Synthesis, Characterization, and Crystal Structure of Neutral Rhenium(V) Complexes with S-Substituted N_2S_2 Ligands

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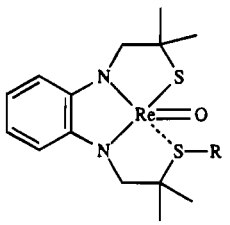
A series of neutral rhenium(V) oxo complexes was synthesized by the reaction of $ReOBr_4^-$ with diamino–thiol–thioether ligands of the type $(RSC(CH_3)_2CH_2NH(o\text{-}C_6H_4)NHCH_2C(CH_3)_2SH$. The complexes were characterized by IR, UV/visible, and ^1H and ^{13}C NMR spectroscopy and by fast-atom-bombardment mass spectroscopy. The single-crystal X-ray structure determination on two of the complexes, where R = $CH_2CH{=}CH_2$ and $CH_2CH_2\text{-}CH_3$, showed them to consist of a square pyramidal $Re^VON_2S_2$ core. $ReO[CH_2{=}CHCH_2SC(CH_3)_2CH_2N(o\text{-}C_6H_4)NCH_2C(CH_3)_2S]$, $C_{17}H_{25}N_2OS_2Re$, crystallizes in the monoclinic space group $P2_1/a$ with $\alpha = 17.899(3)$ Å, $b = 13.910(1)$ Å, $c = 15.936(1)$ Å, $\beta = 104.70(1)°$, $Z = 8$, $D_{calc} = 1.813$ g cm^{-3}, and μ(Cu Kα) = 139.8 cm^{-1}. The propyl complex, $C_{17}H_{27}N_2OS_2Re$, crystallizes in the monoclinic space group $P2_1/a$ with $a = 18.076(1)$ Å, $b = 13.920(1)$ Å, $c = 15.994(1)$ Å, $\beta = 105.09(1)°$, $Z = 8$, $D_{calc} = 1.797$ g cm^{-3}, and μ(Cu Kα) = 138.0 cm^{-1}. The combination of the steric and electronic effects of the aromatic ring fused to the backbone of the N–C–C–N ligand and the S-substitution result in deprotonation of both amine nitrogens and coplanarity of the base of the square pyramidal complex.

Introduction

The chemistry of technetium is of continued interest since the radionuclide ^{99m}Tc (γ-emitter with energy 140 keV and half-life of 6.02 h) is the major isotope used in nuclear medicine.[2-4] We have recently identified a series of aromatic diamino–thiol–thioether ligands (PhAT)[5] that form neutral, lipophilic ^{99m}Tc complexes with potential utility for functional brain imaging.[6] The ^{99m}Tc PhAT complexes can be formed in high yield (>95%) and radiochemical purity (>95%) and are stable for greater than 10 h. Since the concentration of ^{99m}Tc complexes is typically on the order of 10^{-8} M, analyses were based primarily on chromatographic techniques, which meant that the detailed structures of these complexes remained unknown. Often, the chemistry of ^{99m}Tc is studied using macroscopic quantities of the long-lived isomer, ^{99}Tc (β-emitter, $t_{1/2} = 2.12 \times 10^5$ years). However, ^{99}Tc requires a laboratory approved for the handling of β emitters. Since this was unavailable at the time, rhenium was used to obtain a preliminary understanding of the chemistry of the ^{99m}Tc PhAT complexes.



1 R = $CH_2CH{=}CH_2$
2 R = $CH{=}C{=}CH_2$
3 R = $CH_2CH_2CH_3$
4 R = CH_2CH_2OH
5 R = CH_2Ph
6 R = $CH_2C{\equiv}CH$

Figure 1. General structure of the S-substituted ReO–PhAT complexes.

Rhenium is technetium's third row congener and exhibits many of the chemical properties that technetium displays. Theoretically, a Re–PhAT complex will be isostructural with the ^{99m}Tc PhAT complexes that have been prepared for use as brain imaging agents. In addition, the chemistry of radioactive rhenium has assumed medical significance due to the application of ^{186}Re and ^{188}Re labeled radiopharmaceuticals for diagnosis and therapy in nuclear medicine.[7] The synthesis and characterization of a number of rhenium complexes of PhAT ligands are described in this report. The complexes discussed here, shown in Figure 1, are given the trivial name ReO–R–PhAT, where R = 2-propenyl, allenyl, propyl, 2-hydroxyethyl, benzyl, and 2-propynyl.

Experimental Section

Materials and Instrumentation. $KReO_4$ was purchased from Alfa Products or Aldrich Chemical Co. $[Et_4N][ReOBr_4]$ and $[Bu_4N]$-

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(5) Note on nomenclature: PhAT is the acronym used for this ligand stemming from phenyl–amino–thiol compounds. The IUPAC names for this family of compounds are lengthy. For example, the 2-propynyl ligand has the name N^2-(2-mercapto-2-methylpropyl)-N^1-(2-(2-propynylthio)-2-methylpropyl)-1,2-benzenediamine. For simplicity we denote the ligands as R-PhAT, where in this case R = 2-propynyl.

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[$ReOBr_4$] were prepared from $KReO_4$ by published procedures.[8,9] All PhAT ligands were synthesized on a 1−3 g scale using methods reported elsewhere.[6] All solvents were reagent or HPLC grade and were used without further purification. Melting points were obtained with a Mel-Temp melting point apparatus; no stem correction was applied. Infrared spectra were recorded on a Beckman Acculab 8 spectrophotometer except where noted. High field ^1H and ^{13}C NMR spectra were recorded on either a Varian XL200 or Varian XL400 superconducting FT spectrometer. UV spectra were obtained on a Beckman DU-7 UV-visible spectrophotometer. Mass spectra were performed using either a V.G. 70E-HF (high resolution) V.G. ZAB-1F (low resolution) spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and by University of California Chemical Analytical Services, Berkeley, CA.

Analytical thin-layer chromatography (TLC) was performed on Merck aluminum plates precoated with 0.2 mm of silica gel 60 F-254. Unless otherwise noted, chromatographic isolations were accomplished by radial layer chromatography using a Chromatotron Model 7924T (Harrison Research, Palo Alto, CA) with Kieselgel PF silica gel. In all cases, the material to be chromatographed was filtered through a plug of silica gel to remove baseline impurities.

Preparation of Complexes. Complexes were prepared by the same general method, described in detail for complex **1**. In all cases, a fine black precipitate was observed (most probably ReO_2), which was removed by filtration and radial chromatography.

[*SP*-5-15(*R)]-[*S*-(2-Propenyl)phenylene-1,2-diaminobis(2,2-dimethyl-1,2-ethanethiolato)-*N,S,N',S'*] oxorhenium (1).** In a 100 mL three-necked round bottom flask equipped with a reflux condenser, addition funnel, and N_2 inlet, 1.02 g (1.33 mmol, 100 M%) of [Bu_4N]-[$ReOBr_4$] was dissolved in 15 mL of acetone and was cooled to 0 °C. The addition funnel was charged with 2-propenyl-PhAT (0.59 g, 1.82 mmol, 137 M%), 6 mL of MeOH, and 6 mL of H_2O. The pH was adjusted to 13−14 with 10 N NaOH. The cloudy ligand mixture was added dropwise to the $ReOBr_4^-$ solution while stirring. After the addition period, the mixture was warmed to room temperature and the pH was adjusted to 7−9 with 10 N NaOH in 1:1 MeOH/H_2O. After 1 h, the mixture was filtered through a bed of Celite to remove a fine black precipitate (probably ReO_2). The solvent was removed by rotary evaporation and the residue was taken up in 50 mL of CH_2Cl_2. The CH_2Cl_2 was washed with 50 mL of H_2O. The aqueous layer was extracted with 2 × 50 mL of CH_2Cl_2. The combined CH_2Cl_2 layers were washed with 50 mL of saturated NaCl and were dried over anhydrous Na_2SO_4. Removal of the solvent gave 1.82 g of a red oil containing three components detected by UV absorbance on TLC (20% ethyl acetate/hexane: R_f 0.80; R_f 0.74, 1-allyl PhAT; R_f 0.24, red-orange spot). The red-orange component was isolated by radial chromatography (4 mm silica gel plate) using 10−30% ethyl acetate/hexane. Concentration provided 0.68 g (97%) of a red oil which solidified upon trituration with Et_2O to give a red solid, mp 165−168 °C dec. IR (KBr): 928 (vs, Re=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.09 (s, 3H, Me), 1.52 (s, 3H, Me), 1.72 (s, 3H, Me), 1.91 (s, 3H, Me), 3.72 (dd, 1H, J_{vic} = 7.9 Hz, SCH_2), 3.82 (dd, 1H, J_{vic} = 6.4 Hz, SCH_2), 4.11 (d, 1H, J = 12.3 Hz, NCH_2), 4.23 (d, 1H, J = 11.4 Hz, NCH_2), 4.24 (d, 1H, J = 12.3 Hz, NCH_2), 4.37 (d, 1H, J = 11.4 Hz, NCH_2), 5.43 (d, 1H, J_{cis} = 10.2 Hz, =CH_2), 5.54 (d, 1H, J_{trans} = 16.5 Hz, =CH_2), 6.01 (m, 1H, −CH=C), 6.71 (dd, 1H, ArH), 6.75 (dt, 1H, ArH), 6.80 (dt, 1H, ArH), 6.91 (dd, 1H, ArH). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 154.9, 154.0, 130.5, 122.5, 120.1 (2C), 111.7, 110.2, 72.3, 69.3, 66.5, 61.7, 39.1, 30.6, 30.5, 25.3, 23.6. UV (CH_3CN), λ_{max} (ϵ_{max}, M^{-1} cm^{-1}): 310 nm (1.46 × 10^4); 460 nm (423). FAB^+ MS: *m/z* 525 (M + H), 483, 409. Anal. Calcd for $C_{17}H_{25}N_2S_2ReO$: C, 38.99; H, 4.81; N, 5.35; S, 12.24; Re, 35.55. Found: C, 38.83; H, 4.81; N, 5.29; S, 12.79; Re, 35.84.

[*SP*-5-15(*R)]-[*S*-Allenylphenylene-1,2-diaminobis(2,2-dimethyl-1,2-ethanethiolato)-*N,S,N',S'*]oxorhenium (2).** Using the procedure described for the synthesis of **1**, [Et_4N][$ReOBr_4$] (0.95 g, 1.45 mmol) and (2-propynyl)PhAT (0.83 g, 2.57 mmol) were combined in the acetone, MeOH, H_2O, and 10 N NaOH mixture at ambient temperature. Purification by radial chromatography (4 mm silica gel, 5−30% ethyl acetate/hexane) gave **2** (0.22 g, 29%) as an orange solid after trituration with 1:1 Et_2O/petroleum ether and the side product **7** (92 mg) as a colorless oil. **2**: mp 152−155 °C. IR (KBr): 1930 (w, C=C=C), 930 (vs, Re=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 3H, Me), 1.51 (s, 3H, Me), 1.72 (s, 3H, Me), 1.89 (s, 3H, Me), 4.19 (d, 1H, J = 12.4 Hz, NCH_2), 4.24 (d, 1H, J = 11.5 Hz, NCH_2), 4.27 (d, 1H, J = 11.3 Hz, NCH), 4.39 (d, 1H, J = 11.5 Hz, NCH_2), 5.29 (dd, 1H, J = 13.8 Hz, J = 6.3 Hz, =C=CH_2), 5.38 (dd, 1H, J = 13.6 Hz, J = 6.2 Hz, =C=CH_2), 5.98 (t, 1H, J = 6.2 Hz, SCH=), 6.70−6.83 (m, 3H, ArH), 6.91 (dd, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz) 213.0 (=C=), 155.0, 153.9, 120.2 (2C), 111.7, 110.3, 81.6, 79.9, 72.5, 70.1, 67.9, 61.8, 30.6, 30.5, 24.5, 23.5. UV (CH_3CN), λ_{max} (ϵ_{max}): 315 nm (1.73 × 10^4); 466 nm (419). FAB^+ MS: *m/z* 523 (M + H), 483, 409. Anal. Calcd for $C_{17}H_{23}N_2S_2ReO$: C, 39.14; H, 4.44; N, 5.37; S, 12.29; Re, 35.69. Found: C, 39.38; H, 4.55; N, 5.23; S, 12.55; Re, 35.91. **7**: TLC (5% ethyl acetate/hexane) R_f 0.60. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.44 (s, 6H, $C(Me)_2$), 1.47 (s, 3H, Me), 1.51 (s, 6H, $C(Me)_2$), 1.71 (s, 3H, Me), 2.10 (t, 1H, J = 2.7 Hz, =CH), 3.03 (bd, 1H, J = 9 Hz, NCH_2), 3.13−3.19 (m, 2H, NCH_2), 3.21 (m, 2H, SCH_2), 5.76 (bt, 1H, J = 5.6 Hz, NH), 6.58−6.62 (m, 2H, ArH), 7.07−7.21 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 400 Hz): 147.6, 129.9, 128.1, 127.4, 115.3, 110.1, 80.9, 74.4, 70.8, 69.0, 52.5, 49.5, 47.1, 33.2, 31.2, 29.1, 27.7, 27.3 (2C) 16.1. FAB^+ MS: *m/z* 363, 347, 291, 275, 249. Anal. Calcd for $C_{20}H_{30}N_2S_2$: C, 66.25; H, 8.34; N, 7.72; S, 17.68. Found: C, 65.93; H, 8.34, N, 7.91; S, 17.85.

[*SP*-5-15(*R)]-[*S*-Propylphenylene-1,2-diaminobis(2,2-dimethyl-1,2-ethanethiolato)-*N,S,N',S'*-oxorhenium (3).** Using the procedure described for the synthesis of **1**, [Bu_4N][$ReOBr_4$] (2.83 g, 3.68 mmol) and propylPhAT (1.50 g, 4.60 mmol) were combined in the acetone, MeOH, H_2O, and 10 N NaOH mixture at 0 °C. Extraction into $CHCl_3$ gave 3.64 g of a red-orange oil. TLC (20% ethyl acetate/hexane) showed the oil to consist of two new compounds (R_f 0.86 and 0.30, red-orange spot). The products were separated by radial chromatography (4 mm silica gel). Ethyl acetate/hexane (5−20%) was used to isolate **8** (0.22 g) as a yellow solid. Elution with 0−5% Et_2O in $CHCl_3$/hexane (1:1) afforded **3** (1.57 g, 81%) as a dark red solid. **3**: mp 196−206 °C. IR (KBr): 930 (vs, Re=O) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.00 (s, 3H, Me), 1.18 (t, 3H, J = 7.3 Hz, CH_3), 1.51 (s, 3H, Me), 1.72 (s, 3H, Me), 1.89 (s, 3H, Me), 2.00 (m, 2 H, CH_2), 3.01 (m, 2H, SCH_2), 4.12 (d, 1H, J = 12.23 Hz, NCH_2), 4.21 (d, 1H, J = 11.5 Hz, NCH_2), 4.25 (d, 1H, J = 12.1 Hz, NCH_2), 4.37 (d, 1H, J = 11.4 Hz, NCH_2), 6.72−6.93 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 540.3 MHz) δ 155.0, 154.0, 120.0 (2C), 111.6, 110.2, 72.2, 69.0, 65.5, 61.6, 36.4, 30.7, 30.4, 24.6, 23.8, 21.4, 13.2. UV (CH_3CN), λ_{max} (ϵ_{max}) 309 nm (1.43 × 10^4); 453 nm (398). FAB^+ MS: *m/z* 527 (M + H), 279. Anal. Calcd for $C_{17}H_{27}N_2S_2ReO$: C, 38.84; H, 5.18; N, 5.33; S, 12.20; Re, 35.42. Found: C, 38.48; H, 5.07; N, 5.18; S, 11.74; Re, 34.75. 8: ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, 3H, CH_3), 1.37 (s, 6H, $C(Me)_2$), 1.47 (s, 3H, Me), 1.52 (s, 6H, $C(Me)_2$), 1.56 (q, 2H, CH_2), 1.71 (s, 3H, Me), 2.42 (s, 2H, SCH_2), 3.00−3.10 (m, 3H, CH_2N), 3.65 (bd, 1H, CH_2N), 5.77 (t, 1H, NH), 6.57−6.61 (m, 2H, ArH), 7.10 (dt, 1H, ArH), 7.20 (dd, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ 147.7, 129.7, 128.1, 127.4, 115.0, 109.9, 74.2, 68.9, 52.3, 49.4, 33.1, 31.1, 29.6, 29.1, 27.7, 27.6, 22.9, 13.9. FAB^+ MS: *m/z* 367 (M^+), 365, 351, 291, 275, 249. Anal. Calcd for $C_{20}H_{34}N_2S_2$: C, 65.52; H, 9.35; N, 7.64; S, 17.49. Found: C, 64.28; H, 9.15; N, 7.83; S, 17.90.

[*SP*-5-15(*R)]-[*S*-(2-Hydroxyethyl)phenylene-1,2-diaminobis(2,2-dimethyl-1,2-ethanethiolato)-*N,S,N',S'*]oxorhenium (4).** Using the procedure described for the synthesis of **1**, [Bu_4N][$ReOBr_4$] (1.50 g, 1.95 mmol) and 2-hydroxyethyl-PhAT (0.96 g, 2.92 mmol) were allowed to react for 20 min. Radial chromatography using 1:1 Et_2O/$CHCl_3$ afforded 0.74 g (72%) of **4** as an orange solid after trituration with Et_2O, mp 211−213 °C. IR (KBr): 3510 (m, OH), 935 (vs, Re=O) cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 0.93 (s, 3H, Me), 1.43 (s, 3H, Me), 1.60 (s, 3H, Me), 1.87 (s, 3H, Me), 3.04 (dt, 1H, J = 12.5 Hz, SCH_2), 3.40 (m, 1H, SCH_2), 3.81 (m, 1H, OCH_2), 3.91 (m, 1H, OCH_2), 4.11 (d, 1H, J = 11.6 Hz, NCH_2), 4.15 (d, 1H, J = 12.4 Hz, NCH_2), 4.24 (d, 1H, J = 11.5 Hz, NCH_2), 4.29 (d, 1H, J = 12.5 Hz, NCH_2), 5.33 (bs, 1H, OH), 6.68−6.94 (m, 4H, ArH). ^{13}C NMR (DMSO-d_6, 50.3 MHz): 154.6, 153.2, 119.8, 119.6, 111.2, 110.4, 71.4, 67.8, 66.0, 60.8, 57.7, 37.5, 30.4, 29.7, 23.7, 22.7. UV (CH_3CN), λ_{max} (ϵ_{max}, M^{-1} cm^{-1}): 308 nm (1.31 × 10^4); 454 nm (373). FAB^+ MS:

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Table 1. Crystal Data for Structure Determination of ReO−2-propenyl-PhAT (**1**) and ReO−propyl-PhAT (**3**)

property	2-propenyl (**1**)	propyl (**3**)
formula	$C_{17}H_{25}N_2OS_2Re$	$C_{17}H_{27}N_2OS_2Re$
fw	523.73	525.75
cryst size (mm)	0.05 × 0.23 × 0.27	0.02 × 0.10 × 0.18
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$
a (Å)	17.899(3)	18.076(1)
b (Å)	13.910(1)	13.920(1)
c (Å)	15.936(1)	15.994(1)
β (deg)	104.70(1)	105.09(1)
V (Å^3)	3838.0	3885.8
Z	8	8
D_{calc} (g cm^{-3})	1.813	1.797
μ (cm^{-1})	139.8	138.0
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (mono)	Cu Kα	Cu Kα
temp (°C)	23	23
scan mode	ω-2θ	ω-2θ
max 2θ (deg)	120	100
no. of indep reflcns	5681	3976
abs cor	numerical	numerical
transm factors	T_{max} = 0.50 T_{min} = 0.092	T_{max} = 0.75 T_{min} = 0.32
function minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
anomalous dispersion	all non-hydrogen atoms	all non-hydrogen atoms
no. of observns with $I > 3\sigma(I)$	4795	3012
no. of variables	411	415
R (R_w)	0.031, 0.038	0.033, 0.040
peaks in final diff map (e Å^{-3})	<2.9	<1.3

m/z 528 (M + H), 511, 483, 449. Anal. Calcd for $C_{16}H_{26}N_2S_2ReO_2$: C, 36.35; H, 4.96; N, 5.30; S, 12.13; Re, 35.22. Found: C, 36.36; H, 4.66; N, 5.18; S, 11.92; Re, 34.67.

[*SP*-5-15(*R)]-[*S*-Benzylphenylene-1,2-diaminobis(2,2-dimethyl-1,2-ethanethiolato)-*N*,*S*,*N*′,*S*′]oxorhenium (5).** Using the procedure described for the synthesis of **1**, [Et_4N][$ReOBr_4$] (1.50 g, 1.95 mmol) and benzyl-PhAT (1.10 g, 2.92 mmol) were allowed to react for 20 min. The product was filtered through a bed of 40 mL of silica gel, washing with 150 mL of 1:1 $CHCl_3$/Et_2O. The solvent was removed under reduced pressure, and after the residue was allowed to stand overnight, the ReO complex precipitated. The solid was washed with several portions of Et_2O to give 0.51 g (46%) of **5** as a red-brown solid, mp 189−192 °C dec. IR (KBr): 930 (vs, Re=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.95 (s, 3H, Me), 1.41 (s, 3H, Me), 1.66 (s, 3H, Me), 1.83 (s, 3H, Me), 4.13 (d, 1H, J = 12 Hz, NCH_2), 4.22 (AB quartet, 2H, J(AB) = 12 Hz, NCH_2), 4.31 (d, 1H, J = 11 Hz, NCH_2), 4.34 (d, 1H, J = 13 Hz, SCH_2), 4.67 (d, 1H, J = 13 Hz, SCH_2), 6.68−6.96 (m, 4H, ArH), 7.38−7.64 (m, 5H, Ph). ^{13}C NMR (DMSO-d_6, 100.5 MHz): 154.5, 153.1, 134.1−129.0, 119.8, 119.7, 111.3, 110.5, 71.5, 68.0, 67.9, 61.6, 38.4, 30.1 (2C), 23.3, 22.8 (decomposes in DMSO). UV (CH_3CN), λ_{max} (ϵ, M^{-1} cm^{-1}): 316 nm (1.81 × 10^4); 464 nm (428). FAB$^+$ MS: *m/z* 575 (M + H), 557, 495, 429. Anal. Calcd for $C_{21}H_{27}N_2S_2ReO$: C, 43.96; H, 4.74; N, 4.88; S, 11.17; Re, 32.45. Found: C, 44.12; H, 4.69; N, 4.88; S, 11.64; Re, 31.37.

[*SP*-5-15(*R)][*S*-(2-Propynyl)phenylene-1,2-diaminobis(2,2-dimethyl-1,2-ethanethiolato)-*N*,*S*,*N*′,*S*′]oxorhenium (6).** In a 50 mL round-bottom flask, 1.50 g (1.95 mmol) of [Bu_4N][$ReOBr_4$] was dissolved in 20 mL of MeOH. The brown solution was flushed with N_2 and was chilled to 0 °C. 2-Propynyl-PhAT (0.942 g, 2.92 mmol) in 6 mL of MeOH was added to the $ReOBr_4^-$ solution. The solution became a deeper orange. After 15−20 min, 1 mL of 0.1 M NaOH was added and the solution was filtered through 40 mL silica gel. The silica was washed with 150 mL of 1:1 Et_2O/$CHCl_3$. The filtrate was concentrated under reduced pressure and the crude residue was dissolved in 70 mL of $CHCl_3$. The $CHCl_3$ solution was extracted with 50 mL of H_2O. The aqueous layer was extracted with 2 × 50 mL of $CHCl_3$, and the combined organic layers were washed with 50 mL of H_2O and 50 mL of saturated NaCl and were dried (Na_2SO_4). Removal of the solvent gave 1.89 g of a brown oil. The crude product was purified by radial chromatography using a 4 mm silica gel plate and 10−40% ethyl acetate/hexane to elute the product. Concentration of the red band provided 0.56 g (55%) of **6** as a deep red solid, mp 161−166 °C dec. IR ($CHCl_3$): 3310 (m, ≡C−H), 930 (vs, Re=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.17 (s, 3H, Me), 1.49 (s, 3H, Me), 1.71 (s, 3H, Me), 2.06 (s, 3H, Me), 2.46 (t, 1H, J = 3 Hz, aromatic C−H), 3.74 (dd, J = 16.6 Hz, J = 3 Hz, SCH_2), 3.91 (dd, J = 16.4 Hz, J = 3 Hz, SCH_2), 4.23 (d, 1H, J = 12.5 Hz, NCH_2), 4.25 (d, 1H, J = 11.4 Hz, NCH_2), 4.30 (d, 1H, J = 12.5 Hz, NCH_2), 4.35 (d, 1H, J = 11.5 Hz, NCH_2), 6.70−6.83 (m, 3H, ArH), 6.91 (dd, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): 154.7, 153.7, 120.3 (2C), 111.7, 110.2, 77.1, 75.6, 72.2, 69.8, 67.9, 61.8, 30.5 (2C), 26.1, 25.5, 23.3. UV (CH_3CN), λ_{max} (ϵ, M^{-1} cm^{-1}): 317 nm (1.99 × 10^4); 465 nm (389). FAB$^+$ MS: *m/z* 523 (M + H), 497, 483, 481. Anal. Calcd for $C_{17}H_{23}N_2S_2ReO$: C, 39.14; H, 4.44; N, 5.37; S, 12.29; Re, 35.69. Found: C, 38.81; H, 4.40; N, 5.29; S, 13.08; Re, 35.93.

Crystallography

Structure of ReO−2-propenyl-PhAT (1). Diffraction quality crystals were obtained by slow evaporation of **1** from $CHCl_3$/hexane. The crystal data are summarized in Table 1, and atomic coodinates are shown in Table 2. The intensity data were measured on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Cu Kα radiation, ω−2θ scans). The data were corrected for absorption.

The structure was solved by the heavy-atom method, and was refined by full-matrix least squares. Nine reflections, which were strongly affected by extinction, were excluded from the final refinement and difference map. In the final refinement, the nonhydrogen atoms were refined anisotropically, except for the C2's and C3's of the disordered propenyl group, which were refined isotropically. The hydrogen atoms were included in the structure-factor calculations but their parameters were not refined. The major peaks (<2.9 e Å^{-3}) of the final difference map are near the rhenium atoms.

An ORTEP drawing of one of the molecules in the asymmetric unit of **1**, which is the unprimed major rotamer, is shown in Figure 3. Tables containing anisotropic thermal parameters and hydrogen atom locations are available as supplementary material.

Structure of ReO−propyl-PhAT (3). The procedure described above was used to collect data and solve the struture for **3**. Crystal data are shown in Table 1, and atomic coordinates are shown in Table 3. A perspective drawing of one of the molecules of **3**, designated as the unprimed molecule, is shown in Figure 4. Tables containing anisotropic thermal parameters and hydrogen atom locations are available as supplementary material.

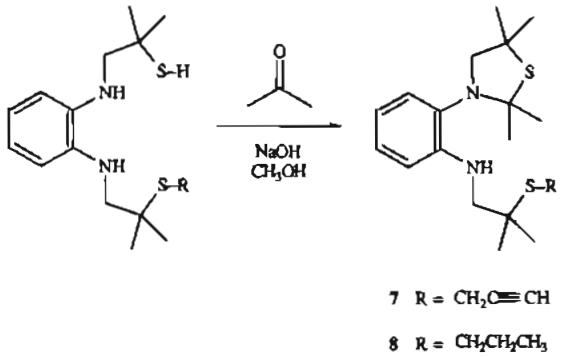

Figure 2. Side reaction of acetone with PhAT ligands.

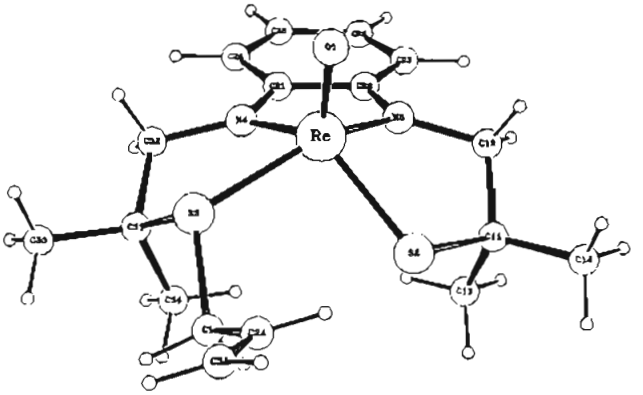

Figure 3. ORTEP drawing of one of the molecules in the asymmetric unit of **1**. The drawing shown is of the major rotamer of the propenyl group.

$[Bu_4N][ReOBr_4]$ and 2-propynyl-PhAT in MeOH. The other complexes may also be accessible in this manner.

In two instances, a side reaction of the ligand with acetone to produce the substituted thiazoles **7** and **8** occurred (Figure 2). This organic side product consumed approximately 15% of the starting ligand but did not interfere with the isolation of the metal complexes.

Table 3. Final Atomic Parameters for Structure **3**[a]

atom	*x*	*y*	*z*	*B* (Å^2)	atom	*x*	*y*	*z*	*B* (Å^2)
Re	0.80340(3)	0.28668(3)	0.48157(3)	2.02(1)	H3A	1.119	0.135	0.630	9.5
S2	0.9065(2)	0.3879(2)	0.5238(2)	2.95(7)	H3B	1.119	0.112	0.530	9.5
S3	0.8759(2)	0.1669(2)	0.4323(2)	2.66(6)	H3C	1.117	0.223	0.562	9.5
O1	0.7749(4)	0.2295(5)	0.5607(5)	3.2(2)	H12A	0.774	0.486	0.571	2.9
N4	0.7374(5)	0.2649(6)	0.3655(5)	2.3(2)	H12B	0.745	0.551	0.483	2.9
N5	0.7475(5)	0.4074(5)	0.4597(6)	2.4(2)	H13A	0.920	0.557	0.420	5.1
C1	0.9786(7)	0.1849(9)	0.4485(8)	3.8(3)	H13B	0.841	0.501	0.374	5.1
C2	1.0175(8)	0.152(1)	0.5456(9)	6.8(5)	H13C	0.837	0.611	0.408	5.1
C3	1.0997(9)	0.156(1)	0.569(1)	8.0(5)	H14A	0.955	0.584	0.580	4.4
C11	0.8601(7)	0.5093(7)	0.5084(7)	2.7(3)	H14B	0.874	0.639	0.575	4.4
C12	0.7767(6)	0.4944(7)	0.5096(7)	2.4(3)	H14C	0.899	0.546	0.638	4.4
C13	0.8648(7)	0.5480(9)	0.4197(8)	4.3(3)	H23	0.633	0.544	0.405	3.8
C14	0.9005(7)	0.5750(8)	0.5818(8)	3.7(3)	H24	0.527	0.524	0.278	4.1
C21	0.6744(6)	0.3275(8)	0.3376(6)	2.4(3)	H25	0.514	0.382	0.198	4.5
C22	0.6823(6)	0.4109(7)	0.3898(7)	2.2(3)	H26	0.606	0.259	0.231	3.9
C23	0.6282(6)	0.4842(8)	0.3688(8)	3.2(3)	H32A	0.720	0.204	0.247	3.6
C24	0.5659(7)	0.4719(9)	0.2953(7)	3.4(3)	H32B	0.726	0.127	0.325	3.6
C25	0.5591(7)	0.3900(9)	0.2481(7)	3.8(3)	H33A	0.904	0.074	0.277	5.0
C26	0.6123(7)	0.3177(9)	0.2675(7)	3.3(3)	H33B	0.830	0.026	0.301	5.0
C31	0.8342(6)	0.1742(8)	0.3146(7)	2.8(3)	H33C	0.819	0.082	0.209	5.0
C32	0.7477(6)	0.1878(8)	0.3081(7)	3.1(3)	H34A	0.921	0.249	0.279	4.7
C33	0.8482(7)	0.0809(9)	0.2719(8)	4.2(3)	H34B	0.837	0.265	0.212	4.7
C34	0.8654(7)	0.2591(9)	0.2742(8)	4.0(3)	H34C	0.859	0.319	0.305	4.7
Re′	0.31185(3)	0.73323(3)	0.01396(3)	2.05(1)	H1A′	0.513	0.752	0.047	4.0
S2′	0.3903(2)	0.6352(2)	−0.0382(2)	2.88(7)	H1B′	0.544	0.858	0.084	4.0
S3′	0.4113(2)	0.8466(2)	0.0656(2)	2.74(7)	H2A′	0.494	0.928	−0.052	4.9
O1′	0.2463(5)	0.7969(5)	−0.0625(5)	3.4(2)	H2B′	0.450	0.828	−0.090	4.9
N4′	0.3042(5)	0.7457(6)	0.1332(5)	2.4(2)	H3A′	0.556	0.852	−0.141	7.6
N5′	0.2655(5)	0.6118(6)	0.0313(5)	2.2(2)	H3B′	0.611	0.856	−0.042	7.6
C1′	0.5023(6)	0.8226(9)	0.0419(7)	3.4(3)	H3C′	0.567	0.756	−0.080	7.6
C2′	0.4975(7)	0.8560(9)	−0.0502(8)	4.1(3)	H12A′	0.233	0.542	−0.084	3.6
C3′	0.5634(8)	0.828(1)	−0.081(1)	6.4(4)	H12B′	0.249	0.470	0.000	3.6
C11′	0.3484(6)	0.5138(8)	−0.0310(8)	3.3(3)	H13A′	0.451	0.458	0.050	4.9
C12′	0.2674(7)	0.5289(7)	−0.0250(8)	3.0(3)	H13B′	0.398	0.512	0.104	4.9
C13′	0.3976(7)	0.4681(8)	0.0545(8)	4.1(3)	H13C′	0.375	0.405	0.064	4.9
C14′	0.3534(7)	0.4533(9)	−0.1087(9)	4.8(3)	H14A′	0.408	0.446	−0.109	5.7
C21′	0.2555(5)	0.6831(7)	0.1611(6)	2.0(2)	H14B′	0.331	0.389	−0.104	5.7
C22′	0.2343(6)	0.6040(7)	0.1016(7)	2.6(3)	H14C′	0.325	0.486	−0.163	5.7
C23′	0.1883(6)	0.5320(7)	0.1220(7)	2.6(3)	H23′	0.174	0.475	0.083	3.1
C24′	0.1619(6)	0.5389(8)	0.1962(7)	2.9(3)	H24′	0.129	0.487	0.209	3.5
C25′	0.1798(6)	0.6148(8)	0.2512(7)	3.0(3)	H25′	0.160	0.619	0.304	3.6
C26′	0.2276(6)	0.6883(9)	0.2319(7)	3.0(3)	H26′	0.241	0.745	0.272	3.6
C31′	0.4262(6)	0.8337(8)	0.1844(7)	3.1(3)	H32A′	0.348	0.799	0.255	3.8
C32′	0.3451(7)	0.8200(8)	0.1946(7)	3.2(3)	H32B′	0.317	0.882	0.182	3.8
C33′	0.4625(7)	0.9264(9)	0.2289(8)	4.6(3)	H33A′	0.515	0.933	0.221	5.5
C34′	0.4757(7)	0.7461(9)	0.2175(8)	4.5(3)	H33B′	0.431	0.983	0.202	5.5
H1A	0.990	0.254	0.440	4.5	H33C′	0.465	0.923	0.292	5.5
H1B	0.998	0.144	0.407	4.5	H34A′	0.528	0.7857	0.210	5.5
H2A	1.001	0.085	0.553	8.0	H34B′	0.479	0.736	0.280	5.3
H2B	0.999	0.196	0.585	8.0	H34C′	0.453	0.688	0.184	5.3

[a] The parameters of the hydrogen atoms were not refined. Standard deviations are in parentheses.

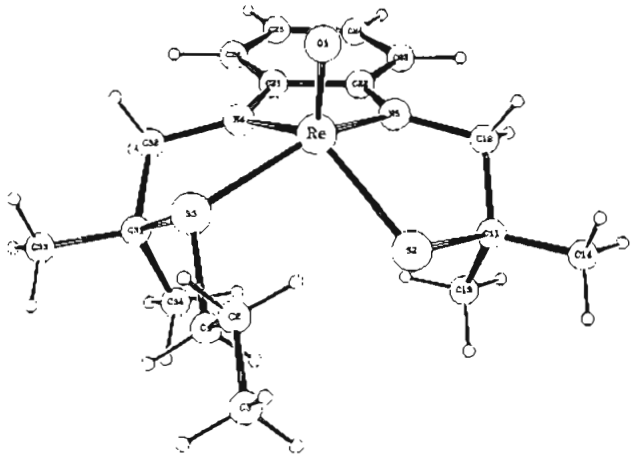

Figure 4. ORTEP drawing of one of the molecules (designated as unprimed) in the asymmetric unit of **3**.

Characterization. The six complexes **1**−**6** were soluble in polar organic solvents and were characterized by elemental analysis, IR, UV/visible, ^{1}H NMR, and ^{13}C NMR spectroscopy, and FAB$^+$ mass spectrometry. The infrared spectra of the ReO−R-PhAT complexes showed a strong absorption in the range 928−935 cm^{-1} characteristic of the Re=O stretching frequency in monooxo square pyramidal Re(V) complexes.[10,13] This absorption is on the low end of the range for rhenium oxo complexes (for instance, a ReO−bis(mercaptoacetamido)propanoate complex[14] absorbs at 950−970 cm^{-1}) and may indicate a weakening of the R=O bond as a result of stronger Re−N bonding. In addition, the propenyl, allenyl, and propynyl complexes all exhibited the expected weak C=C multiple bond stretch (1635, 1930, and 2120 cm^{-1}, respectively), which implies that there is little coordination of the π-electrons to the metal. This was substantiated by making the propyl complex **3** and the hydroxyethyl complex **4**, which showed no unexpected spectroscopic differences.

The ^{1}H and ^{13}C NMR spectra of these complexes showed typical resonances for $ReON_2S_2$ chelates.[15] Both the NH and the SH signals are lost in the Re complex, indicating deprotonation and coordination. The loss of both nitrogen hydrogens, which is unusual in amines, may be attributed to the greater acidity imparted to the aniline-like amine hydrogens by conjugation with the aromatic ring. Although *trans* alkoxo ligands are known for both technetium(V)[16,17] and rhenium(V)[18] oxo compounds, the presence of an O−H resonance in the ^{1}H NMR spectrum of **4** (5.33 ppm) supports the assumption that the alcohol does not interact with the metal center.

The square-pyramidal oxorhenium core causes the methylene and the *gem*-dimethyl units from the $NCH_2C(CH_3)_2S$ groups to be diastereotopic, since now these moieties can reside either *syn* or *anti* with respect to the oxo ligand. In the ^{1}H NMR spectra the CH_2 group appears as an AB quartet at 4.11−4.39 ppm with a geminal coupling constant J_{ab} = 11−13 Hz. The two equivalent sets of *gem*-dimethyl groups in the ligand, either adjacent to the thiolate or to the thioether moiety, now appear as four singlets in both the ^{1}H and ^{13}C NMR spectra.

Table 4. Selected Bond Distances (Å) for Compounds **1** and **3**

	1		3	
bond	unprimed	primed	unprimed	primed
Re−S2	2.293(2)	2.281(2)	2.293(3)	2.277(3)
Re−S3	2.381(2)	2.373(2)	2.379(3)	2.372(3)
Re−O1	1.687(5)	1.695(4)	1.685(8)	1.712(7)
Re−N4	1.965(5)	1.960(6)	1.952(7)	1.956(8)
Re−N5	1.947(5)	1.945(5)	1.945(8)	1.938(8)

The alkyl side chain of the complexes also has the option of residing either *syn* or *anti* with respect to the Re=O bond; however, only a single set of resonances was found in the NMR spectrum. A typical example is the proton NMR spectrum of **5**, which shows two 1-proton doublets (4.34 and 4.67 ppm; J = 13 Hz) for the diastereotopic benzyl hydrogens adjacent to the thioether. This suggests that there is only one isomer and that this isomer is the sterically favored *anti* isomer. This finding is in strong agreement with Davison's results in which he obtained only the *anti* diastereomer when amide−thiol−thioether ligands were treated with Tc(V).[11] He also indicated by variable temperature NMR experiments that there may be a high barrier to inversion for the coordinated thioether.

Further characterization was provided by the UV−visible spectra. All of these complexes exhibited intense absorbance at about 310 nm (ϵ 13 000−20 000), with a much weaker band in the visible region (453−466 nm), resulting in the orange-rust to red-brown colors. The high-intensity peak in the UV region is probably a result of ligand to metal charge-transfer transitions, whereas the lower energy band presumably arises from a d−d transition of Re(V).[14] In addition, the fast atom bombardment mass spectrum of the complexes gave a characteristic peak corresponding to molecular ion [ReO−R(PhAT)-H$^+$].

Crystallography. The single-crystal X-ray analysis of ReO-allyl PhAT (**1**) (Figure 3) and ReO−propyl-PhAT (**3**) (Figure 4) showed this class of compounds to be five coordinate and to have distorted square-pyramidal geometries with the oxo group occupying the apical position. Unlike aliphatic N_2S_2 ligands, however, in which the plane about the N−C−C−N base tends to be puckered,[19,20] the aromatic ring in the PhAT complex forces the base of the pyramid to be almost flat due to the coplanarity of the N−C−C−N bonds. The X-ray analysis also revealed that the side chain (**1**, R = 2-propenyl; **3**, R = propyl) occupied the least sterically hindered position, *anti* with respect to the oxo ligand. For both complexes, the unit cell contained two independent molecules (designated as unprimed and primed), that is, two molecules not related by crystallographic symmetry. The conformations of two independent molecules in both complexes are similar. Drawings of one independent molecule for **1** and **3** are shown in Figures 3 and 4, respectively. In addition, the propenyl group in **1** was disordered in the crystal; for each independent molecule, it was resolved into two moieties.

The average rhenium−oxygen bond distance (Table 4) of 1.685−1.712 Å is in the range for other rhenium(V) oxo complexes.[9,21,22] A recent review by Melnik and Van Lier lists several examples of structural parameters of Tc(V) complexes for comparison.[23] The Re−S distances are also within the ranges of other M−S bond lengths and, as expected, the weaker

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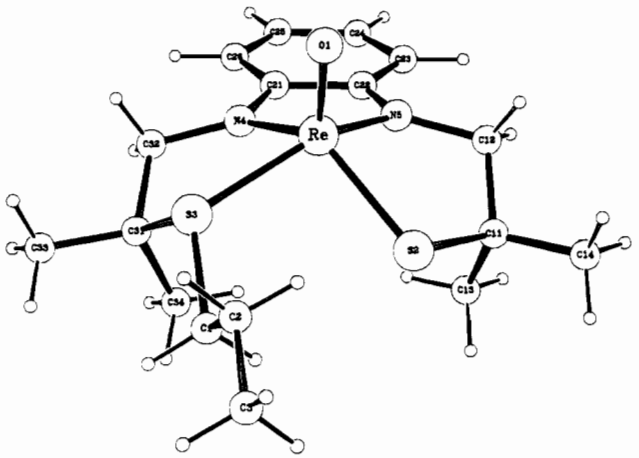

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Characterization. The six complexes **1**−**6** were soluble in polar organic solvents and were characterized by elemental analysis, IR, UV/visible, ^{1}H NMR, and ^{13}C NMR spectroscopy, and FAB$^+$ mass spectrometry. The infrared spectra of the ReO−R-PhAT complexes showed a strong absorption in the range 928−935 cm^{-1} characteristic of the Re=O stretching frequency in monooxo square pyramidal Re(V) complexes.[10,13] This absorption is on the low end of the range for rhenium oxo complexes (for instance, a ReO−bis(mercaptoacetamido)propanoate complex[14] absorbs at 950−970 cm^{-1}) and may indicate a weakening of the R=O bond as a result of stronger Re−N bonding. In addition, the propenyl, allenyl, and propynyl complexes all exhibited the expected weak C=C multiple bond stretch (1635, 1930, and 2120 cm^{-1}, respectively), which implies that there is little coordination of the π-electrons to the metal. This was substantiated by making the propyl complex **3** and the hydroxyethyl complex **4**, which showed no unexpected spectroscopic differences.

The ^{1}H and ^{13}C NMR spectra of these complexes showed typical resonances for $ReON_2S_2$ chelates.[15] Both the NH and the SH signals are lost in the Re complex, indicating deprotonation and coordination. The loss of both nitrogen hydrogens, which is unusual in amines, may be attributed to the greater acidity imparted to the aniline-like amine hydrogens by conjugation with the aromatic ring. Although *trans* alkoxo ligands are known for both technetium(V)[16,17] and rhenium(V)[18] oxo compounds, the presence of an O−H resonance in the ^{1}H NMR spectrum of **4** (5.33 ppm) supports the assumption that the alcohol does not interact with the metal center.

The square-pyramidal oxorhenium core causes the methylene and the *gem*-dimethyl units from the $NCH_2C(CH_3)_2S$ groups to be diastereotopic, since now these moieties can reside either *syn* or *anti* with respect to the oxo ligand. In the ^{1}H NMR spectra the CH_2 group appears as an AB quartet at 4.11−4.39 ppm with a geminal coupling constant J_{ab} = 11−13 Hz. The two equivalent sets of *gem*-dimethyl groups in the ligand, either adjacent to the thiolate or to the thioether moiety, now appear as four singlets in both the ^{1}H and ^{13}C NMR spectra.

Table 4. Selected Bond Distances (Å) for Compounds **1** and **3**

	1		**3**	
bond	unprimed	primed	unprimed	primed
Re−S2	2.293(2)	2.281(2)	2.293(3)	2.277(3)
Re−S3	2.381(2)	2.373(2)	2.379(3)	2.372(3)
Re−O1	1.687(5)	1.695(4)	1.685(8)	1.712(7)
Re−N4	1.965(5)	1.960(6)	1.952(7)	1.956(8)
Re−N5	1.947(5)	1.945(5)	1.945(8)	1.938(8)

The alkyl side chain of the complexes also has the option of residing either *syn* or *anti* with respect to the Re=O bond; however, only a single set of resonances was found in the NMR spectrum. A typical example is the proton NMR spectrum of **5**, which shows two 1-proton doublets (4.34 and 4.67 ppm; J = 13 Hz) for the diastereotopic benzyl hydrogens adjacent to the thioether. This suggests that there is only one isomer and that this isomer is the sterically favored *anti* isomer. This finding is in strong agreement with Davison's results in which he obtained only the *anti* diastereomer when amide−thiol−thioether ligands were treated with Tc(V).[11] He also indicated by variable temperature NMR experiments that there may be a high barrier to inversion for the coordinated thioether.

Further characterization was provided by the UV−visible spectra. All of these complexes exhibited intense absorbance at about 310 nm (ϵ 13 000−20 000), with a much weaker band in the visible region (453−466 nm), resulting in the orange-rust to red-brown colors. The high-intensity peak in the UV region is probably a result of ligand to metal charge-transfer transitions, whereas the lower energy band presumably arises from a d−d transition of Re(V).[14] In addition, the fast atom bombardment mass spectrum of the complexes gave a characteristic peak corresponding to molecular ion [ReO−R(PhAT)-H$^+$].

Crystallography. The single-crystal X-ray analysis of ReO-allyl PhAT (**1**) (Figure 3) and ReO−propyl-PhAT (**3**) (Figure 4) showed this class of compounds to be five coordinate and to have distorted square-pyramidal geometries with the oxo group occupying the apical position. Unlike aliphatic N_2S_2 ligands, however, in which the plane about the N−C−C−N base tends to be puckered,[19,20] the aromatic ring in the PhAT complex forces the base of the pyramid to be almost flat due to the coplanarity of the N−C−C−N bonds. The X-ray analysis also revealed that the side chain (**1**, R = 2-propenyl; **3**, R = propyl) occupied the least sterically hindered position, *anti* with respect to the oxo ligand. For both complexes, the unit cell contained two independent molecules (designated as unprimed and primed), that is, two molecules not related by crystallographic symmetry. The conformations of two independent molecules in both complexes are similar. Drawings of one independent molecule for **1** and **3** are shown in Figures 3 and 4, respectively. In addition, the propenyl group in **1** was disordered in the crystal; for each independent molecule, it was resolved into two moieties.

The average rhenium−oxygen bond distance (Table 4) of 1.685−1.712 Å is in the range for other rhenium(V) oxo complexes.[9,21,22] A recent review by Melnik and Van Lier lists several examples of structural parameters of Tc(V) complexes for comparison.[23] The Re−S distances are also within the ranges of other M−S bond lengths and, as expected, the weaker

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Table 5. Selected Bond Angles (deg) for Compounds **1** and **3**

	1		3	
bond	unprimed	primed	unprimed	primed
O1−Re−N4	115.2(2)	115.8(2)	114.2(3)	116.1(4)
O1−Re−N5	107.3(2)	108.0(3)	107.3(4)	108.0(3)
S2−Re−O1	116.3(1)	115.7(2)	117.0(2)	115.5(3)
S3−Re−O1	102.8(2)	102.6(1)	102.7(3)	103.0(3)
S2−Re−S3	92.8(6)	92.2(6)	93.0(1)	92.2(1)
S2−Re−N4	128.3(2)	128.4(2)	128.6(3)	128.3(2)
S2−Re−N5	82.0(1)	82.5(1)	82.3(3)	82.2(3)
Re−S3−C31	100.4(2)	101.0(3)	100.7(4)	100.8(4)
Re−S3−C1	118.7(2)	118.5(3)	119.0(4)	116.8(4)
C1−S3−C31	105.0(4)	105.9(3)	105.6(6)	107.4(5)
Re−N4−C21	115.6(3)	116.8(4)	116.7(6)	117.9(6)
Re−N4−C32	124.6(3)	123.6(4)	124.6(6)	123.8(7)
Re−N5−C12	120.6(3)	119.8(5)	121.1(6)	121.1(7)
Re−N5−C22	117.6(4)	118.3(4)	117.7(7)	117.8(6)

Re−S(thioether) bond is approximately 0.09 Å longer than the Re−S(thiolate) bond. Analogous to Davison's compounds,[11] the C1−S2−C31 bond angle is 105−107° about the thioether ligand, which implies sp^3 hybridization at the sulfur atom (Table 5). The angles about the amine nitrogen atoms (that is Re−N−C) approximate 120° (Table 5), suggesting significant sp^2 hybridization.

The unique structural feature of the complexes reported here is the combination of an aromatic ring fused to the backbone of the N_2S_2 base and the alkyl substitution on one of the thiol sulfurs. We can hypothesize two effects of the aromatic ring: (1) an electronic effect, enhancing acidity of the amine nitrogens and resulting in deprotonation and coordination of both sites; and (2) a steric effect imparting rigidity to the N−C−C−N portion of the ligand, resulting in an almost flat base to the square pyramidal complex and enhancing the formation and stability of the complex by an entropy effect. The results of this structural study with rhenium tend to confirm properties of the corresponding ^{99m}Tc complexes that were inferred from indirect evidence.[6] Deprotonation and coordination of both amine nitrogens result in a neutral complex, and the S-substituent is retained in the metal complexes.

In conclusion, the ReO−R-PhAT complexes can be readily synthesized by reacting $[R_4N][ReOBr_4]$ with the PhAT ligands. The results from the syntheses and structural analyses of the rhenium compounds will aid in the preparation and characterization of the ^{99}Tc complex of PhAT ligands.

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Supplementary Material Available: Tables of final atomic parameters for hydrogen atoms, anisotropic thermal parameters, and a full listing of bond distances and angles (10 pages). Ordering information is given on any current masthead page.