sulfur due to the formation of the S−M bond. When both $\sigma-\pi$ bonding exists, back-donation of electron density from a low-

(14) Rybtchinski, B.; BenDavid, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786−3793.

lying metal d_π-orbital can occur, which results in an increase in the S−O bond order and a decrease in the S−M bond length. The molecular orbital picture of DMSO[15] shows that the LUMO (SO-π*) is only slightly higher in energy than the HOMO (S lone-pair) and is available for M−d_π orbital overlap only when the S−O vector is either coplanar or perpendicular with the metal coordination plane. Assuming that the MO picture of the sulfoxide(s) present in this study is similar to that calculated for DMSO, the sulfoxide bonding observed in both *rac*-**3** and *rac*-**4** (and one of the two sulfurs in *meso*-**4**) is σ-only, as the observed ω is approximately 32° (cf. Table 2). The orientation of the sulfoxide in *meso*-**4**, in which the oxygen atom occupies an axial position, would suggest that $d_\pi-\pi$* back-donation is possible. If this were possible, then a contraction of the Pd−S bond distance would occur with respect to the other Pd−S distance. Since this is not the case, then the mode of bonding for this sulfur is σ-only and the observed elongation must be attributable to the steric interactions that exist between the isopropyl group and adjacent ligated chloride.

Solution Stability, Behavior, and Dynamics of Bis(sulfoxide)-Pincer Pd(II) Complexes. The complexes prepared in this study were sufficiently soluble in $CHCl_3$, CH_2Cl_2, and CH_3CN to allow spectroscopic characterization, but were sparingly soluble in either benzene or toluene. The chloro derivatives were stable upon exposure to air, but *rac*-**3** yielded the aquo complex when exposed to the same conditions. The general observation to note is that the two *rac*-diastereomers, *rac*-**3** and *rac*-**4**, were significantly more stable in solution when compared to their *meso*-counterparts. This is, in part, evidenced by the inability to isolate *meso*-**3**, but is also bolstered by the reactivity of *meso*-**4** when exposed to slurried silica. For example, *rac*-**4** was readily chromatographed using silica gel chromatography without any noticeable decomposition. The *meso* complex always showed partial decomposition when exposed to the same environment, as evidenced by the retention of a black substance at the top of the column. The susceptibility of *meso*-**4** to undergo partial decomposition under these conditions is rationalized by the fact that the Pd(II) is more loosely bound within the chelating framework when compared to the *rac*-**4**.

The air and acid stability observed for *rac*-**4** allowed for the examination of additional solution studies. Of particular interest is the propensity of *rac*-**4** to form a μ-chloro-bridged dimer in methanol solution. Some of the initial studies involving 2,6-$(R_2NCH_2)_2C_6H_3PdCl$ (R = Me, Me(NCN)PdCl) pincer complexes revealed that an unsupported μ-Cl-$[Pd(MeNCN)]_2^+$ dimer formed when a stoichiometric amount of MeNCNPdCl was added to $[(MeNCN)Pd(OH_2)]BF_4$.[16] The molecular structure of this species revealed that the average Pd−Cl distance of 2.461(4) Å was slightly longer than the norm and that the Pd−Cl−Pd angle was 134.8°. Surprisingly, during the course of characterization of *rac*-**4** via postive-ion mode electrospray mass spectrometry (ESI-MS) using methanol solutions in which the concentration of *rac*-**4** was 1 mM, the presence of a species with molecular mass of 818.925 amu was detected. This mass corresponds exactly with the mass expected for $[2,6\text{-}(^i PrS(O)CH_2))_2C_6H_3Pd]_2\text{-}\mu^2\text{-}Cl$. Interestingly, of the cationic species detected under these conditions, the dimer is the major species present. Subsequent dilution of the sample resulted in a diminution of the mass corresponding to the dimer with a concomitant increase in the intensity of the peak of the cationic monomer (390.988 amu). These data suggest that, in polar solvents, displacement of the chloride occurs and that dimer formation occurs to some degree.

Several reports exist adequately describing the solution dynamics of a number of R(NCN)MX complexes (M = Pt(II)[17] and Ni(II)[18]), as well as Me(SCS)PdCl.[5b] The molecular structures of either NCN′ complexes or ^{R}-(SCS)PdCl suggest that the hydrogens α to the point of chelation should be diastereotopic. Indeed at room temperature, Me(SCS)PdCl displays a single resonance for the benzylic hydrogens, but upon cooling to −40 °C two sets of AB quartets were observed, which was indicative of the presence of two diastereomers present in solution. In this particular system, the source of exchange was due to either sulfur-inversion or rotation about the Pd−C_{ipso} bond. The authors were unable to unambiguously determine which pathway was operative. In the case of the NCN′-pincer adducts, the source of exchange is exclusively due to M−C_{ipso} bond rotation. Previous work showed that a single resonance is found for the benzylic hydrogens even at −83 °C,[16] which indicates that the observed resonance is time-averaged between the two species.

For the two racemic products observed in this study, the solid state structure shows that the two alkyl substituents occupy axial positions. Since the sulfur is configurationally stable, the only internal exchange operation is rotation about the Pd−C_{ipso} bond. Therefore, this process would result in a species in which both isopropyl groups are situated in equatorial positions. A consequence of this rotation occurring in solution is that two diastereomers would be present in solution and the observed AB-quartet present at room temperature would be the time-averaged resonance of the two diastereomers. The benzylic hydrogens α to the sulfoxide moiety, either bound or free, are always diastereotopic. In the slow exchange limit, two sets of AB-quartets are possible since exchange would occur between two diastereomers whose benzyl hydrogens are magnetically inequivalent due to the positioning of the isopropyl groups. Variable-temperature ^{1}H NMR of *rac*-**4**, using either CD_2Cl_2 or $CDFCl_2$ to obtain −80 or −130 °C, respectively, showed no broadening due to any exchange process. The only complex to exhibit exchange on the NMR time scale (400.13 MHz) was *rac*-**3**. In fact, two exchange processes exist, as detected by variable-

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temperature ^{1}H NMR. A recent report showed that acetonitrile ligation to the Pd(II) center of an SCS-pincer complex is very weak.[5i] Therefore, it is of no surprise that the first exchange process occurred at room temperature and is attributable to exchange between free and coordinated acetonitrile. It should be noted that crystalline material of *rac*-**3** contains free CH_3CN molecules within the lattice. Indeed, in CD_3CN, the benzylic hydrogens of *rac*-**3** appear as a well-defined AB quartet (5.041, 4.956 ($^2J_{AB}$ = 15.8 Hz)), but in either CD_2Cl_2 or $CDFCl_2$ at 25 °C, substantial broadening of all resonances was observed. Cooling the sample down to −33 °C resulted in sharper resonances and yielded the appearance of a single resonance at 2.371 ppm (bound acetonitrile), ca. 0.4 ppm downfield from free acetonitrile. Additional cooling of the sample to −130 °C (in $CDFCl_2$) resulted in broadening of all of the resonances, which is suggestive of time-averaging of the benzylic hydrogens between the two diastereomers brought about by rotation about the Pd−C_{ipso} bond. Observation of time-averaging at −130 °C in *rac*-**3**, but not *rac*-**4**, could be a consequence of the difference in Pd−C_{ipso} bond lengths (cf. Table 2). The shorter Pd−C_{ipso} bond observed in *rac*-**3** clearly provides a slightly higher barrier to rotation, and the temperature required to access the intermediate time regime for *rac*-**4** is not experimentally accessible at this field strength (400.132 MHz).

Conclusions

Complexation of bis(sulfoxide)-pincer ligands occurred with Pd(II) in which the isolated yields of the C_2-symmetric diastereomer varies from either fair to good depending upon the synthetic method of choice. The *meso*-diastereomer was found to be inherently less stable than its C_2-symmetric counterpart, as evidenced by the inability to isolate *meso*-**3** and the instability of *meso*-**4** with respect to *rac*-**4** when exposed to acid. The complexes were fully characterized, when possible, by ^{1}H NMR, FT-IR, and X-ray crystallography. Both ^{1}H NMR and FT-IR spectroscopic methods support the notion that *S*-ligation to Pd(II) is the exclusive mode of bonding, as evidenced by the approximately 1 ppm downfield shift of hydrogens α to the sulfoxide and the increase of the ν_{SO} stretching frequency of the chelated complexes. Definitive evidence to support this spectroscopic data comes from the X-ray crystallographically determined molecular structures of *rac*-**3**, *rac*-**4**, and *meso*-**4**. The molecular structures showed that *S*-ligation was the only mode of ligation. Electrospray mass spectrometry of *rac*-**4** in methanol provided evidence for the formation of the μ^2-chloride dimer in solution. Detection of the 14e cationic monomer suggests that the bis(sulfoxide)-pincer framework is capable of supporting the Pd(II) in a more reactive, Lewis acidic form. Experiments are in progress to determine the extent of its reactivity and selectivity as a Lewis acid-based catalyst.

Experimental Section

All materials, unless otherwise specified, were obtained from Acros, Aldrich, or TCI-America and were used without purification. When necessary, work was performed in a Vacuum Atmospheres dri-box or using Schlenk techniques under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX 400 at operating frequencies of 400.132 and 100.625 MHz, respectively. Dichlorofluoromethane-d_1 ($CDFCl_2$) was prepared according to a literature procedure[19] and purified by bulb-to-bulb distillation from CaH_2. All chemical shifts are reported relative to internal TMS ($CDCl_3$) or relative to solvent residual. FT-IR data were collected using a Nicolet Magna-IR 560 spectrometer employing 1 cm^{-1} resolution. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Fast atom bombardment (FAB) mass spectrometry was performed on a VG7070E magnetic sector mass spectrometer. Electrospray mass spectrometry was operated in the positive-ion mode using a Micromass QTOF II (Beverly, MA). Samples, in the appropriate solvent, were directly infused using a syringe pump operating at 5 uL/min. High-resolution spectra were recorded with poly-D-alanine as an internal molecular weight standard. X-ray analyses were performed using a Bruker SMART CCD system operating at −80 °C (vide infra).

1,3-(^{i}PrSCH$_2$)$_2$C$_6$H$_4$, 1. α,α′-Bis(isopropylthio)-*m*-xylene, **1**, was synthesized using a procedure similar to Loeb et al. for 1,2,4,5-(^{t}BuSCH$_2$)$_4$C$_6$H$_2$.[5c] Isolated yield for a 57.1 mmol reaction: 96.7%. Bp: 185−187 °C (5 mTorr). ^{1}H NMR (C_6D_6): δ (TMS) 7.326 (s, 1H, Ar*H*), 7.093 (m, 3H, Ar*H*), 3.502 (s, 4H, ArCH_2S^{i}Pr), 2.597 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, SC*H*(CH$_3$)$_2$), 1.084 (d, $^3J_{HH}$ = 6.7 Hz, 12H, SCH(CH_3)$_2$). HR FAB-MS (MH$^+$) obsd (theor): 255.1252 (255.1241) (4.3 ppm).

***rac/meso*-(^{i}PrS(O)CH$_2$)$_2$C$_6$H$_4$, *rac/meso*-2.** *rac/meso*-**2** was prepared from **1** using a previously published procedure,[6a] with the exception that flash chromatography (6:3:1 of EtOAc/CH_2Cl_2/MeOH) was employed to remove the bis(sulfone), 1,3-(^{i}PrS(O)$_2$CH$_2$)$_2$C$_6$H$_4$, or monosulfone-monosulfoxide impurities. A reaction based on 5.0 g of **1** resulted in the isolation of 5.40 g (86.2%) of pure *rac/meso*-1,3-(^{i}PrS(O)CH$_2$)$_2$C$_6$H$_4$. ^{1}H NMR ($CDCl_3$): δ (TMS) 7.386 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar*H*), 7.298 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ar*H*), AB-system, both *rac* and *meso* H_B overlap, but there is resolution between the two for H_A; *rac*-**2** 3.927 and 3.863 (2H, $^2J_{AB}$ = 13.2 Hz, ArCH_2S), *meso*-**2** 3.927 and 3.856 (2H, $^2J_{AB}$ = 13.2 Hz, ArCH_2S), *rac*-**2** 2.718 (sept, $^3J_{HH}$ = 6.8 Hz, SC*H*(CH$_3$)$_2$), *meso*-**2** 2.718 (sept, $^3J_{HH}$ = 6.8 Hz, SC*H*(CH$_3$)$_2$), *rac*-**2** 1.336 and 1.303 (d, $^3J_{HH}$ = 6.8 Hz, SCH(CH_3)$_2$), *meso*-**2** 1.334 and 1.299 (d, $^3J_{HH}$ = 6.8 Hz,SCH(CH_3)$_2$). ^{13}C NMR (100.625 MHz, δ, $CDCl_3$): *rac*/*meso*-**2**, aromatic 131.53, 131.44, 131.38, 129.78, 129.75, 129.38, 54.56, 54.53 (Ar*C*H$_2$S(O)CH(CH$_3$)$_2$), 48.92, 48.83 (ArCH$_2$S(O)*C*H(CH$_3$)$_2$), 16.48, 16.47, 14.10, 14.08 (ArCH$_2$S(O)CH(*C*H$_3$)$_2$), (C$_{ipso}$), 139.54 (C$_{ortho}$), 127.92 (C$_{para}$), 123.16 (C$_{meta}$), 67.07 (C$_{benzyl}$), 57.10 (C$_{methine}$), 15.60 and 15.43 (C$_{methyl}$). FT-IR (KBr, cm^{-1}): 1054s (ν_{SO}), 1034s (ν_{SO}), 1021s (ν_{SO}), 1015s (ν_{SO}), 807m (ν_{CS}), 713m (ν_{CS}). Mp (uncorrected): 93.8−94.4 °C. HR-FAB-MS (MH$^+$) obsd (theor): 287.1142, (287.1139) (1.0 ppm).

Preparation and isolation of *rac*-[(^{i}PrS(O)CH$_2$)$_2$C$_6$H$_4$Pd(NCMe)][BF$_4$], *rac*-3. To a solution of a 286.5 mg amount (1.0 mmol) of *rac/meso*-**2** and 1.0 mmol of 2,6-di-*tert*-butylpyridine in 20 mL of dried MeCN was added a 444.2 mg amount (1.0 mmol) of [Pd(MeCN)$_4$)]BF$_4$ in 5 mL of MeCN. The solution was stirred for 2 h at 25 °C. The solution volume was reduced to about 5 mL and then filtered to remove the solid. The filtrate was concentrated and layered with dry Et_2O. The resultant pale yellow-orange crystalline material (suitable for X-ray) was collected, washed with 2 × 0.5 mL of CH_2Cl_2, and dried in vacuo for 24 h. This yielded 196 mg (26%) of *rac*-**3**. ^{1}H NMR (δ ppm, in CD_3CN): 7.277 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar*H*), 7.184 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ar*H*), AB 5.041, 4.956 ($^2J_{AB}$ = 15.8 Hz, 4H, ArCH_2S), 3.210 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, Me$_2$C*H*S), 1.947 (s, 3H, *Me*CNPd), 1.478 and 1.422 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{13}C NMR (100.625 MHz, δ, $CDCl_3$): 152.46 (C$_{ipso}$), 138.87 (C$_{ortho}$), 129.90 (C$_{para}$), 124.78 (C$_{meta}$), 67.02 (C$_{benzyl}$), 58.61 (C$_{methine}$), 17.92 and 14.74 (C$_{methyl}$). FT-IR (KBr, cm^{-1}): 1118s (ν_{SO}), 883m, 789m (ν_{CS}). The molecular structure of *rac*-**3**

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revealed an acetonitrile molecule in the lattice. Samples of *rac*-**3** submitted for C, H, and N elemental analysis were of X-ray quality crystals and yielded the following values for $C_{16}H_{24}BNO_2F_4S_2Pd{\cdot}CH_3CN$: obsd, C 38.85, H 4.81, N 4.92; theor, C 38.55 H 4.85 N 4.99_5.

Preparation of *rac*-4 from *rac*-3. To a 50 mL flask, 477.5 mg (0.92 mmol) of *rac*-**3** and 655.3 mg (12.25 mmol) of ground NH_4Cl were added along with 15 mL of dried MeCN. The mixture was stirred for 6 h at 50 °C and filtered to remove undissolved solid. The filtrate was evaporated under vacuo, and the resultant residue was extracted with CH_2Cl_2. Evaporation of the CH_2Cl_2 solution in vacuo yielded 370.0 mg (94%) of *rac*-**4**. ^{1}H NMR (δ ppm, in CD_2Cl_2): 7.22 (dd, $^3J_{HH} = 7.0$ Hz, 1H, Ar*H*), 7.14 (d, $^3J_{HH} = 7.6$ Hz, 2H, Ar*H*), 4.92 and 4.84 (AB, $^2J_{AB} = 16.4$ Hz, 4H, ArCH_2S), 3.35 (sept, $^3J_{HH} = 7.0$ Hz, 2H, Me_2CHS), 1.57 and 1.50 (d, $^3J_{HH} = 7.0$ Hz, 12H, CH*Me*2). ^{13}C NMR (100.625 MHz, δ, $CDCl_3$): 158.01 (C_{ipso}), 138.77 (C_{ortho}), 128.04 (C_{para}), 122.849 (C_{meta}), 67.69 (C_{benzyl}), 57.86 ($C_{methine}$), 16.61 and 15.20 (C_{methyl}). FT-IR (KBr, cm^{-1}): 1121s (ν_{SO}), 1110s (ν_{SO}), 878m (ν_{CS}), 788m (ν_{CS}). Crystals of *rac*-**4** suitable for X-ray were obtained from slow evaporation of solvent in a 1:8 CH_2Cl_2/hexane solution at 22 °C. Elemental analysis was performed on X-ray quality crystals with the following values for $C_{14}H_{21}O_2S_2ClPd$: theor (obsd): C 39.35 (39.44), H 4.95 (4.76). HR-ESI-MS (M^+, MeOH): obsd 391.0022; theor 391.0018 (1.0 ppm).

Preparation of *rac*-4 from *rac/meso*-2 and $PdCl(BF_4)(NCPh)_2$. To a 100 mL flask containing 50 mL of CH_2Cl_2 were added 500 mg of $PdCl_2(NCPh)_2$ (1.3 mmol) and 373.4 mg of *rac/meso*-**2** (1.3 mmol) with vigorous stirring. Complete dissolution of the solid material required about 15 min and yielded a yellowish-brown solution. To this solution, 253 mg of $AgBF_4$ (1.3 mmol) was added and the solution stirred for 2 h at room temperature. After this time, the undissolved precipitate was removed by filtration and the filtrate was evaporated under vacuo with gentle heating to yield a dark brown oil. Washing the oil with cold CH_3OH (5 mL) yielded a yellow-brown powder. The CH_3OH wash was collected and the powder was triturated under cold CH_3OH (2 × 5 mL). The resultant solid was dried under vacuo and then recrystallized from an ethyl acetate/CH_2Cl_2/CH_3OH (6:3:1) solution yielding 227 mg (0.531 mmol) of *rac*-**4** (40.8% yield based on *rac/meso*-**2** and 81.7% yield based on *rac*-**2**). The spectroscopic and HR-ESI-MS (MeOH) properties were identical to *rac*-**4** prepared by the alternative method (vide supra). The mother liquor was evaporated to yield a yellowish-brown solid, which was dissolved in ethyl acetate. Slow evaporation of this solution resulted in the formation of colorless needles. Collection of the needles via filtration followed by drying under vacuo for 24 h resulted in 50 mg of *meso*-**4** (0.117 mmol; 9% yield based on *rac*/*meso*-**2** and 18% yield based on *meso*-**2**). Spectroscopic data for *meso*-**4**. ^{1}H NMR (δ ppm, in $CDCl_3$): 7.22 (dd, $^3J_{HH} = 7.2$ Hz, 1H, Ar*H*), 7.14 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ar*H*), 4.904 and 4.694 (AB, $^2J_{AB} = 16.2$ Hz, 4H, ArCH_2S), 3.654 (sept, $^3J_{HH} = 6.8$ Hz, 2H, Me_2CHS), 1.617 and 1.595 (d, $^3J_{HH} = 6.8$ Hz, 12H, CHMe_2). ^{13}C NMR (100.625 MHz, δ, $CDCl_3$): 157.36 (C_{ipso}), 139.54 (C_{ortho}), 127.92 (C_{para}), 123.16 (C_{meta}), 67.07 (C_{benzyl}), 57.10 ($C_{methine}$), 15.60 and 15.43 (C_{methyl}). FT-IR (KBr, cm^{-1}): 1121 (ν_{SO}), 1095 (ν_{SO}), 879 (ν_{CS}), 791 (ν_{CS}). HR-ESI-MS (M^+, MeOH): obsd, 391.0029; theor, 391.0018 (2.8 ppm).

X-ray Analysis. X-ray diffraction measurements of *rac*-**3**, *rac*-**4**, and *meso*-**4** were collected using a Bruker SMART CCD system at −80 °C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames/series) that were well distributed in reciprocal space. Data frames were collected [Mo Kα] with 0.2° wide ω-scans for 10 s. Five complete ω-scan series, 909 frames, were collected, with an additional 200 frames a repeat of the first series for redundancy and decay purposes. The crystal-to-detector distance was 4.973 cm, thus providing a complete sphere of data to $2\theta_{max} = 55°$. The total number of reflections collected were corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS.[20] The experimental parameters for each complex are presented in Table 1.

Structural Determination and Refinement. All crystallographic calculations were achieved using a personal computer (PC) with dual Pentium 450 MHz processors and 384MB of extended memory. The SHELXTL[21] program package was implemented, XPREP, to determine the probable space group and set up the initial files. The structures were determined by direct methods with the successful location of nearly all atoms using the program XS.[22] The structure was refined with XL.[23] After the initial refinement difference Fourier cycle, additional atoms were located and input. After several of these refinement difference Fourier cycles, all of the atoms were refined isotropically, then anisotropically. The only disorder present in all three complexes was that observed with one of the isopropyl groups of *rac*-**4**. One methyl group (10A/10B) was modeled as a two-site disorder with the SOFs being 57.658% and 42.342%. The hydrogen atoms for *rac*-**3** were located and refined isotropically, but hydrogen atoms for *rac*-**4** and *meso*-**4** were placed in calculated positions. A final difference Fourier map was featureless, indicating that the structure is therefore both correct and complete.

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Supporting Information Available: Crystal structure data for *rac*-**3**, *rac*-**4**, and *meso*-**4** including tables of atomic parameters, anisotropic thermal parameters, bond distances, and bond angles. Interested readers are able to obtain this material free of charge via the Internet at http://pubs.acs.org.

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