

# Thermal Stability of Tris(3,5-dimethylpyrazolyl)hydridoboratorhenium(V)(oxo)-(1,2-dithiolate) and -(1,2-monothiodiolate) Complexes and DFT Studies of C–S Bond Cleavage

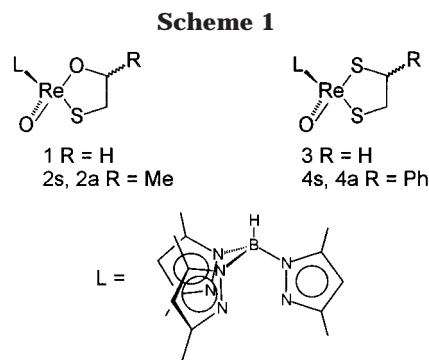
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Rhenium(V) complexes are prepared by reductive cyclocondensation of alkane-1,2-dithiols or alkane-1-thio-1,2-diols with  $\text{Tp}'\text{ReO}_3$  ( $\text{Tp}' = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{hydridoborate}$ ) and  $\text{PPh}_3$ . One complex,  $\text{Tp}'\text{Re}(\text{O})(\text{SCH}_2\text{CH}_2\text{S})$ , was characterized by X-ray crystallography. Unlike the corresponding 1,2-diolato compounds, these sulfur analogues are thermally stable in hydrocarbon solvents for more than one week at 120 °C. To evaluate whether the barrier to cycloreversion was thermodynamic or kinetic in origin, DFT calculations were performed at the B3LYP/LACVP\*\* level. Comparison of calculated reaction energies reveals that substitution of each sulfur raises the predicted  $\Delta E_{\text{rxn}}$  for alkene cycloreversion by about 10 kcal/mol.

The formation and cleavage of carbon–chalcogen bonds mediated by transition metals is fundamental to a large number of chemical transformations. Previous work in our laboratories has focused on C–O bond cleavage mediated by rhenium as a mechanistic model for processes that form new C–O bonds.<sup>1</sup> One question raised in these investigation was whether sulfur analogues would exhibit similar behavior. C–S bond cleavage is a critical component of hydrodesulfurization of fossil fuel sources;<sup>2</sup> this provides ample impetus for examining the chemistry of rhenium thiodiolates. An early report by Herrmann suggested that  $(\eta\text{-C}_5\text{Me}_5)\text{-Re}(\text{O})(\text{SCH}_2\text{CH}_2\text{S})$  thermally decomposed to ethylene, although no tractable rhenium-containing products were seen.<sup>3</sup> Recent work by Rauchfuss and co-workers has hinted that there may be a thermochemical similarity between rhenium sulfides and rhenium oxides in that C–S bond formation from reaction of  $\text{ReS}_4^-$  and alkenes can be observed<sup>4,5</sup> if the alkene is strained or the product is trapped with an appropriate Lewis base. We report here that direct analogues of  $\text{Tp}'\text{Re}(\text{O})(\text{diolate})$  ( $\text{Tp}' = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{hydridoborate}$ ) are thermally stable to at least 120 °C and that DFT calculations reveal that the thermodynamics of this system strongly



favor formation of thiodiolates based on the weak S–Re  $\pi$  interaction.

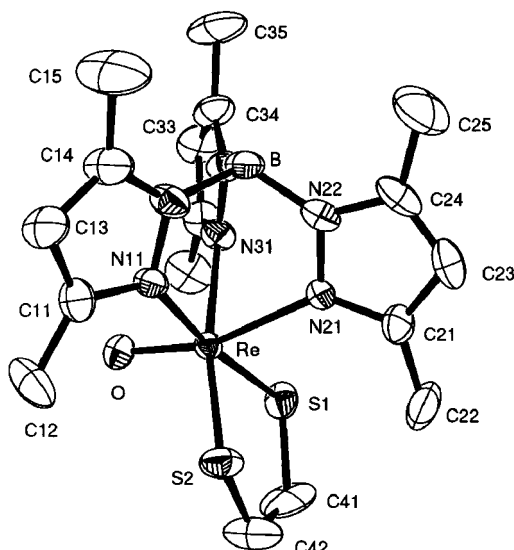
## Results

Mono- and dithiolate complexes can be easily prepared in a procedure analogous to formation of  $\text{Tp}'\text{Re}(\text{O})(1,2\text{-diolate})$  complexes.<sup>6</sup> In-situ reduction of  $\text{Tp}=\text{ReO}_3$  with  $\text{PPh}_3$  in THF presumably leads to the dioxo complex;<sup>7</sup> condensation with a 2-mercapto alcohol or a 1,2-dithiol results in formation of the complexes shown in Scheme 1. These were isolated in 40–80% yield after column chromatography. The compounds were moderately air- and water-stable, particularly in the solid state.

X-ray crystallography of **4** shows the solid state structure of the dithiodiolate (Figure 1). The structure is quite similar to both  $(\text{HBpz}_3)\text{Re}(\text{O})(\text{SCH}_2\text{CH}_2\text{S})$  (**5**) and  $(\text{Bpz}_4)\text{Re}(\text{O})(\text{OCH}_2\text{CH}_2\text{O})$  (**6**), but several features are notable. The relatively short Re=O bond (1.668 Å)

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**Figure 1.** ORTEP from the X-ray crystallographic analysis of **3**. Hydrogen atoms are omitted for clarity. Notable bond lengths: Re=O 1.668(5) Å; Re–S1 2.286(2) Å; Re–N11 2.189(5) Å; Re–N31 2.193(5) Å; Re–N21 2.275(5) Å.

is consistent with the formal triple bond necessary for coordinative saturation, but the nonmethylated compound **5** actually has a longer rhenium oxo bond (1.694 Å). The trans effect of the oxo ligand lengthens one Re–N bond; this has been noted for a number of pyrazolyl rhenium compounds.<sup>8</sup> Of considerable interest is the flattening of the rhenium dithiolate ring. The S–C–S dihedral angle is only 12°. In contrast, dithiolates reported by Rauchfuss et al. have similar dihedral angles of approximately 40°, as does **5**.

All the Tp' mono- and dithiolate complexes in Scheme 1 are thermally stable in benzene or toluene (sealed under vacuum) at 120 °C for at least one week. Under these conditions, no alkene or new rhenium compound is seen by NMR spectroscopy, and the concentration of the thiodiolate relative to 1,4-di-*tert*-butylbenzene included as an internal standard is unchanged ( $\pm 3\%$ ). By contrast, the least reactive oxygen analogue, Tp'Re(O)(OCH<sub>2</sub>CH<sub>2</sub>O), decomposes to Tp=ReO<sub>3</sub> and CH<sub>2</sub>=CH<sub>2</sub> with a half-life of 13 h at 120 °C.<sup>6</sup> Not even the placement of a phenyl ring, which in the diolate series lowers  $\Delta H^\ddagger$  by 5 kcal/mol, has any detectable impact on thermal stability.

Computational studies were performed on these systems using the hybrid B3LYP method. The basis set chosen (LACVP\*\*) consists of the 6-31G\*\* basis set for all atoms except the rhenium; a Hay–Wadt effective core potential<sup>9</sup> (ECP) is applied to the metal atom. This ECP includes corrections for relativistic effects and explicitly treats outer core 6s and 6p electrons. Initial structures were subjected to a preliminary molecular mechanics optimization of the ligands (freezing the coordination geometry at Re at an arbitrary guess with pseudooctahedral coordination), then full optimization at the B3LYP level was performed. This procedure, when applied to the oxygenated analogues, provides

**Table 1.** Calculated Energies and Vibrational Frequencies of Rhenium Compounds at Optimized Geometries

compound	$E$ , B3LYP/LACVP** (Hartree)	calcd $\nu_{\text{Re=O}}$ , cm <sup>-1</sup>	obsd $\nu_{\text{Re=O}}$ , cm <sup>-1</sup>
Tp'Re(O)(OCH <sub>2</sub> CH <sub>2</sub> O)	-1321.8216	949	959
<b>1</b>	-1644.7989	955	961
<b>3</b>	-1967.7795	947	941
TpRe(O)(OCH <sub>2</sub> CH <sub>2</sub> O)	-1085.8884	953	964 <sup>a</sup>
TpRe(O)(SCH <sub>2</sub> CH <sub>2</sub> O)	-1408.8722	940	
TpRe(O)(SCH <sub>2</sub> CH <sub>2</sub> S)	-1731.8547	947	951 <sup>b</sup>
Tp'ReO <sub>3</sub>	-1243.1956	913	910 <sup>c</sup>
Tp'ReO <sub>2</sub> S	-1566.1558	900	
Tp'ReOS <sub>2</sub>	-1889.1185	897	
TpReO <sub>3</sub>	-1007.2579	908	909 <sup>d</sup>
TpReO <sub>2</sub> S	-1330.2221	946	
TpReOS <sub>2</sub>	-1653.1899	927	
CH <sub>2</sub> CH <sub>2</sub> (6-31G**) )	-78.5938		

<sup>a</sup> Reference 27. <sup>b</sup> Reference 8a. <sup>c</sup> Reference 28. <sup>d</sup> Reference 29.

energies that are in reasonable accord with both our own thermochemical measurements and other published calculations for closely related systems.<sup>10</sup> Frequency analysis revealed all optimized structures were stationary points (no imaginary vibrations). Energies of optimized structures are listed in Table 1. Specific details for the optimized structures are found in the Supporting Information.

## Discussion

The quality of the computational results can be benchmarked by a number of measurements. Comparison of the Re=O stretching frequencies with those observed in the infrared spectrum shows that, in general, calculated frequencies (scaled by 0.9614)<sup>11</sup> agree to within 10 cm<sup>-1</sup> with observed IR bands. Overall reaction energetics are slightly more positive than expected for formation of LReO<sub>3</sub> and alkene; cycloreversion of unstrained alkenes is known to be favorable, while cycloaddition of norbornene to Tp'ReO<sub>3</sub> is observed (for cycloreversion,  $\Delta G^\circ < 0$ ).<sup>6</sup> The estimate for relief of ring strain in the latter reaction is 5.7 kcal/mol, so including a  $T\Delta S$  term of 9–12 kcal/mol (based on a  $\Delta S$  value of 20–40 cal/(mol·K)), cycloreversion of ethylene from the diolate should have a  $\Delta H_{\text{rxn}}$  of near zero. Thus, the positive values calculated for  $\Delta E$  may reflect either problems due to phase (gas phase calculations vs solution phase experiments) or a systematic problem with the methodology. The fact that, experimentally, Tp'ReO<sub>3</sub> precipitates upon cycloreversion of the diolate suggests that phase is a significant variable that has a significant impact on the overall thermodynamics, but one that is probably consistent across the compounds compared here given that all experiments are conducted in hydrocarbon solvents (benzene or toluene). At worst, the computational results provide a qualitative comparison of the different reactions.

One aspect of the calculated structures conflicts with the experimental structure. As noted above, the solid shows a fairly flat dithiolate ring, where the S–C–S angle is only 12°. Yet the optimized calculated structure shows a dihedral angle more in accord with structures

(8) (a) Tisato, F.; Bolzati, C.; Duatti, A.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1993**, *32*, 2042–2048. (b) Paulo, A.; Pires de Matos, A.; Santos, I.; Fernanda, M.; Carvalho, N. N.; Pombeiro, A. J. L. *Inorg. Chem.* **1994**, *33*, 4729–4737.

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(11) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

**Table 2. Calculated Energies of Reaction**

reaction	$\Delta E$ , Hartree	$\Delta E$ , kcal/mol <sup>a</sup>
TpRe(O)(OCH <sub>2</sub> CH <sub>2</sub> O) → TpReO <sub>3</sub> + CH <sub>2</sub> CH <sub>2</sub>	+0.0367	+23.0 (+15.5)
Tp'Re(O)(OCH <sub>2</sub> CH <sub>2</sub> O) → Tp'ReO <sub>3</sub> + CH <sub>2</sub> CH <sub>2</sub>	+0.0322	+20.2 (+17.1)
TpRe(O)(SCH <sub>2</sub> CH <sub>2</sub> O) → TpReO <sub>2</sub> S + CH <sub>2</sub> CH <sub>2</sub>	+0.0563	+35.3 (+34.6)
<b>1</b> → Tp'ReO <sub>2</sub> S + CH <sub>2</sub> CH <sub>2</sub>	+0.0493	+30.9 (+28.5)
TpRe(O)SCH <sub>2</sub> CH <sub>2</sub> S → TpReOS <sub>2</sub> + CH <sub>2</sub> CH <sub>2</sub>	+0.0710	+44.6 (+42.8)
<b>3</b> → Tp'ReOS <sub>2</sub> + CH <sub>2</sub> CH <sub>2</sub>	+0.0672	+42.2 (+41.3)

<sup>a</sup> Values in parentheses include zero-point energy corrections derived from vibrational analysis.

**Table 3. Bond Lengths and Angles for 3<sup>a</sup>**

measurement	X-ray structure	B3LYP/LACVP** structure
Re=O	1.668(5)	1.696
Re–S	2.2757(18)	2.330
	2.2858(17)	2.333
Re–N	2.189(5)	2.201
	2.193(5)	2.202
	2.275(5)	2.365
C–S	1.808(10)	1.855
	1.822(10)	1.860
C–C	1.455(14)	1.518
O–Re–S	103.30(18)	104.7
	103.10(18)	102.3
S–Re–S	86.82(7)	86.5
N–Re–N	79.0(2)	78.6
	78.2(2)	77.9
	87.2(2)	87.6
S–C–C–S	12	43.0

<sup>a</sup> Comparison of X-ray structure with computationally optimized model. Bond distances are in angstroms, bond angles and torsions in degrees. Uncertainties in the crystal structure measurement are standard deviations.

reported by Rauchfuss et al.; the dihedral angle in the calculated structure is 43° (identical to that seen experimentally for **5**). Structural data for other rhenium dithiolates indicate a staggered geometry for the ring and an S–C–C–S dihedral angle that can vary from 14° to almost 48°.<sup>12</sup> Solution phase NMR studies indicate average dihedral angles of 36°, based on measured vicinal proton–proton coupling constants of 7.5 and 6 Hz.<sup>13</sup> (Other compounds show coupling constants consistent with a similar average dihedral angle in solution of 33–38°; see Supporting Information.) The dichotomy suggests that motion in the ring has a very low barrier. The flattening relative to **5** is probably due to steric interactions with the ring methyl groups in solution or to crystal packing effects in the solid.<sup>14</sup> The bonds to rhenium are calculated to be somewhat shorter than found in the X-ray structure, but other bond lengths are consistent. Comparison of structural metrics is summarized in Table 3.

(12) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Nicholson, T.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1339–1345.

(13) Dihedral/coupling constant relationships were calculated from a Karplus-type relationship corrected for the electronegativity of substituents. See: Haasnoot, C. A. G.; DeLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783–2792. A Javascript-based program for calculating coupling constants from dihedral angles is available at <http://www.spectroscopynow.com/Spy/tools/proton-proton.html>.

(14) A search of 42 ethanedithiolate complexes in the Cambridge Crystallographic Structure Database showed 97 unique dihedrals in a range from 3.4° to 64.1°, with an average of 45.8°. A histogram of this analysis is in the Supporting Information.

The most significant result of this investigation is that for each substitution of sulfur for oxygen  $\Delta E$  for the cycloreversion becomes more endothermic by approximately 10 kcal/mol. This supports the assertion that the absence of reactivity observed for complexes **1–4** originates in a thermodynamic barrier rather than a kinetic one. It is notable that in the chemistry of ReS<sub>4</sub><sup>−</sup> with alkenes, the kinetic barrier between sulfide and dithiolate appears to be low and that the system can be driven to the dithiolate by trapping with a Lewis base (a thiol).<sup>4</sup> This can be understood by noting that the cycloaddition formally created a site of unsaturation at the metal. In our case, two features enhance the thermodynamic stability of the dithiodiolate. The trispyrazolylborate is itself a strong  $\sigma$  donor to the metal, and the six-coordinate complexes are inherently closer to coordinative saturation than are the thiol-trapped dithiolates of Rauchfuss et al. Second, the ancillary oxo ligand is a better  $\pi$  donor (minimally because of the short Re–O bond), enhancing the triple bond nature of the rhenium oxo.

The general resistance of these thiodiolates to cycloreversion, as well as the importance of the tripodal Tp' ligand, is illustrated by their behavior in mass spectrometry. Rhenium diolates exhibit a marked tendency to lose alkene from the parent ion.<sup>6</sup> However, none of these thio analogues show a significant (M – alkene)<sup>+</sup> signal. There is an (M – pyrazole – alkene)<sup>+</sup> signal, suggesting that loss of the alkene can occur only after fragmentation of a pyrazole ligand from the parent ion. The only evidence of ring fragmentation of any sort is in the propane-1-thio-1,2-diolate **2**, for which loss of a mass 46 fragment suggests cleavage of the C–C bond with loss of either acetaldehyde or thioformaldehyde.

That the oxo is a better  $\pi$  donor is reinforced by examining the overall thermochemistry suggested by the calculations. Even granting that the  $\sigma$  component of the M=X bond is affected by the bond length contraction (M=O from 1.95 to 1.72 Å; M=S from 2.33 to 2.16 Å), the more important contributor to the change in thermochemistry is probably a weakening of the M=S  $\pi$  bond relative to that of the M=O bond. As seen in Table 2, this amounts to approximately 10 kcal/mol for each oxygen substituted by sulfur. One clear prediction of this work is that Tp'ReS<sub>3</sub> should react efficiently with alkenes. In fact, any thio analogue of Tp'ReO<sub>3</sub> should be thermodynamically capable of cycloaddition to an alkene, and further cycloaddition chemoselectivity will be for the units S=Re=S > O=Re=S > O=Re=O.

Methylation of the pyrazoles appears to have a minimal effect, changing  $\Delta E$  for the alkene extrusion by less than 3 kcal/mol. This minor electronic effect is consistent with other experimental measurements and much smaller than the effect seen in methylating a cyclopentadienyl ring.<sup>15</sup> This reinforces the view of the pyrazole–Re bond being strongly  $\sigma$  type in nature. Surprisingly, though, our X-ray structure shows a shorter Re=O for **3** compared to the nonmethylated **5**, despite the expectation that the more electron rich donor should weaken and therefore lengthen the Re=O bond.

(15) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077–5083.



## Experimental Section

General procedures have been described elsewhere.<sup>6</sup> Tp'ReO<sub>3</sub> was prepared via a published procedure,<sup>16</sup> and thiodiols and dithiols were used as received from Aldrich or prepared from epoxides using literature methods.<sup>17</sup>

**Synthesis of Complexes 1–4.** Similar procedures were used for all compounds. A representative preparation of **3** is presented here; full characterization of all compounds (<sup>1</sup>H and <sup>13</sup>C NMR, IR, HRMS) is listed in the Supporting Information.

**Tris(3,5-dimethylpyrazolyl)hydridoboratorhenium(V)(oxo)(ethane-1,2-dithiolate) (3).** Triphenylphosphine (60.9 mg, 0.236 mmol), Tp'ReO<sub>3</sub> (100 mg, 0.188 mmol), and 1, 2-ethanedithiol (53 mg, 0.561 mmol) were placed in a round-bottom flask with freshly ground molecular sieves (0.5 g) and 12 mg of *p*-toluenesulfonic acid hydrate. These reagents were dissolved in 30 mL of THF and stirred under argon for 15 h at room temperature. The mixture was filtered, and the filtrate evaporated to dryness. Chromatography of the residue (silica, 1:1 hexane/dichloromethane) and removal of solvent gave 97 mg of the product as a brown solid (0.164 mmol, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.05 s, 2H; 5.50 s, 1H; 4.10 m, 2H; 3.60 m, 2H; 2.90 s, 6H; 2.55 s, 6H; 2.18 s, 3H; 2.12 s, 3H. As with other Tp and Tp' complexes, the borohydride proton signal was not identified because it is substantially broadened by the <sup>11</sup>B quadrupole and thus not structurally diagnostic. Iterative fitting of the signals at 4.1 and 3.6 ppm as an AA'BB' system led to a good fit with *J* values of −12 Hz (*J*<sup>AB</sup> = *J*<sup>A'B'</sup>), 5.95 Hz (*J*<sup>AA'</sup>), 7.54 Hz (*J*<sup>BB'</sup>), 7.42 Hz (*J*<sup>AB</sup>), and 6.87 Hz (*J*<sup>BB'</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 156.0, 153.9, 145.9, 143.1, 108.9, 108.1, 51.1, 17.2, 16.2, 13.0. IR: 2532 (B–H); 941 (Re=O) cm<sup>−1</sup>. MS (FAB): 592 (M<sup>+</sup>), 497 (M − pz)<sup>+</sup>, 469, 374.

**Computational Details.** Preliminary structure generation and molecular mechanics optimization of ligands was performed on Spartan, v. 5.1,<sup>18</sup> using the Sybyl force field for all atoms except rhenium and fixing the geometry of rhenium. The following bond lengths were fixed: Re=O 1.72 Å, Re–O 1.95 Å, Re–N 2.1 Å, Re–S 2.28 Å, Re=S 1.85 Å. These preliminary structures were then fully optimized with Jaguar, v. 4.1,<sup>19</sup> using B3LYP methodology and the LACVP\*\* basis set. Frequency analysis was performed using the final Hessian from the optimization. In cases where geometry optimization did not succeed directly, the structure was subjected to preliminary optimization without polarization functions, followed by final optimization with polarization functions.

**Crystallography.** Crystals of **3** were grown by vapor diffusion of water into a saturated solution of **4** in CH<sub>3</sub>CN at 10 °C over 5 days; crystals were collected by filtration. Determination of the crystallographic parameters, data collection, and structure solution and refinement were done as described elsewhere,<sup>20</sup> with the following details. A small block of approximate dimensions 0.1 × 0.1 × 0.1 mm<sup>3</sup> was mounted on the end of a Pyrex fiber using some epoxy glue. An automated routine was used to find and center 15 reflections with 15° < 2θ < 35°. The crystal was indexed, and the lattice parameters were refined against this list. The reflection list was then expanded to include 65 reflections with 35° < 2θ < 57.3°. All unique data, including a small set of redundant reflections, were collected (−1 − *h*, −1 − *k*, −1 − *l*). Monitoring of three standards during data collection did not indicate any decay of the reflection intensities with time. Given the high

### Table 4. Crystallographic Data for 3

identification code	KG120100
empirical formula	C <sub>17</sub> H <sub>26</sub> BN <sub>6</sub> OReS <sub>2</sub>
fw	591.57
temperature	290(2) K
wavelength	1.54178 Å
cryst syst	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
unit cell dimens	<i>a</i> = 8.5673(5) Å, α = 90° <i>b</i> = 11.4116(12) Å, β = 90° <i>c</i> = 22.8696(19) Å, γ = 90°
volume	2235.9(3) Å <sup>3</sup>
<i>Z</i>	4
density (calcd)	1.757 Mg/m <sup>3</sup>
abs coeff	12.535 mm <sup>−1</sup>
<i>F</i> (000)	1160
cryst size	0.10 × 0.10 × 0.10 mm <sup>3</sup>
θ range for data collection	3.87 to 67.41°
index ranges	−10 ≤ <i>h</i> ≤ 1, −1 ≤ <i>k</i> ≤ 13, −27 ≤ <i>l</i> ≤ 1
no. of reflns collected	2817
no. of ind reflns	2627 [ <i>R</i> (int) = 0.0332]
completeness to θ = 67.41°	92.9%
abs corr	analytical
max. and min. transmn	0.3670 and 0.3670
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
no. of data/restraints/params	2627/0/255
goodness-of-fit on <i>F</i> <sup>2</sup>	1.069
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0284, w <i>R</i> 2 = 0.0721
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0300, w <i>R</i> 2 = 0.0744
absolute structure param	0.000(19)
extinction coeff	0.00035(4)
largest diff peak and hole	0.868 and −0.831 e Å <sup>−3</sup>

linear absorption coefficient of this compound for Cu Kα radiation, the data were corrected for the effects of absorption anisotropy by means of a face indexed method, as programmed in Platon.<sup>21</sup>

Examination of the systematic extinctions, coupled with the fact that the intensity statistics calculated for this data set strongly suggested an acentric space group,<sup>22</sup> led to the choice of the space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (#19). The structure was solved by direct methods as programmed in SHELXS-90.<sup>23</sup> This solution clearly showed the ReN<sub>3</sub>OS<sub>2</sub> core of the molecule. The solution was expanded by successive cycles of least squares refinements followed by Fourier synthesis using the program SHELXL-97.<sup>24</sup> In the final cycle of least squares refinement all non-hydrogen atoms were refined using anisotropic thermal displacement coefficients. All hydrogen atoms were placed in idealized positions, and their displacement parameters were fixed to be either 1.5 times (methyl group hydrogen atoms) or 1.2 times (all other hydrogen atoms) that of the atom to which it was attached. Refinement of the Flack parameter yielded a value of −0.001(19), indicating that the model depicted corresponds to the correct absolute structure.<sup>25</sup> The chirality of the compound arises from the torsion of the tris-pyrazolylborate ligand about the imaginary Re–B axis. Indubitably, if an exhaustive characterization of all the crystals was undertaken, several crystals with the opposite handedness would also be found, as is known in several other similar systems.<sup>26</sup>

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**Supporting Information Available:** Characterization data for **1**, **2**, and **4**, results of a CSD search on torsional angles in metal ethanedithiolate complexes, tables of fractional coordinates, bond lengths and angles for **3**, and calculated optimized structures for all rhenium complexes. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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