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Exploring oxorhenium '3+1' mixed-ligand complexes carrying the S-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbazate [ONS]/monothiol [S] donor set: synthesis and characterization

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Abstract

The reaction of $\text{ReOCl}_3(\text{PPh}_3)_2$ with the potentially tridentate ligand S-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbazate ([ONS] donor set) and *para*-substituted benzenethiols [$\text{C}_6\text{H}_4\text{X}-4\text{-SH}$] (where X=H, F, Cl, Br and OCH_3) in the presence of Et_3N afforded a series of integrated '3+1' oxorhenium(V) complexes with general formula $[\text{ReO}\{\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=N-N=C(SCH}_2\text{Ph)-S}\}(\eta^1\text{-C}_6\text{H}_4\text{X-4-S})]$. The molecular structure of $[\text{ReO}\{\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=N-N=C(SCH}_2\text{Ph)-S}\}(\eta^1\text{-C}_6\text{H}_4\text{F-4-S})]$ (**4**) was determined by single-crystal X-ray analysis. Complex **4** consists of a central oxorhenium(V) core with phenolic oxygen, azomethine nitrogen and thiol sulfur donor from the thiosemicarbazone Schiff base ligand and one sulfur donor from monothiol ligand completing a distorted square pyramidal environment. Crystal data for **4**, $\text{C}_{21}\text{H}_{16}\text{FN}_2\text{O}_2\text{S}_3\text{Re}$: orthorhombic, $P2_12_12_1$, $a=5.6682(3)$, $b=11.6600(6)$, $c=31.697(2)$ Å, $V=2094.9(2)$ Å³, $Z=4$.

Keywords

Crystal structures; Oxorhenium complexes; Dithiocarbazate complexes

1. Introduction

^{99m}Tc has become the radionuclide of choice in diagnostic nuclear medicine by virtue of its optimal nuclear properties (γ -emitter, $E_{\text{max}}=140$ keV, $t_{1/2}=6$ h) as well as its convenient availability from commercial ⁹⁹Mo/⁹⁹Tc generator columns [1]. The half-life of ^{99m}Tc of 6 h and the absence of tissue-damaging corpuscular radiation allow the injection of activities of more than 30 mCi with low radiation exposure to the patient [2]. The half-life is yet sufficiently long to study organs lying deep in the body and can be collimated so as to be effectively detected with NaI(Tl) scintillation counters. The relatively stable ⁹⁹Tc isotope may be used to develop technetium chemistry and to model technetium pharmaceuticals [3]. Furthermore, the radionuclides of rhenium, the Group 7 congener of Tc, are β -emitters with suitable properties for therapeutic applications (¹⁸⁶Re, $E_{\text{max}}=1.07$ MeV, $t_{1/2}=90$ h; ¹⁸⁸Re, $E_{\text{max}}=2.12$ MeV, $t_{1/2}=17$ h) [4]. In addition, the rhenium isotopes possess the advantage of a photon emission at approximately the same energy as that of ^{99m}Tc, making it possible to monitor the biodistribution of rhenium radiopharmaceuticals with the same equipment employed for the ^{99m}Tc agents [5].

The chemistry of technetium and rhenium has been well documented [6], and significant efforts continue to develop new chelating agents for these two elements due to their rich redox chemistry and often complicated coordination modes. A major class of technetium and rhenium complexes are represented by the tetradentate $[N_xS_{(4-x)}]$ oxometal(V) core. Diamidedithiol $[N_2S_2]$ and triamidethiol $[N_3S]$ donors form stable anionic MO^{3+} core complexes, while the former can also form either cationic or neutral MO^{3+} complexes by fine tuning of pH value. One major problem which has hindered the applications of many of these systems has been the inevitable formation of multiple isomers differing in their pharmacokinetic properties. As an alternative, '3+1' chemistry has been extensively investigated. All these '3+1' systems contain a dianionic tridentate ligand carrying at least one sulfur donor group, such as [SSS], [SOS], [SN(R)S], [SNN(R)], or [ONS] donor atom sets (R=various alkyl or aryl-substitute pendant groups) and a monodentate thiol, which usually bears the receptor avid moiety. The '3+1' approach simplifies to some extent the formidable amount of organic synthesis, as compared to that required for the conjugation of a tetradentate chelate to a pharmacophore group [7]. Another advantage of these '3+1' systems is that they avoid the existence of *syn/anti* isomers and enantiomers which are often produced in the tetradentate systems [8]. Recent evidence has revealed that the complexes are unstable in vitro and in vivo due to the metabolism and replacement of the monothiolate ligand through transchelation by the physiological thiols cysteine and glutathione, which eventually leads to hydrophilic metabolic products of these compounds in thiolate-rich tissues such as liver [9]. However, the stability of these '3+1' complexes is strongly dependent on small structural variations of the tridentate/monothiol ligand sets, especially of the tridentate ligands. For example, [SN(CH₃)S] donor complexes are significantly more stable than [SSS] complexes. To better understand the synergistic effects of the '3+1' type of oxometal metal complexes, significant efforts to develop new tridentate ligands must be undertaken. As part of our continuing elaboration [10] of the coordination chemistry of Tc(V) and Re(V) complexes in order to provide new methodologies for radiolabeling of chemotactic peptides, we have developed quite a few [ONS] tridentate donors, such as Schiff base salicylaldehyde-2-mercaptoanil [11] and 6-thiomethyl-2-pyridinemethanol [12]. The ReO^{3+} core complexes of these ligands are characterized by an almost ideal square pyramidal configuration of the ReO^{3+} core.

In the preparation of Schiff base salicylaldehyde-2-mercaptoanil, a cycloaddition byproduct 2-(2-hydroxyphenyl)benzothiazole is almost inevitable, which functions as a bidentate ligand to compete with the incoming monothiols. Prolonged reaction time enhances the amount of '3+2' complex $[ReO(\eta^3-OC_6H_4-CH=NC_6H_4-2-S)(\eta^2-OC_6H_4C=NC_6H_4-2-S)]$ [13]. To avoid such complications, we herein report the synthesis and characterization of a series of '3+1' [ONS]/[S] complexes. The tridentate [ONS] ligand is *S*-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbamate, and the monothiols are *para*-substituted benzenethiols ($C_6H_4X-4-SH$) (where X=H, F, Cl, Br and OCH₃). The X-ray crystal structure of $[ReO(\eta^3-OC_6H_4-2-CH=N-N=C(SCH_2Ph)-S)(\eta^1-C_6H_4F-4-S)]$ (**4**) is also reported.

2. Experimental

2.1. General considerations

NMR spectra were recorded on a Bruker DPX 300 (¹H 300.10 MHz) spectrometer in CDCl₃ (δ 7.27 ppm). IR spectra were recorded as KBr pellets with a Perkin–Elmer Faragon 1000 FT-IR spectrometer. Elemental analyses for carbon, hydrogen and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel F-254 glass-backed plates. Visualization was achieved by UV illumination. Flash chromatography was performed according to Still [14] using Aldrich silica gel (70-230 mesh). *S*-Benzylthiocarbamate was prepared by a standard method [15]. $ReOCl_3(PPh_3)_2$ was prepared according to the literature [16].

2.2. Synthesis

2.2.1. Preparation of S-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbazate

(1)—The compound was readily obtained by condensation of salicylaldehyde (2.44 g, 20 mmol) and S-benzylthiocarbazate (3.96 g, 20 mmol) in an ethanolic solution (50 cm³) [17]. A pale-yellow fluffy microcrystalline solid was obtained upon standing at 4°C overnight. Yield: 3.87 g, 64%. FT-IR (cm⁻¹, KBr pellet): 3110 (OH), 2975 (NH), 1619 (C=N), 1570 (C=O), 1041 (C=S). ¹H NMR (CDCl₃, ppm): 10.22 (s br, 1H, OH), 9.98 (s, 1H, CH=N thiole form), 8.72 (s, 1H, CH=N thione form), 8.00 (s, 1H, ArH), 6.90–7.05 (m, 2H, ArH), 7.25–7.45 (m, 6H, ArH), 4.60 (s, 2H, CH₂Ph). *Anal.* Calc. for C₁₅H₁₄N₂OS₂: C, 59.60; H, 4.64; N, 9.27. Found: C, 59.93; H, 4.78; N, 9.31%.

2.2.2. Preparation of the intermediate [ReOCl{η³-OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(PPh₃)] (2)

—To a stirred suspension of trichlorobis(triphenylphosphine)rhenium(V) oxide (83 mg, 0.1 mmol) in chloroform (30 cm³) was added S-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbazate (**1**) (33 mg, 0.11 mmol), and the mixture was refluxed until the green–yellow color of the precursor turned to dark-red. After being cooled to room temperature, the reaction mixture was washed with water. The organic layer was separated from the mixture and dried over Na₂SO₄. The volume was reduced to 3 cm³ and then purified on silica gel column using gradient eluent (from 100% CHCl₃ to 100% acetone). Yield: 57 mg, 77%. FT-IR (cm⁻¹, KBr pellet): 1603 (C=N), 1534 (C=O), 937 (Re=O). ¹H NMR (CDCl₃, ppm): 9.31 (s br, 1H, CH=N), 7.0–7.8 (m, 24H, PPh₃ and ArH), 4.59 (s br, 2H, CH₂Ph). *Anal.* Calc. for C₃₃H₂₇N₂O₂ClPRe: C, 53.84; H, 3.67; N, 3.81. Found: C, 54.13; H, 3.83; N, 3.75%.

2.2.3. General procedure for the preparation of '3+1' complexes [ReO{η³-OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η¹-C₆H₄X-4-S)] where X=H (**3**), F (**4**), Cl (**5**), Br (**6**) and OCH₃ (**7**)

—To a stirred suspension of trichlorobis(triphenylphosphine)rhenium(V) oxide (83 mg, 0.1 mmol) in CHCl₃ (30 cm³) was added dropwise with stirring a CHCl₃ solution (5 cm³) consisting of 1 equiv. of S-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbazate (**1**) and 1 equiv. of the benzenethiol [C₆H₄X-4-S] (X=H, F, Cl, Br and OCH₃) (0.1 mmol). A reddish brown solution formed immediately, which turned into a bright red solution when Et₃N (2 drops) was added. The reaction was stirred under reflux for 20 min, concentrated and purified by flash chromatography. The eluent first applied was CHCl₃ to remove PPh₃ and trace amounts of unreacted thiols; then 10% acetone/CHCl₃ was used to obtain the product as a red solid. X-ray quality crystals for compound **4** were grown by slow diffusion of ethyl ether into a solution of the compound dissolved in minimum amount of CH₂Cl₂.

2.2.3.1. [ReO{η³-OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η¹-C₆H₅-S)] (3**):** Yield: 35 mg, 57%. FT-IR (cm⁻¹, KBr pellet): 1605 (C=N), 1538 (C=O), 987 (Re=O). ¹H NMR (CDCl₃, ppm): 9.37 (s br, 1H, CH=N), 6.6–7.8 (m, 14H, ArH), 4.60 (s br, 2H, CH₂Ph). *Anal.* Calc. for C₂₁H₁₇N₂O₂S₃Re: C, 41.24; H, 2.78; N, 4.58. Found: C, 40.95; H, 2.67; N, 4.65%.

2.2.3.2. [ReO{η³-OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η¹-C₆H₄F-4-S)] (4**):** Yield: 40 mg, 64%. FT-IR (cm⁻¹, KBr pellet): 1606 (C=N), 1541 (C=O), 987 (Re=O). ¹H NMR (CDCl₃, ppm): 9.38 (s br, 1H, CH=N), 7.0–7.8 (m, 13H, ArH), 4.57 (s br, 2H, CH₂Ph). *Anal.* Calc. for C₂₁H₁₆N₂O₂FS₃Re: C, 40.06; H, 2.54; N, 4.45. Found: C, 39.81; H, 2.68; N, 4.31%.

2.2.3.3. [ReO{η³-OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η¹-C₆H₄Cl-4-S)] (5**):** Yield: 44 mg, 68%. FT-IR (cm⁻¹, KBr pellet): 1601 (C=N), 1545 (C=O), 984 (Re=O). ¹H NMR (CDCl₃, ppm): 9.35 (s br, 1H, CH=N), 7.0–7.8 (m, 13H, ArH), 4.62 (s br, 2H, CH₂Ph). *Anal.* Calc. for C₂₁H₁₆N₂O₂ClS₃Re: C, 39.04; H, 2.48; N, 4.34. Found: C, 39.39; H, 2.65; N, 4.15%.

2.2.3.4. [ReO{ η^3 -OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η^1 -C₆H₄Br-4-S)] (6): Yield: 43 mg, 62%. FT-IR (cm⁻¹, KBr pellet): 1605 (C=N), 1537 (C-O), 982 (Re=O). ¹H NMR (CDCl₃, ppm): 9.42 (s br, 1H, CH=N), 7.1–7.8 (m, 13H, ArH), 4.53 (s br, 2H, CH₂Ph). *Anal.* Calc. for C₂₁H₁₆N₂O₂BrS₃Re: C, 36.52; H, 2.32; N, 4.06. Found: C, 36.95; H, 2.10; N, 4.37%.

2.2.3.5. [ReO{ η^3 -OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η^1 -C₆H₄OCH₃-4-S)] (7): Yield: 37 mg, 57%. FT-IR (cm⁻¹, KBr pellet): 1610 (C=N), 1535 (C-O), 981 (Re=O). ¹H NMR (CDCl₃, ppm): 9.37 (s br, 1H, CH=N), 7.2–7.6 (m, 13H, ArH), 4.58 (s br, 2H, CH₂Ph), 3.61 (s, OCH₃). *Anal.* Calc. for C₂₂H₁₉N₂O₃S₃Re: C, 41.19; H, 2.96; N, 4.37. Found: C, 40.90; H, 3.05; N, 4.11%.

2.3. X-ray crystallography

The selected crystals of **4** were measured with a Siemens P4 diffractometer equipped with the SMART CCD system [18] and using graphite-monochromated Mo K α radiation ($\lambda=0.71073$ Å). The data collection was carried out at 89(5) K. The data were corrected for Lorentz and polarization effects, and absorption corrections were made using SADABS [19]. Neutral atom scattering factors were taken from Cromer and Waber [20]. Anomalous dispersion corrections were taken from those of Creagh and McAuley [21]. All calculations were performed using SHELXL [22]. The structures were solved by direct methods [23] and all of the non-hydrogen atoms were located from the initial solution. After locating all the initial non-hydrogen atoms in each structure, the models were refined against F^2 , initially using isotropic and later anisotropic thermal displacement parameters until the final value of $\Delta/\sigma_{\max}$ was less than 0.001. At this point the hydrogen atoms were located from the electron density difference map and a final cycle of refinements was performed, until the final value of $\Delta/\sigma_{\max}$ was again less than 0.001. No anomalies were encountered in the refinements. The relevant parameters for crystal data, data collection, structure solution and refinement are summarized in Table 1, and important bond lengths and angles in Table 2. A complete description of the details of the crystallographic methods is given in Section 5.

3. Results and discussion

The Schiff base *S*-benzyl-3-[(2-hydroxyphenyl)-methylene]dithiocarbazate (**1**) was readily prepared by condensation of salicylaldehyde with *S*-benzylthiocarbazate in ethanol solution as a fluffy pale-yellow crystalline solid. The free ligand exhibits a $\nu(\text{C}=\text{S})$ vibration in its FT-IR spectrum at 1041 cm⁻¹, and does not display the band at approximately 2570 cm⁻¹ associated with $\nu(\text{S}-\text{H})$ [24], indicating that it exists in the thione form **A** in the solid state as shown in Scheme 1. The thione group is relatively unstable and tends to convert to the more stable C-S bond by enethiolization, if there is at least one proton adjacent to the thione group [25]. In fact, both thione and thiolo tautomeric forms are present in solution. ¹H NMR spectrum of the free ligand indicates that the ratio of thione/thiolo tautomers is approximately 77/23 in CHCl₃ by the measurement of integration for the CH=N imine proton.

On metal complexation, the ligand is found in the dianionic thiol form, involving deprotonation of the phenolic and SH group of **B** (Scheme 1) as is apparent from the disappearance of its $\nu(\text{OH})$ (3110 cm⁻¹) and $\nu(\text{NH})$ (2975 cm⁻¹) bands, as well as from the absence of any $\nu(\text{SH})$ or $\nu(\text{C}=\text{S})$ vibrations [26]. The [ONS] mode of metal complexation, i.e. through phenolic oxygen, azomethine nitrogen and thiol sulfur of **B**, is ascertained from the red-shift (15–20 cm⁻¹) of the $\nu(\text{C}=\text{N})$ [27] and blue-shift (30–35 cm⁻¹) of the $\nu(\text{C}-\text{O})$ vibrations of the parent ligand (1619 and 1570 cm⁻¹, respectively) [28]. The tendency of the Schiff base to shift the equilibrium from thione form **A** to thiolo form **B** may be attributed to stabilization arising from the conjugation of the -C=N-N=C group upon coordination to the ReO(V) core [29]. Moreover, comparison of the ¹H NMR spectrum of the free ligand (**1**) with its ReO(V)

complexes reveals that (i) the phenolic proton of the ligand disappears, (ii) the azomethine proton signal is shifted downfield [30], and (iii) the position of the SCH₂ proton resonance attributed to the *S*-benzyl group of (**1**), occurring at around δ 4.60 ppm, virtually remains unaltered during complexation. This supports the mode of coordination suggested by the IR data, with additional evidence that the sulfur atom in the CH₂Ph group is not involved in coordination.

The '3+1' complexes **3–7** can be prepared conveniently through one-pot synthesis of the tridentate Schiff-base ligand (**1**) and the monodentate thiols with ReOCl₃(PPh₃)₂ in the presence of Et₃N to neutralize HCl that is produced during the reaction. The neutral five-coordinated 16-electron complexes [31] can be purified via flash column chromatography on silica gel. Elemental analyses, provided in Section 2, are in good agreement with the proposed formulations. The IR spectra exhibit the characteristic Re=O stretching vibration at around 985 cm⁻¹ [32].

The ORTEP diagram of complex **4** is given in Fig. 1. Selected bond lengths and angles for complex **4** are given in Table 2. As shown in Fig. 1, the structure of **4** is prototypical of '3+1' complexes with the [MO]³⁺ core. The rhenium site exhibits distorted square pyramidal geometry with the basal plane defined by phenol oxygen, azomethine nitrogen and thiolate sulfur donors of the [ONS] tridentate ligand and thiolate donor of the monodentate moiety and the axial position occupied by the oxygen group. The distorted five-coordinate geometry may be quantitatively evaluated by using the trigonality index, τ , described by Addison [33]. The measurement uses the two largest angles contained in the mean basal plane, which expressed in the form $(\beta - \alpha)/60$ give a unitless value ranging from 0 to 1 with $\tau=0$ for perfect square pyramid, and $\tau=1$ for ideal trigonal bipyramid. The τ value of 0.31 for **4** is higher than those reported previously in this laboratory in the investigation of [ONS]/[S] '3+1' complexes [11,12], but still falls in the range of [SSS]/[S] and [SOS]/[S] complexes [10]. The rhenium is situated 0.713 Å above the basal plane defined by the four coordinated atoms. The N(1)–C(7) distance of 1.312(9) Å and the valence angles at N(1) of 111.5(6), 125.8(5) and 122.5(4)° confirm that the N(1) site is sp² hybridized and the ligand in the Schiff base form. The neutrality of the complex requires a dianionic ligand in the pheno-late-azaenethiolate form as confirmed by bond lengths and bond angles within the ligand chain. The N(2)–C(8) distance of 1.296(9) Å and the C(8)–N(2)–N(1) bond angle of 111.7(6)° are consistent with an N(2)–C(8) double bond and sp² hybridization at the N(2) site. The S(1)–C(8) distance of 1.774(7) Å is characteristic of a C–S single bond. The average bond lengths of Re=O, Re–O, Re–N and Re–S are 1.683, 1.979, 2.081 and 2.886 Å, respectively. The Re–S bonds are identical within statistical limits. These values are in agreement with those of analogous oxorhenium complexes observed [11].

4. Conclusion

A new series of '3+1' oxorhenium complexes based on trifunctional [ONS] Schiff base *S*-benzyl-3-[(2-hydroxyphenyl)methylene]dithiocarbazate and monodentate thiols have been prepared. The Schiff base exists in the thione form **A** in the solid state and as thione/thiolate tautomers in solution. Upon complexation with oxorhenium(V), the thione form is completely enethiolized and the ligand acts as a dianionic thiol. This type of [ONS] tridentate Schiff base avoids the possibility of cycloaddition byproduct as encountered in the condensation of salicylaldehyde and 2-aminothiophenol, yet the reactivity is virtually the same.

Complexes of the oxotechnetium(V) and oxorhenium(V) cores with '3+1' ligand environments have provided a convenient method for manipulation of the geometric features of size and shape and of the substituent steric and electronic constraints in the development of an important class of radiopharmaceuticals. The compounds of this study illustrate that the general methodology of the '3+1' ligand chemistry may be extended to the synthesis of [ONS]/[S]

oxorhenium(V) complexes. The geometry and charge of the monodentate thiol ligand may be easily manipulated to produce complexes of various size, shapes and charges for clinical development. Synthesis of analogous [ONS]/[S] TcO(V) complexes and in vitro and in vivo stability of such complexes are now in progress and will be reported elsewhere.

5. Supplementary material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Scheme 1.

Fig. 1.
ORTEP drawing of [ReO{η³-OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η¹-C₆H₄F-4-S)] (4). Ellipsoids correspond to 50% probability.

Table 1

Summary of crystal, intensity, collection, and refinement data for complex [ReO{ η^3 -OC₆H₄-2-CH=N-N=C(SCH₂Ph)-S}(η^1 -C₆H₄F-4-S)] (**4**)

Crystal data	
Empirical formula	C ₂₁ H ₁₆ FN ₂ O ₂ S ₃ Re
Formula weight	629.74
Crystal size (mm)	0.2×0.1×0.1
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	
<i>a</i> (Å)	5.6682(3)
<i>b</i> (Å)	11.6600(6)
<i>c</i> (Å)	31.697(2)
<i>V</i> (Å ³)	2094.9(2)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.997
<i>F</i> (000)	1216
λ (Å)	0.71073
μ (mm ⁻¹)	6.130
Data collection	
θ Range (°)	1.28–28.29
<i>h,k,l</i>	–7/7, –13/15, –41/27
No. of reflections	13 943
No. of unique data	5008
<i>R</i> _{int} (%)	4.01
Structure solution and refinement	
Parameters refined	271
Final indices (2 σ data), <i>R</i> ₁ (<i>wR</i> ₂) ^a	0.0328, 0.0825
All data, <i>R</i> ₁ (<i>wR</i> ₂)	0.0359, 0.0898
Goodness-of-fit <i>S</i> (<i>F</i> ²)	1.101
Largest difference peak and hole (e Å ⁻³)	1.113 and –2.040

^aWhere $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $wR_2 = \left[\Sigma \left[w(F_o^2 - F_c^2)^2 \right] / \Sigma \left[w(F_o^2)^2 \right] \right]^{1/2}$.

Table 2

Selected bond distances (Å) and angles (°) for complex $[\text{ReO}\{\eta^3\text{-OC}_6\text{H}_4\text{-2-CH=N-N=C(SCH}_2\text{Ph)-S}\}(\eta^1\text{-C}_6\text{H}_4\text{F-4-S})]$ (**4**)

Re(1)–O(1)	1.683(5)	S(2)–C(9)	1.822(7)
Re(1)–O(2)	1.979(5)	S(3)–C(16)	1.791(7)
Re(1)–N(1)	2.081(6)	F(1)–C(19)	1.366(8)
Re(1)–S(1)	2.278(2)	N(1)–C(7)	1.312(9)
Re(1)–S(3)	2.300(2)	N(1)–N(2)	1.432(8)
S(1)–C(8)	1.774(7)	N(2)–C(8)	1.296(9)
S(2)–C(8)	1.731(7)	O(2)–C(1)	1.345(8)
O(1)–Re(1)–O(2)	115.8(2)	C(8)–S(1)–Re(1)	98.9(2)
O(1)–Re(1)–N(1)	107.9(2)	C(8)–S(1)–Re(1)	98.9(2)
O(2)–Re(1)–N(1)	84.3(2)	C(8)–S(2)–C(9)	102.1(3)
O(1)–Re(1)–S(1)	107.7(2)	C(16)–S(3)–Re(1)	106.5(2)
O(2)–Re(1)–S(1)	136.5(2)	C(7)–N(1)–N(2)	111.5(6)
N(1)–Re(1)–S(1)	80.6(2)	C(7)–N(1)–Re(1)	125.8(5)
O(1)–Re(1)–S(3)	106.3(2)	N(2)–N(1)–Re(1)	122.5(4)
O(2)–Re(1)–S(3)	83.3(2)	C(8)–N(2)–N(1)	111.7(6)
N(1)–Re(1)–S(3)	145.8(2)	C(1)–O(2)–Re(1)	127.2(4)
S(1)–Re(1)–S(3)	86.87(6)		