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Access to Central Carbon Chirality through Cycloplatination of 1-(2-Pyridinylthio)propanone by *cis*-[$PtCl_2$(*S*-SOMe(*p*-tolyl))]. The Crystal Structure of (S_sS_c)-[Pt{py{SCHC(O)Me}-2}Cl(SOMe(*p*-tolyl))]

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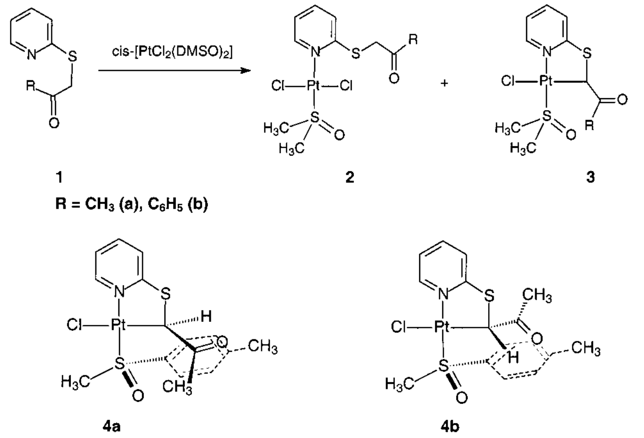
Cycloplatination of the prochiral sp^3 C−H bond of 1-(2-pyridinylthio)propanone (py{SCH_2C(O)Me}-2, **1a**) by *cis*-[$PtCl_2(SOMe_2)$] in dry ethanol affords [Pt{py{SCHC(O)Me}-2}Cl($SOMe_2$)] (**3a**) in 77% isolated yield without any side product. The same reaction using the chiral complex *cis*-[$PtCl_2$(*S*-SOMe(*p*-tolyl))] (the absolute configuration of sulfur is indicated for the *coordinated* ligand) leads to two cycloplatinated diastereoisomers, **4a** (S_sR_c) and **4b** (S_sS_c), in 12.9 and 33.7% yield, respectively (de 44.6%). Their absolute configuration was deduced from the analysis of the ^1H NMR spectra and confirmed by an X-ray structural investigation of **4b**. Diastereomer **4b** was shown to react with PPh_3 to give the enantiomer [Pt{py{SCHC(O)Me}-2}Cl(PPh_3)] with the central carbon chirality only. Rather surprisingly, attempted cycloplatination of py{SCH_2C(O)Ph}-2 (**1b**) by *cis*-[$PtCl_2(SOMe_2)$] affords the cycloplatinated complex [Pt{py{SCHC(O)Ph}-2}Cl($SOMe_2$)] (**3b**) in a miserable yield.

Introduction

We are currently interested in synthesis, reactivity, and catalytic properties of cyclopalladated and cycloplatinated complexes with sulfoxides including enantiomerically pure ones.[1−5] Previously, we presented evidence that the platinum(II) complex with enantiomerically pure sulfoxide *cis*-[$PtCl_2$(*S*-SOMe(*p*-tolyl))] reacts with a ferrocene derivative to afford a pair of cycloplatinated diastereomerers with the element of planar chirality, which are extremely easy to separate and to convert into the individual planar chiral enantiomers.[2] In this work, we extend this method to sp^3 C−H bond activation and show that 1-(2-pyridinylthio)propanone (**1a**) reacts with *cis*-[$PtCl_2$(*S*-SOMe(*p*-tolyl))] (the absolute configuration of sulfur is indicated for the *coordinated* ligand) to give separable diastereomers **4a** and **4b** (45% de, Scheme 1). Achiral cyclometalation of the sp^3 C−H bond of ligand **1a**, as well as of its phenyl substituted analogue **1b**, by palladium(II) and gold(III) complexes has been described,[6,7] but this is the first report in the literature demonstrating the asymmetric cycloplatination of the sp^3 C−H bond.

Scheme 1



Results and Discussion

Cycloplatination of 1a by *cis*-[$PtCl_2(SOMe_2)$]. It has been first demonstrated that the achiral complex *cis*-[$PtCl_2(SOMe_2)_2$] reacts with **1a** to form cycloplati-

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Table 1. Reaction Conditions and Yields of Complexes 2a and 3b on Interaction between 1a and *cis*-[PtCl$_2$(SOMe$_2$)]

run	conditions	ratio [**1a**]:[Pt^{II}]	solvent	yield of **2a** (%)	yield of **3a** (%)
1	8 h, 22 °C	1:1.3	MeOH	55.7[a]	6.5
2	16 h, reflux	1.1:1	MeOH	38.4[a]	16
3	24 h, reflux	1:1	MeOH	38.3[a]	23.2
4	8 h, reflux	1:1	EtOH	0	77.4
5	24 h, reflux	1:1	CH_3CN	49.5	1.2
6	24 h, reflux	**2a** → **3a**[a]	MeOH		55

[a] Conversion of **2** into **3**.

nated compound **3a**. In fact, this interaction may lead to two compounds, viz., *N*-bound complex **2a** and *C*,*N*-chelate **3a**. Table 1 summarizes the results of the interaction between *cis*-[PtCl$_2$(SOMe$_2$)$_2$] and **1a**. As seen from Table 1, the target compound **3a** is better synthesized in refluxing dry ethanol for 8 h. The consequences of a transition from methanol to ethanol as solvent are worth mentioning. In contrast to MeOH, in which a considerable amount of **2a** is formed, the reaction in ethanol leads exclusively to the target compound in high yield. Although the data in Table 1 show that initially formed complex **2a** transforms gradually into **3a** in refluxing MeOH (cf. runs 1−3), a large quantity of **2a** is still present in the reaction mixture. The reason for the different chemistry observed in two similar solvents is that complex **2a**, a plausible precursor of **3a** formed as shown by eqs 1 and 2,[8] is significantly more soluble in ethanol than in methanol. Precipitation of **2a** from the methanol solution must noticeably slow its cycloplatination into complex **3a**.

$$\textit{cis}\text{-}[\mathrm{PtCl_2(SOMe_2)_2}] + \mathrm{ROH} \rightleftharpoons [\mathrm{PtCl_2(SOMe_2)(ROH)}] + \mathrm{SOMe_2} \quad (1)$$

$$[\mathrm{PtCl_2(SOMe_2)(ROH)}] + \mathbf{1} \rightleftharpoons \mathbf{2} + \mathrm{ROH} \quad (2)$$

Together with the analytical data, the structures of **2a** and **3a** were assigned on the basis of the ^{1}H NMR spectral information. In particular, the CH_2 resonance in **2a** is a singlet without Pt satellites, and its integral intensity corresponds to two hydrogens. The intensity of the corresponding proton in complex **3a** is twice as low as in **2a**, the resonance is shifted upfield, and, importantly, the Pt−H coupling constant equals 97 Hz. The latter is direct evidence that Pt^{II} is σ-bound to the sp^3-carbon.

Asymmetric Cycloplatination of 1a. The data in Table 1 obtained for *cis*-[PtCl$_2$(SOMe$_2$)$_2$] were further used for selecting the most favorable conditions for the cycloplatination of **1a** by the chiral complex *cis*-[PtCl$_2$(*S*-SOMe(*p*-tolyl))]. The reaction was run at a [**1a**]:[Pt^{II}] molar ratio 1:1, in refluxing dry ethanol for 4−6 h. The diastereomers formed were separated using preparative thin-layer chromatography on silica gel. As a result, diastereomers **4a** and **4b** were isolated in 12.9 and 33.7% yield, respectively (de 44.6%). The ^{1}H NMR spectral data for **4a** and **4b** allow assigning the absolute configuration of the asymmetric sp^3-carbon. Naturally, the conclusions are based on the observation that the absolute configuration at sulfur does not change during the cycloplatination.[2] The evidence is in the chemical shifts of the SCH_3, $COCH_3$, and SCHC protons. The former singlet is seen at δ 3.62 and 3.64 for **4a** and **4b**, respectively, indicative of similar environments of the SCH_3 group in both diastereomers. If the chloro ligand is the closest “neighbor” of the sulfoxide methyl group (see structures **4a** and **4b**), the $COCH_3$ and SCHC protons should be differently shielded by the sulfoxide tolyl ring. In particular, the SCHC and $COCH_3$ hydrogens are shielded in **4a** and **4b**, respectively, and the corresponding resonances are thus shifted upfield.[9] In fact, the effect of the aromatic ring current of the tolyl group of **4a** accounts for the SCHC resonance at δ 4.23. In contrast, the SCHC resonance is observed at δ 4.50 for **4b**, since the SCHC hydrogen and the tolyl group are more spatially separated. The same argument is equally applicable to the $COCH_3$ resonance observed at δ 2.25 and 1.76 for **4a** and **4b**, respectively. The resonance at the highest field is seen when the methyl group is strongly shielded by the tolyl group in diastereomer **4b**. To this end, the ^{1}H NMR spectral data allow us to assign the absolute configuration at the sp^3 chiral carbon, which is *R* and *S* for **4a** and **4b**, respectively, and this conclusion was confirmed by the X-ray structural investigation of **4b**.

Structures of **4a** and **4b** help to reveal the origin of diastereoselectivity during the cycloplatination. Our recent structural and kinetic studies of cycloplatination of aryl oximes by *cis*-[PtCl$_2$(SOMe$_2$)$_2$] are indicative of the intermediacy of the [PtCl$_2$(N∧CH)(SOMe$_2$)] species, where N∧CH is *N*-coordinated aryl oxime.[8] Assuming that (i) a similar mechanism is operative here and (ii) the C−H bond cleavage involves the late, product-like transition state, i.e., similar to products **4a** and **4b**, it may be postulated that the transition state leading to **4b** has lower energy due to the favorable hydrophobic interaction between the $COCH_3$ methyl group and the tolyl ring of the coordinated sulfoxide.

By the example of the more stable stereoisomer **4b** it was demonstrated that **4** reacts with an equimolar amount of triphenylphosphine. The expected substitution of the sulfoxide by PPh_3 takes place. The same was previously observed for the planar chiral cycloplatinated dimethylaminomethylferrocene.[2]

X-ray Structural Investigation of 4b. The crystal structure of complex **4b** is shown in Figure 1. As seen, its geometry is in a full accord with that derived from the ^{1}H NMR information. This concerns both the coordination square at platinum(II) and the absolute configuration of the asymmetric carbon. The asymmetric unit contains one molecule of **4b**. The geometry around platinum(II) deviates only slightly from the square planar arrangement, with angles between 84.9° and 93.3° in the plane. Due to the high value for the anomalous dispersion of Pt, the configuration of C(6) could be determined with a very high accuracy. All ligands exhibit a geometry that agrees with the ideal geometry expected for the correspondingly hybridized atoms, thus indicating the lack of strong interactions between adjacent molecules in the crystal. Only C(6) exhibits a significantly distorted geometry (tetrahedral

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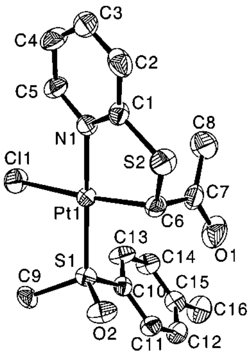

Figure 1. Crystal structure of complex **4b**. Ellipsoids represent a 70% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths in Å: Pt−C(6) 2.052(8), Pt−N(1) 2.055(7), Pt−S(1) 2.221(2), Pt−Cl(1) 2.371(2).

angles are in the range 105.3−114.0°). This distortion is due to the steric requirements of the five-membered ring. The ring has an envelope conformation. It is slightly distorted due to the very different bond lengths within the ring. The "tip" of the envelope is formed by C(6). The average bond lengths the of the pyridyl and phenyl groups are 1.374 and 1.384 Å, respectively, and all C−C−C angles in these rings are 120° within a 3σ range.

Attempted Cycloplatination of 1b by *cis*-[PtCl$_2$(SOMe$_2$)$_2$]. It was surprising to find out that the reaction between **1b** and *cis*-[PtCl$_2$(SOMe$_2$)$_2$] was not as clean as for **1a** under identical conditions. The major product precipitated turned out to be a light yellow, obviously polymeric, material, which was sparingly soluble in hot dimethyl sulfoxide only. The target platinacycle **3b** was isolated from the mother liquor in 3 and 1.5% yield when the reaction was run in methanol and ethanol, respectively. The ^{1}H NMR of the polymer recorded in DMSO-d_6 did not show any signal with Pt satellites. The carbonyl stretching frequency was observed at 1670 cm^{-1}. Other strong band in the IR spectrum is seen at 1120 cm^{-1} and can be attributed to the coordinated dimethyl sulfoxide.[10] Attempts to split the polymer by treating it with ligands such as pyridine or triphenylphosphine in benzene at reflux or in dimethyl sulfoxide at 100 °C for 5−6 h failed. However, the extensive refluxing of the material in methanol or ethanol results in a slow accumulation of complex **3b**. In particular, after refluxing 100 mg of the polymer in 35 mL of methanol for 24 h and filtering the hot solution, 10 mg of chromatographically pure **3b** was recovered from the filtrate. Interestingly, polymeric palladium(II)-containing products based on **1b** were obtained previously.[11]

In conclusion, we have shown that the use of chiral sulfoxides coordinated to platinum(II) is a tool for asymmetric cycloplatination of sp^3 C−H bonds. The diastereoselectivity of this process is higher than that previously reported for the sp^2 C−H activation of the ferrocene derivatives, affording compounds with planar chirality.[2] To our knowledge, this is the first example of asymmetric C−H cleavage by platinum(II) at the sp^3-hybridized carbon. Asymmetric catalytic reactions,[12,13] for example, hydrolysis of amino acid esters and amides,[14,15] are a potential field of applications of the chiral platinum metalacycles.

Experimental Section

General Procedures. The starting complexes were prepared according to Price et al.[16] In particular, *cis*-[PtCl$_2$(*S*-SOMe(*p*-tolyl)] was prepared by adding a 3-fold excess of *R*-methyl (*p*-tolyl) sulfoxide (Fluka) to a solution of K$_2$PtCl$_4$ in 5 mL of water, and the mixture was stirred for 48 h to form a white precipitate (90%). Ligands **1a**,**b** were obtained as described elsewhere.[7,17] ^{1}H NMR spectra were recorded on a Bruker CXP-200 instrument.

Complex 2a (Run 5, Table 1). Ligand **1a** (143 mg, 0.856 mmol) and *cis*-[PtCl$_2$(SOMe$_2$)$_2$] (361 mg, 0.856 mmol) were mixed in 25 mL of dry acetonitrile and refluxed for 24 h. After refluxing for 12 h, the reaction mixture was a yellow homogeneous solution containing mostly **2a** and a small amount of **3a** (TLC, Silufol plates, 1:1 benzene/acetone as eluent; R_f = 0.5 and 0.7, respectively). The reaction mixture was kept at −5 °C for 7 days. Complex **2a** as a white precipitate was filtered off, washed with dry MeCN, and dried in the air (206.6 mg). The mother liquor was concentrated to 5 mL and subjected to TLC (Silufol plates) using 1:1 benzene/acetone as eluent. As a result, 10 and 5 (1.2%) mg of complexes **2a** and **3a**, respectively, were isolated. Total yield of **2a** was 49.5%. Anal. (after crystallization of **2a** from dry MeCN) Found: C, 23.35; H, 2.85; N, 2.89; Cl, 12.29. Calcd for C$_{10}$H$_{15}$NS$_2$O$_2$Cl$_2$-Pt: C, 23.49; H, 2.96; N, 2.74; Cl, 13.87. Mp: 195 °C. ^{1}H NMR (CD$_3$CN/CDCl$_3$, δ, J in Hz): 2.38 (s, COCH$_3$), 3.50 and 3.60 (s, SCH$_3$, $J_{\rm PtH}$ 24.4), 4.17 (s, CH$_2$), 7.22 (t, 1H, py-H4, $J_{\rm HH}$ 6.8), 7.30 (d, 1H, py-H3, $J_{\rm HH}$ 7.1), 7.79 (t, 1H, py-H5, $J_{\rm HH}$ 6.78), 8.77 (d, 1H, py-H6, $J_{\rm HH}$ 7.07, $J_{\rm PtH}$ 45.8).

Complex 3a (Run 4, Table 1). Ligand **1a** (159 mg, 0.95 mmol) and *cis*-[PtCl$_2$(SOMe)$_2$] (401 mg, 0.95 mmol) were mixed in 25 mL of dry ethanol and refluxed for 8 h. The products formed were analyzed by TLC (Silufol plates, 7:3 benzene/acetone). The yellow precipitate formed was filtered off from the hot reaction mixture, washed with ethanol, and air-dried (233 mg). This turned out to be chromatographically pure complex **3a** (R_f 0.65). The mother liquor was kept in the refrigerator for 2 days to afford an extra 116 mg of **3a**. Total yield: 77.4%. Anal. (after crystallization from dry EtOH) Found: C 25.56; H. 3.14; Pt, 41.05. Calcd for C$_{10}$H$_{14}$NS$_2$O$_2$-ClPt: C, 25.29; H, 2.97; Pt, 41.08. Mp: 228−230 °C. ^{1}H NMR (CD$_3$CN/CDCl$_3$, δ, J in Hz): 2.30 (s, COCH$_3$, $J_{\rm PtH}$ 9.6), 3.49 and 3.61 (s, SCH$_3$, $J_{\rm PtH}$ 24), 4.52 (s, CH, $J_{\rm PtH}$ 97.3), 7.08 (t, 1H, py-H4, $J_{\rm HH}$ 7.9), 7.61 (d, 1H, py-H3, $J_{\rm HH}$ 7.0), 7.73 (t, 1H, py-H5, $J_{\rm HH}$ 7.85), 8.96 (d, 1H, py-H6, $J_{\rm HH}$ 6.7, $J_{\rm PtH}$ 30.5).

Complex 3b. Complex *cis*-[PtCl$_2$(SOMe)$_2$] (334 mg, 0.79 mmol) was suspended in 18 mL of dry MeOH and stirred by a magnetic bar for 1 h at room temperature. A solution of **1b** (181 mg, 0.79 mmol) in 5 mL of MeOH was then added to the white suspension, and the resulting mixture was refluxed for 17 h. TLC showed the presence of two compounds with R_f 0.0 and 0.55 (9:1 benzene/acetone). The light yellow precipitate formed was filtered off, washed with dry MeOH, and air-dried

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(394 mg, R_f 0.0, presumably polymer). The mother liquor was concentrated to 5 mL and kept for 3 days at 5 °C. The yellow crystals formed were separated, washed with hexane, and air-dried to give 14 mg of complex **3b** (3.3%, R_f 0.55). The same result was obtained in ethanol as solvent, where the yield of **3b** was as low as 1.5%. Anal. Found: C, 32.0; H, 3.0; Pt, 36.3. Calcd for $C_{15}H_{16}ClNO_2PtS_2 \cdot H_2O$: C, 32.5; H, 3.3; Pt, 35.2. Mp: >230 °C (dec). ^{1}H NMR ($CDCl_3$, δ, J in Hz): 2.64 (s, SCH_3, J_{PtH} 23) and 3.51 (s, SCH_3, J_{PtH} 24), 5.37 (s, CH, J_{PtH} 95.7), 7.06 (td, 1H, py-H4, J_{HH} 6.8 and 2.0), 7.4−8.10 (m, 8H), 8.96 (d, 1H, py-H6, J_{HH} 6.7, J_{PtH} 32). The compound with R_f 0.0 is soluble in hot DMSO only.

Complexes 4. Ligand **1** (61.1 mg, 0.336 mmol) and *cis*-[$PtCl_2$(*S*-SOMe(*p*-tolyl))] (210 mg, 0.336 mmol) were refluxed in 15 mL of dry ethanol for 4 h. After 5 min the reaction mixture became a homogeneous yellow solution. The TLC analysis (Silufol plates, 9:1 benzene/acetone) showed the presence of two products (R_f = 0.7 and 0.65). The reaction mixture was kept at 5 °C for 3 days. The dark yellow solid formed was filtered and air-dried (27 mg, R_f 0.4). The mother liquor was concentrated to afford a purple oil residue, which was treated by preparative TLC (silica 32−63, 40 μm; 9:1 benzene/acetone). Bands containing two diastereomers of **4** were collected (R_f 0.65 (**4a**) and 0.7 (**4b**)) and washed with EtOH; the solvent was removed using a rotary evaporator and dried in vacuo. TLC analysis (Silufol plates) of thus isolated diastereomers indicated that each fraction is slightly contaminated by the corresponding counterpart. Therefore, extra multiple TLC purification using Silufol UV-254 plates and a benzene/acetone mixture (9:1) as an eluent was essential. Each time 10−15 mg of impure **4a** or **4b** was introduced, and the plates were then treated as indicated above using $CHCl_3$ for the washing. Lemon-white diastereomer **4b** (68 mg, 33.7%) is a stable solid in the air, whereas diastereomer **4a** (26 mg, 12.9%) is a white milk-like oil which is less stable even at 5 °C. Total yield of **4a** and **4b** is 46.6%. **4a**: Anal. Found: C, 29.30; H, 3.07; N, 2.00. Calcd for $C_{16}H_{18}ClNO_2PtS_2 \cdot CHCl_3 \cdot H_2O$: C, 29.66, H, 3.07, N, 2.03. ^{1}H NMR (CD_3CN, δ, J in Hz): 2.25 (s, $COCH_3$), J 9.0), 2.41 (s, $ArCH_3$), 3.62 (s, SCH_3, J 22.2), 4.24 (s, CH, J 89.6), 7.09 (td, H5, J 8.2, 1.6), 7.41, 7.45, 7.96, and 8.00 (AA′BB′, C_6H_4), 7.56 (dd, H3, J 8, 1), 7.74 (td, H4, J 7.1, 1.66), 8.88 (d, H6, J 4.8, 32.4). **4b**: Anal. Found: C, 34.81; H, 3.35; N, 2.46. Calcd for $C_{16}H_{18}ClNO_2PtS_2$: C, 34.88; H, 3.29; N, 2.54. Mp: 210−211 °C. ^{1}H NMR (CD_3CN, δ, J in Hz): 1.76 (s, $COCH_3$), J 9.0), 2.40 (s, $ArCH_3$), 3.64 (s, SCH_3, J 22.9), 4.51 (s, CH, J 92.6), 7.11 (td, H5, J 7, 1.5), 7.39, 7.43, 8.04, and 8.09 (AA′BB′, C_6H_4), 7.60 (dd, H3, J 8, 1), 7.75 (td, H4, J 7.3, 1.66), 8.96 (d, J 6.0, 32.9).

Crystal Structure Determination of 4b. An irregularly shaped, yellow crystal of approximate size 0.2 × 0.15 × 0.1 mm^3 was mounted to a glass capillary. Diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer[18,19] using AgKα radiation. A total of 15 950 reflections were collected. The data set showed monoclinic symmetry, and the systematic extinction ($0k0$:$k = 2n$) led to the possible space groups $P2_1$ and $P2_1/m$, of which the former, noncentrosymmetric one could be confirmed during the structure solution. A numerical absorption correction was applied.[20] The platinum, sulfur, and chlorine atoms could be localized using direct methods;[21] all other atoms were found during subsequent difference Fourier analyses. All non-hydrogen atoms were refined with anisotropic displacement parameters against F^2 using full-matrix least-squares refinements.[22] The hydrogen atoms were refined using a riding model. The absolute configuration could be determined with high accuracy (Flack parameter $x = -0.005$ (0.016)). The crystal data are summarized in Table 2.

Table 2. Crystal Data for 4b

chemical formula	$PtC_{16}H_{18}ClNO_2S_2$
source	synthetic
habit	0.25 × 0.20 × 0.15 mm^3, irregular shape
lattice constants	$a = 764.03(2)$ pm
	$b = 1076.51(2)$ pm
	$c = 1098.74(4)$ pm
	$\beta = 93.6815(9)°$
temperature	297(2) K
radiation	Ag Kα, $\lambda = 56.08$ pm, graphite monochromator
space group	$P2_1$
abs coeff	$\mu = 44.3$ cm^{-1}
transmn factors	$T_{min} = 0.5578$
	$T_{max} = 0.7835$
abs corr	numerical
diffractometer	Bruker-Nonius KappaCCD
refln range	$6.4° < 2\theta < 42.7°$
	$-9 < h < 9$
	$-13 < k < 13$
	$-14 < l < 14$
no. of reflns:	9834
no. of unique reflns	4061
R-factors	$R_{int} = 4.6\%$
	$R_1 = 3.9\%$ (all data)
	$wR_2 = 8.5\%$ (all data)
	$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$,
	$P = (\max(F_o^2, 0) + 2F_c^2)/3$
Flack param	$x = -0.005(0.016)$

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Supporting Information Available: Tables of X-ray experimental details, positional and thermal parameters, bond lengths, and bond angles for the crystal structure **4b** as well as Figures 1S and 2S, showing the unit cell in a projection along (1 0 0) and in a stereographic view. This material is available free of charge via the Internet at http://pubs.acs.org.

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