Supporting Information for:

Effect of the Ancillary Ligand on the Mechanism for CO Migratory Insertion in High Valent Oxorhenium Complexes

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Crystal Structure Report for 6

Crystal description
A red block-like specimen of $C_6H_{11}O_2ReS_3$, approximate dimensions 0.290 mm x 0.362 mm x 0.378 mm, was used for the X-ray crystallographic analysis. Instrument description The X-ray intensity data were measured.
Data collection The total exposure time was 3.59 hours. Integration The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 20288 reflections to a maximum θ angle of 34.97° (0.62 Å resolution), of which 2340 were independent (average redundancy 8.670, completeness = 100.0%, R_{int} = 3.84%, R_{sig} = 1.84%) and 2250 (96.15%) were greater than $2\sigma(F^2)$. Unit cell The final cell constants of a = 9.1938(3) Å, b = 11.5524(4) Å, c = 9.6348(3) Å, volume = 1023.32(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 9971 reflections above 20 σ(I) with 5.505° < 2θ < 72.78°. Scaling Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.561. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0890 and 0.1230.

Structure solution The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P n m a, with Z = 4 for the formula unit, $C_6H_{11}O_2ReS_3$. Structure refinement The final anisotropic full-matrix least-squares refinement on F^2 with 66 variables converged at R1 = 1.70%, for the observed data and wR2 = 4.24% for all data. The goodness-of-fit was 1.096. The largest peak in the final difference electron density synthesis was 1.083 $e^-/Å^3$ and the largest hole was -1.038 $e^-/Å^3$ with an RMS deviation of 0.146 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.580 g/cm^3 and F(000), 744 e^-. Structure Packing Sample and crystal data

Table S1. Sample and crystal data for **6.**

Identification code	rds218	
Chemical formula	$C_6H_{11}O_2ReS_3$	
Formula weight	397.53	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.290 x 0.362 x 0.378 mm	
Crystal habit	red block	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 9.1938(3) Å	α = 90°
	b = 11.5524(4) Å	β = 90°
	c = 9.6348(3) Å	γ = 90°
Volume	1023.32(6) $Å^3$	
Z	4	
Density (calculated)	2.580 g/cm^3	
Absorption coefficient	12.445 mm^{-1}	
F(000)	744	

Data collection and structure refinement

Table S2. Data collection and structure refinement for **6.**

Theta range for data collection	2.75 to 34.97°
Index ranges	-14<=h<=14, -18<=k<=17, -14<=l<=15
Reflections collected	20288
Independent reflections	2340 [R(int) = 0.0384]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.1230 and 0.0890
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2340 / 0 / 66
Goodness-of-fit on F^2	1.096
Δ/σ_{max}	0.002
Final R indices	2250 data; I>2σ(I) R1 = 0.0170, wR2 = 0.0420
	all data R1 = 0.0179, wR2 = 0.0424
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0214P)^2+0.7351P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0054(2)
Largest diff. peak and hole	1.083 and -1.038 eÅ^{-3}
R.M.S. deviation from mean	0.146 eÅ^{-3}

Atomic coordinates and equivalent isotropic displacement parameters

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **6**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Re1	0.42781(2)	0.25	0.43961(2)	0.01046(4)
S1	0.48672(7)	0.25	0.20412(7)	0.01313(10)
S2	0.33441(6)	0.43012(4)	0.39483(6)	0.01704(9)
O1	0.5880(2)	0.25	0.5259(3)	0.0216(4)
O2	0.1390(2)	0.25	0.5780(2)	0.0188(4)
C1	0.4028(2)	0.3747(2)	0.1235(2)	0.0207(4)
C2	0.4134(3)	0.47261(19)	0.2274(3)	0.0245(4)
C3	0.2706(3)	0.25	0.5945(3)	0.0135(4)
C4	0.3327(3)	0.25	0.7407(3)	0.0197(5)

Bond lengths

Table S4. Bond lengths (Å) for **6**.

Re1-O1	1.691(2)	Re1-C3	2.077(3)
Re1-S2	2.2920(5)	Re1-S2	2.2920(5)
Re1-S1	2.3327(6)	S1-C1	1.809(2)
S1-C1	1.809(2)	S2-C2	1.836(2)
O2-C3	1.221(3)	C1-C2	1.514(4)
C1-H1A	0.99	C1-H1B	0.99
C2-H2A	0.99	C2-H2B	0.99
C3-C4	1.520(4)	C4-H4A	0.98
C4-H4B	0.98	C4-H4C	0.98

Bond angles

Table S5. Bond angles (°) for **6**.

O1-Re1-C3	104.63(11)	O1-Re1-S2	114.759(14)
C3-Re1-S2	82.79(3)	O1-Re1-S2	114.759(14)
C3-Re1-S2	82.79(3)	S2-Re1-S2	130.42(3)
O1-Re1-S1	106.03(9)	C3-Re1-S1	149.34(7)
S2-Re1-S1	84.483(15)	S2-Re1-S1	84.483(15)
C1-S1-C1	105.53(16)	C1-S1-Re1	108.56(7)
C1-S1-Re1	108.56(7)	C2-S2-Re1	105.06(7)
C2-C1-S1	106.47(16)	C2-C1-H1A	110.4
S1-C1-H1A	110.4	C2-C1-H1B	110.4
S1-C1-H1B	110.4	H1A-C1-H1B	108.6
C1-C2-S2	110.83(15)	C1-C2-H2A	109.5
S2-C2-H2A	109.5	C1-C2-H2B	109.5
S2-C2-H2B	109.5	H2A-C2-H2B	108.1
O2-C3-C4	119.5(2)	O2-C3-Re1	126.6(2)
C4-C3-Re1	113.89(19)	C3-C4-H4A	109.5
C3-C4-H4B	109.5	H4A-C4-H4B	109.5
C3-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5		

Torsion angles

Table S6. Torsion angles (°) for **6**.

C1-S1-C1-C2	154.01(11)	Re1-S1-C1-C2	37.78(16)
S1-C1-C2-S2	-54.39(18)	Re1-S2-C2-C1	46.44(18)

Anisotropic displacement parameters

Table S7. Anisotropic atomic displacement parameters ($Å^2$) for **6**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	0.00798(5)	0.01102(5)	0.01237(5)	0	-0.00002(3)	0
S1	0.0123(2)	0.0126(2)	0.0145(2)	0	0.00267(18)	0
S2	0.01895(19)	0.00994(17)	0.0222(2)	-0.00136(15)	0.00423(16)	0.00160(14)
O1	0.0112(8)	0.0346(13)	0.0189(9)	0	-0.0044(7)	0
O2	0.0123(8)	0.0284(11)	0.0157(8)	0	0.0011(6)	0
C1	0.0217(8)	0.0215(9)	0.0191(8)	0.0076(7)	0.0037(7)	0.0049(7)
C2	0.0280(10)	0.0133(8)	0.0322(11)	0.0067(7)	0.0095(8)	0.0008(7)
C3	0.0137(9)	0.0131(9)	0.0138(9)	0	0.0002(8)	0
C4	0.0185(11)	0.0268(14)	0.0139(11)	0	-0.0033(9)	0

Hydrogen atom coordinates and isotropic atomic displacement parameters

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **6**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1A	0.4542	0.3952	0.0367	0.025
H1B	0.2997	0.3583	0.1012	0.025
H2A	0.3614	0.5412	0.1911	0.029
H2B	0.5168	0.4939	0.2406	0.029
H4A	0.3423	0.1701	0.7736	0.03
H4B	0.2672	0.2927	0.8026	0.03
H4C	0.4285	0.2872	0.7403	0.03

Crystal Structure Report for 4

Crystal description
A lustrous brown block-like specimen of $C_{11}H_{15}OReS_3$, approximate dimensions 0.277 mm x 0.311 mm x 0.433 mm, was used for the X-ray crystallographic analysis. Instrument description The X-ray intensity data were measured.
Data collection

Table S9: Data collection details for **4**.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/
Phi	39.595	45.14	-314.79	-100.00	-23.00	0.50	512	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	-90.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	78.57	-36.90	-211.74	78.26	0.50	188	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	-135.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	135.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	3.85	-355.37	0.00	-54.74	0.50	205	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	-45.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	-180.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	90.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	-11.15	-114.43	270.00	54.74	0.50	205	10.00	0.71073	50	30.0
Omega	39.595	45.14	-313.07	45.00	-54.74	0.50	201	10.00	0.71073	50	30.0
Omega	39.595	-26.15	-129.43	153.00	54.74	0.50	205	10.00	0.71073	50	30.0

A total of 2722 frames were collected. The total exposure time was 7.56 hours. Integration The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 130975 reflections to a maximum θ angle of 40.44° (0.55 Å resolution), of which 17155 were independent (average redundancy 7.635, completeness = 99.8%, R_{int} = 2.83%, R_{sig} = 1.81%) and 15860 (92.45%) were greater than $2\sigma(F^2)$. Unit cell The final cell constants of a = 15.7482(7) Å, b = 9.5141(4) Å, c = 18.5449(8) Å, β = 103.734(2)°, volume = 2699.1(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 746 reflections above 20 σ(I) with 5.003° < 2θ < 68.95°. Scaling Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.640. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0688 and 0.2335.

Structure solution Structure refinement The final anisotropic full-matrix least-squares refinement on F^2 with 289 variables converged at R1 = 2.54%, for the observed data and wR2 = 5.34% for all data. The goodness-of-fit was 1.292. The largest peak in the final difference electron density synthesis was 3.084 $e^-/Å^3$ and the largest hole was -2.241 $e^-/Å^3$ with an RMS deviation of 0.161 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.193 g/cm^3 and F(000), 1696 e^-. Structure Packing.

Sample and crystal data

Table S10. Sample and crystal data for **4.**

Identification code	rds240
Chemical formula	$C_{11}H_{15}OReS_3$
Formula weight	445.61
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal size	0.277 x 0.311 x 0.433 mm
Crystal habit	lustrous brown block
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 15.7482(7) Å α = 90°
	b = 9.5141(4) Å β = 103.734(2)°
	c = 18.5449(8) Å γ = 90°
Volume	2699.1(2) $Å^3$
Z	8
Density (calculated)	2.193 g/cm^3
Absorption coefficient	9.444 mm^{-1}
F(000)	1696

Data collection and structure refinement

Table S11. Data collection and structure refinement for **4.**

Theta range for data collection	2.26 to 40.44°
Index ranges	-28<=h<=28, -17<=k<=17, -33<=l<=33
Reflections collected	130975
Independent reflections	17155 [R(int) = 0.0283]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.2335 and 0.0688
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	17155 / 0 / 289
Goodness-of-fit on F^2	1.292
Δ/σ_{max}	0.004
Final R indices	15860 data; I>2σ(I) R1 = 0.0254, wR2 = 0.0527
	all data R1 = 0.0289, wR2 = 0.0534
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0129P)^2+4.5608P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	3.084 and -2.241 eÅ^{-3}
R.M.S. deviation from mean	0.161 eÅ^{-3}

Atomic coordinates and equivalent isotropic displacement parameters

Table S12. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **4**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Re1	0.53406(2)	0.84972(2)	0.16180(2)	0.01109(10)
S1	0.63761(3)	0.87985(5)	0.09502(3)	0.01444(7)
S2	0.52296(3)	0.09439(5)	0.15433(3)	0.01360(7)
S3	0.38521(3)	0.85613(5)	0.11907(3)	0.01559(8)
O1	0.57159(11)	0.80628(18)	0.25189(8)	0.0191(3)
C1	0.66234(14)	0.0684(2)	0.09632(13)	0.0171(3)
C2	0.57918(14)	0.1533(2)	0.08476(12)	0.0164(3)
C3	0.40999(14)	0.1440(2)	0.11593(13)	0.0186(3)
C4	0.35227(15)	0.0337(2)	0.13900(13)	0.0198(4)
C5	0.51550(14)	0.6454(2)	0.10847(11)	0.0156(3)
C6	0.59651(13)	0.56238(19)	0.11020(11)	0.0141(3)
C7	0.62447(15)	0.5351(2)	0.04544(12)	0.0180(3)
C8	0.69808(17)	0.4522(2)	0.04703(15)	0.0232(4)
C9	0.74547(16)	0.3960(2)	0.11362(16)	0.0247(4)
C10	0.71916(16)	0.4240(2)	0.17890(15)	0.0230(4)
C11	0.64584(15)	0.5057(2)	0.17686(12)	0.0187(3)
Re2	0.46807(2)	0.41600(2)	0.32737(2)	0.01179(2)
S4	0.61720(3)	0.40299(5)	0.36342(3)	0.01513(8)
S5	0.47473(3)	0.17070(5)	0.33275(3)	0.01508(8)
S6	0.37036(3)	0.38933(5)	0.40020(3)	0.01629(8)
O2	0.42681(12)	0.46304(19)	0.23816(9)	0.0213(3)
C12	0.64570(14)	0.2237(2)	0.34115(13)	0.0203(4)
C13	0.58794(14)	0.1154(2)	0.36488(13)	0.0192(3)
C14	0.42508(15)	0.1138(2)	0.40693(13)	0.0187(3)
C15	0.34337(15)	0.2018(2)	0.39966(15)	0.0224(4)
C16	0.49251(14)	0.6189(2)	0.38192(11)	0.0158(3)
C17	0.41192(13)	0.7038(2)	0.37872(10)	0.0144(3)
C18	0.36666(15)	0.7664(2)	0.31194(11)	0.0182(3)
C19	0.29116(16)	0.8449(2)	0.30838(12)	0.0204(4)
C20	0.25902(15)	0.8628(2)	0.37169(13)	0.0189(3)
C21	0.30231(15)	0.7997(2)	0.43784(12)	0.0178(3)
C22	0.37789(14)	0.7215(2)	0.44125(11)	0.0154(3)

Bond lengths

Table S13. Bond lengths (Å) for **4**.

Re1-O1	1.6861(15)	Re1-C5	2.1694(19)
Re1-S1	2.2878(5)	Re1-S3	2.2901(5)
Re1-S2	2.3360(5)	S1-C1	1.834(2)
S2-C3	1.815(2)	S2-C2	1.818(2)
S3-C4	1.830(2)	C1-C2	1.510(3)
C1-H1A	0.99	C1-H1B	0.99
C2-H2A	0.99	C2-H2B	0.99
C3-C4	1.515(3)	C3-H3A	0.99
C3-H3B	0.99	C4-H4A	0.99
C4-H4B	0.99	C5-C6	1.494(3)
C5-H5A	0.99	C5-H5B	0.99
C6-C7	1.398(3)	C6-C11	1.402(3)
C7-C8	1.396(3)	C7-H7	0.95
C8-C9	1.389(4)	C8-H8	0.95
C9-C10	1.395(4)	C9-H9	0.95
C10-C11	1.385(3)	C10-H10	0.95
C11-H11	0.95	Re2-O2	1.6879(16)
Re2-C16	2.171(2)	Re2-S4	2.2874(5)
Re2-S6	2.2898(5)	Re2-S5	2.3372(5)
S4-C12	1.836(2)	S5-C13	1.818(2)
S5-C14	1.819(2)	S6-C15	1.834(2)
C12-C13	1.507(3)	C12-H12A	0.99
C12-H12B	0.99	C13-H13A	0.99
C13-H13B	0.99	C14-C15	1.514(3)
C14-H14A	0.99	C14-H14B	0.99
C15-H15A	0.99	C15-H15B	0.99
C16-C17	1.494(3)	C16-H16A	0.99
C16-H16B	0.99	C17-C22	1.398(3)
C17-C18	1.406(3)	C18-C19	1.392(3)
C18-H18	0.95	C19-C20	1.395(3)
C19-H19	0.95	C20-C21	1.390(3)
C20-H20	0.95	C21-C22	1.392(3)
C21-H21	0.95	C22-H22	0.95

Bond angles

Table S14. Bond angles (°) for **4**.

O1-Re1-C5	102.10(8)	O1-Re1-S1	116.10(6)
C5-Re1-S1	84.36(6)	O1-Re1-S3	116.01(6)
C5-Re1-S3	81.38(6)	S1-Re1-S3	127.730(19)
O1-Re1-S2	107.86(6)	C5-Re1-S2	149.99(5)
S1-Re1-S2	84.030(17)	S3-Re1-S2	84.082(18)
C1-S1-Re1	106.96(7)	C3-S2-C2	103.81(10)
C3-S2-Re1	109.56(7)	C2-S2-Re1	107.88(7)
C4-S3-Re1	105.70(8)	C2-C1-S1	110.31(14)
C2-C1-H1A	109.6	S1-C1-H1A	109.6
C2-C1-H1B	109.6	S1-C1-H1B	109.6
H1A-C1-H1B	108.1	C1-C2-S2	106.64(14)
C1-C2-H2A	110.4	S2-C2-H2A	110.4
C1-C2-H2B	110.4	S2-C2-H2B	110.4
H2A-C2-H2B	108.6	C4-C3-S2	107.90(15)
C4-C3-H3A	110.1	S2-C3-H3A	110.1
C4-C3-H3B	110.1	S2-C3-H3B	110.1
H3A-C3-H3B	108.4	C3-C4-S3	111.37(15)
C3-C4-H4A	109.4	S3-C4-H4A	109.4
C3-C4-H4B	109.4	S3-C4-H4B	109.4
H4A-C4-H4B	108.0	C6-C5-Re1	116.22(13)
C6-C5-H5A	108.2	Re1-C5-H5A	108.2
C6-C5-H5B	108.2	Re1-C5-H5B	108.2
H5A-C5-H5B	107.4	C7-C6-C11	117.7(2)
C7-C6-C5	121.40(18)	C11-C6-C5	120.90(18)
C8-C7-C6	121.1(2)	C8-C7-H7	119.5
C6-C7-H7	119.5	C9-C8-C7	120.3(2)
C9-C8-H8	119.9	C7-C8-H8	119.9
C8-C9-C10	119.4(2)	C8-C9-H9	120.3
C10-C9-H9	120.3	C11-C10-C9	120.0(2)
C11-C10-H10	120.0	C9-C10-H10	120.0
C10-C11-C6	121.6(2)	C10-C11-H11	119.2
C6-C11-H11	119.2	O2-Re2-C16	101.85(8)
O2-Re2-S4	115.49(6)	C16-Re2-S4	81.71(6)
O2-Re2-S6	116.83(6)	C16-Re2-S6	83.88(6)
S4-Re2-S6	127.501(19)	O2-Re2-S5	108.03(6)
C16-Re2-S5	150.09(5)	S4-Re2-S5	84.315(18)
S6-Re2-S5	83.907(18)	C12-S4-Re2	105.87(7)
C13-S5-C14	103.32(11)	C13-S5-Re2	109.47(7)
C14-S5-Re2	107.84(7)	C15-S6-Re2	106.97(8)
C13-C12-S4	111.87(15)	C13-C12-H12A	109.2
S4-C12-H12A	109.2	C13-C12-H12B	109.2
S4-C12-H12B	109.2	H12A-C12-H12B	107.9
C12-C13-S5	108.63(16)	C12-C13-H13A	110.0

S5-C13-H13A	110.0	C12-C13-H13B	110.0
S5-C13-H13B	110.0	H13A-C13-H13B	108.3
C15-C14-S5	106.09(15)	C15-C14-H14A	110.5
S5-C14-H14A	110.5	C15-C14-H14B	110.5
S5-C14-H14B	110.5	H14A-C14-H14B	108.7
C14-C15-S6	110.26(15)	C14-C15-H15A	109.6
S6-C15-H15A	109.6	C14-C15-H15B	109.6
S6-C15-H15B	109.6	H15A-C15-H15B	108.1
C17-C16-Re2	114.06(13)	C17-C16-H16A	108.7
Re2-C16-H16A	108.7	C17-C16-H16B	108.7
Re2-C16-H16B	108.7	H16A-C16-H16B	107.6
C22-C17-C18	117.75(19)	C22-C17-C16	121.44(17)
C18-C17-C16	120.80(18)	C19-C18-C17	121.2(2)
C19-C18-H18	119.4	C17-C18-H18	119.4
C18-C19-C20	120.12(19)	C18-C19-H19	119.9
C20-C19-H19	119.9	C21-C20-C19	119.4(2)
C21-C20-H20	120.3	C19-C20-H20	120.3
C20-C21-C22	120.4(2)	C20-C21-H21	119.8
C22-C21-H21	119.8	C21-C22-C17	121.24(19)
C21-C22-H22	119.4	C17-C22-H22	119.4

Torsion angles

Table S15. Torsion angles (°) for **4**.

Re1-S1-C1-C2	-42.36(16)	S1-C1-C2-S2	53.93(17)
C3-S2-C2-C1	-158.01(14)	Re1-S2-C2-C1	-41.81(15)
C2-S2-C3-C4	146.04(15)	Re1-S2-C3-C4	31.03(17)
S2-C3-C4-S3	-49.88(19)	Re1-S3-C4-C3	46.60(17)
Re1-C5-C6-C7	-112.41(18)	Re1-C5-C6-C11	69.4(2)
C11-C6-C7-C8	1.1(3)	C5-C6-C7-C8	-177.13(19)
C6-C7-C8-C9	-0.5(3)	C7-C8-C9-C10	-0.4(3)
C8-C9-C10-C11	0.7(3)	C9-C10-C11-C6	-0.1(3)
C7-C6-C11-C10	-0.8(3)	C5-C6-C11-C10	177.4(2)
Re2-S4-C12-C13	-45.25(17)	S4-C12-C13-S5	48.12(19)
C14-S5-C13-C12	-144.24(15)	Re2-S5-C13-C12	-29.55(16)
C13-S5-C14-C15	158.83(16)	Re2-S5-C14-C15	42.98(17)
S5-C14-C15-S6	-54.6(2)	Re2-S6-C15-C14	42.33(19)
Re2-C16-C17-C22	106.44(19)	Re2-C16-C17-C18	-72.2(2)
C22-C17-C18-C19	0.8(3)	C16-C17-C18-C19	179.5(2)
C17-C18-C19-C20	0.0(3)	C18-C19-C20-C21	-1.0(3)
C19-C20-C21-C22	1.1(3)	C20-C21-C22-C17	-0.3(3)
C18-C17-C22-C21	-0.7(3)	C16-C17-C22-C21	-179.39(19)

Anisotropic displacement parameters

Table S16. Anisotropic atomic displacement parameters ($Å^2$) for **4**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	0.01044(3)	0.01147(3)	0.01117(3)	0.00109(2)	0.00221(2)	-0.00135(2)
S1	0.01272(19)	0.01225(17)	0.01972(19)	0.00063(14)	0.00656(15)	-0.00067(14)
S2	0.01252(18)	0.01256(17)	0.01573(17)	-0.00127(13)	0.00336(14)	-0.00057(14)
S3	0.01116(18)	0.01665(19)	0.01872(19)	-0.00016(15)	0.00308(15)	-0.00208(15)
O1	0.0207(7)	0.0204(7)	0.0148(6)	0.0031(5)	0.0017(5)	-0.0022(6)
C1	0.0127(8)	0.0132(7)	0.0262(9)	0.0027(6)	0.0061(7)	-0.0018(6)
C2	0.0153(8)	0.0129(7)	0.0214(8)	0.0029(6)	0.0053(6)	-0.0011(6)
C3	0.0136(8)	0.0162(8)	0.0262(9)	0.0010(7)	0.0052(7)	0.0031(6)
C4	0.0136(8)	0.0194(9)	0.0275(10)	-0.0005(7)	0.0069(7)	0.0013(7)
C5	0.0155(8)	0.0115(7)	0.0192(7)	0.0009(6)	0.0028(6)	-0.0016(6)
C6	0.0158(8)	0.0098(6)	0.0163(7)	0.0011(5)	0.0033(6)	-0.0028(5)
C7	0.0233(10)	0.0134(7)	0.0192(8)	0.0002(6)	0.0088(7)	-0.0030(7)
C8	0.0256(11)	0.0157(8)	0.0329(11)	-0.0032(8)	0.0163(9)	-0.0049(7)
C9	0.0148(9)	0.0152(8)	0.0450(14)	-0.0019(8)	0.0088(9)	-0.0032(7)
C10	0.0178(9)	0.0162(8)	0.0315(11)	0.0029(7)	-0.0009(8)	-0.0009(7)
C11	0.0200(9)	0.0163(8)	0.0184(8)	0.0031(6)	0.0020(7)	-0.0001(7)
Re2	0.01029(3)	0.01355(3)	0.01108(3)	0.00075(2)	0.00166(2)	-0.00147(2)
S4	0.01097(18)	0.0182(2)	0.01632(18)	-0.00098(15)	0.00330(14)	-0.00253(15)
S5	0.01177(19)	0.01400(18)	0.01876(19)	-0.00367(14)	0.00220(15)	-0.00064(14)
S6	0.0144(2)	0.01283(18)	0.0241(2)	0.00064(15)	0.00938(17)	-0.00043(15)
O2	0.0219(8)	0.0254(8)	0.0143(6)	0.0023(5)	-0.0005(5)	-0.0023(6)

C12	0.0134(8)	0.0241(9)	0.0245(9)	-0.0077(7)	0.0065(7)	-0.0008(7)
C13	0.0125(8)	0.0172(8)	0.0266(9)	-0.0043(7)	0.0021(7)	0.0018(6)
C14	0.0158(8)	0.0136(7)	0.0277(9)	0.0019(7)	0.0074(7)	-0.0011(6)
C15	0.0165(9)	0.0132(8)	0.0403(12)	0.0025(8)	0.0126(8)	-0.0014(6)
C16	0.0153(8)	0.0140(7)	0.0177(7)	0.0017(6)	0.0032(6)	-0.0014(6)
C17	0.0157(8)	0.0116(7)	0.0148(7)	0.0014(5)	0.0015(6)	-0.0018(6)
C18	0.0210(9)	0.0174(8)	0.0153(7)	0.0045(6)	0.0028(6)	0.0002(7)
C19	0.0194(9)	0.0184(8)	0.0205(8)	0.0058(7)	-0.0009(7)	-0.0006(7)
C20	0.0145(8)	0.0146(8)	0.0261(9)	0.0010(6)	0.0020(7)	-0.0020(6)
C21	0.0173(9)	0.0167(8)	0.0194(8)	-0.0017(6)	0.0045(6)	-0.0024(6)
C22	0.0173(8)	0.0134(7)	0.0150(7)	-0.0001(5)	0.0027(6)	-0.0010(6)

Hydrogen atom coordinates and isotropic atomic displacement parameters

Table S17. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **4**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1A	0.7018	1.0936	0.1446	0.021
H1B	0.6926	1.0904	0.0566	0.021
H2A	0.5422	1.1375	0.0343	0.02
H2B	0.5928	1.2548	0.0909	0.02
H3A	0.3981	1.2373	0.1350	0.022
H3B	0.3981	1.1490	0.0611	0.022
H4A	0.2908	1.0498	0.1121	0.024
H4B	0.3558	1.0426	0.1928	0.024
H5A	0.4771	0.5888	0.1324	0.019
H5B	0.4843	0.6590	0.0559	0.019
H7	0.5929	0.5736	-0.0004	0.022
H8	0.7158	0.4342	0.0024	0.028
H9	0.7953	0.3391	0.1147	0.03
H10	0.7515	0.3869	0.2248	0.028
H11	0.6286	0.5238	0.2217	0.022
H12A	0.6400	0.2159	0.2870	0.024
H12B	0.7074	0.2046	0.3663	0.024
H13A	0.6032	0.1065	0.4196	0.023
H13B	0.5965	0.0228	0.3433	0.023
H14A	0.4101	0.0127	0.4017	0.022
H14B	0.4657	0.1292	0.4559	0.022
H15A	0.3161	0.1807	0.4414	0.027
H15B	0.3008	0.1779	0.3528	0.027
H16A	0.5226	0.6038	0.4346	0.019
H16B	0.5324	0.6733	0.3585	0.019
H18	0.3880	0.7548	0.2685	0.022
H19	0.2615	0.8863	0.2627	0.024
H20	0.2080	0.9175	0.3696	0.023
H21	0.2802	0.8101	0.4810	0.021
H22	0.4069	0.6794	0.4869	0.018

Crystal Structure Report for **2**

Crystal description
A light orange block-like specimen of $C_6H_{13}OReS_3$, approximate dimensions 0.062 mm x 0.198 mm x 0.198 mm, was used for the X-ray crystallographic analysis. Instrument description The X-ray intensity data were measured.
Data collection The total exposure time was 5.04 hours. Integration The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38793 reflections to a maximum θ angle of 38.00° (0.58 Å resolution), of which 5539 were independent (average redundancy 7.004, completeness = 99.6%, R_{int} = 3.18%, R_{sig} = 2.06%) and 5069 (91.51%) were greater than $2\sigma(F^2)$. Unit cell The final cell constants of a = 7.2497(3) Å, b = 18.0720(7) Å, c = 8.0726(3) Å, β = 104.951(2)°, volume = 1021.84(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 242 reflections above 20 σ(I) with 4.512° < 2θ < 65.69°. Scaling Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.297.

Structure solution Structure refinement The final anisotropic full-matrix least-squares refinement on F^2 with 101 variables converged at R1 = 2.18%, for the observed data and wR2 = 4.30% for all data. The goodness-of-fit was 1.071. The largest peak in the final difference electron density synthesis was 3.079 $e^-/Å^3$ and the largest hole was -1.702 $e^-/Å^3$ with an RMS deviation of 0.161 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.493 g/cm^3 and F(000), 720 e^-. Structure Packing Sample and crystal data

Data collection and structure refinement

Table S18. Data collection and structure refinement for **2**.

Theta range for data collection	2.25 to 38.00°
Index ranges	-12<=h<=11, -31<=k<=31, -13<=l<=13
Reflections collected	38793
Independent reflections	5539 [R(int) = 0.0318]
Coverage of independent reflections	99.6%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5539 / 0 / 101
Goodness-of-fit on F^2	1.071
Δ/σ_{max}	0.003
Final R indices	5069 data; I>2σ(I) R1 = 0.0218, wR2 = 0.0420
	all data R1 = 0.0257, wR2 = 0.0430
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0158P)^2+1.4364P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	3.079 and -1.702 eÅ^{-3}
R.M.S. deviation from mean	0.161 eÅ^{-3}

Atomic coordinates and equivalent isotropic displacement parameters

Table S19. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **2**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Re1	0.30650(2)	0.34175(2)	0.82402(2)	0.01193(2)
S1	0.16705(7)	0.43813(3)	0.93085(6)	0.01387(8)
S2	0.51370(7)	0.33950(3)	0.10090(7)	0.01510(8)
S3	0.58208(8)	0.34492(3)	0.73564(8)	0.01839(9)
O1	0.1808(2)	0.26199(9)	0.7879(2)	0.0200(3)
C1	0.2610(3)	0.43668(13)	0.1645(3)	0.0174(4)
C2	0.4747(3)	0.42321(13)	0.2133(3)	0.0176(4)
C3	0.7582(3)	0.34716(12)	0.0816(3)	0.0204(4)
C4	0.7642(3)	0.30787(13)	0.9176(3)	0.0222(4)
C5	0.2006(3)	0.39774(13)	0.5822(3)	0.0195(4)
C6	0.9839(3)	0.40478(15)	0.5239(3)	0.0247(5)

Bond lengths

Table S20. Bond lengths (Å) for **2**.

Re1-O1	1.6901(15)	Re1-C5	2.157(2)
Re1-S3	2.2890(5)	Re1-S1	2.2911(5)
Re1-S2	2.3498(6)	S1-C1	1.833(2)
S2-C2	1.823(2)	S2-C3	1.824(2)
S3-C4	1.830(3)	C1-C2	1.516(3)
C1-H1A	0.99	C1-H1B	0.99
C2-H2A	0.99	C2-H2B	0.99
C3-C4	1.513(3)	C3-H3A	0.99
C3-H3B	0.99	C4-H4A	0.99
C4-H4B	0.99	C5-C6	1.525(3)
C5-H5A	0.99	C5-H5B	0.99
C6-H6A	0.98	C6-H6B	0.98
C6-H6C	0.98		

Bond angles

Table S21. Bond angles (°) for **2**.

O1-Re1-C5	101.16(9)	O1-Re1-S3	116.27(6)
C5-Re1-S3	80.88(6)	O1-Re1-S1	116.28(6)
C5-Re1-S1	84.01(6)	S3-Re1-S1	127.138(19)
O1-Re1-S2	109.47(6)	C5-Re1-S2	149.33(6)
S3-Re1-S2	84.36(2)	S1-Re1-S2	83.743(18)
C1-S1-Re1	107.07(7)	C2-S2-C3	104.96(10)
C2-S2-Re1	108.41(7)	C3-S2-Re1	108.33(8)
C4-S3-Re1	104.33(8)	C2-C1-S1	110.68(14)
C2-C1-H1A	109.5	S1-C1-H1A	109.5
C2-C1-H1B	109.5	S1-C1-H1B	109.5
H1A-C1-H1B	108.1	C1-C2-S2	106.45(15)
C1-C2-H2A	110.4	S2-C2-H2A	110.4
C1-C2-H2B	110.4	S2-C2-H2B	110.4
H2A-C2-H2B	108.6	C4-C3-S2	106.66(15)
C4-C3-H3A	110.4	S2-C3-H3A	110.4
C4-C3-H3B	110.4	S2-C3-H3B	110.4
H3A-C3-H3B	108.6	C3-C4-S3	110.69(15)
C3-C4-H4A	109.5	S3-C4-H4A	109.5
C3-C4-H4B	109.5	S3-C4-H4B	109.5
H4A-C4-H4B	108.1	C6-C5-Re1	114.59(15)
C6-C5-H5A	108.6	Re1-C5-H5A	108.6
C6-C5-H5B	108.6	Re1-C5-H5B	108.6
H5A-C5-H5B	107.6	C5-C6-H6A	109.5
C5-C6-H6B	109.5	H6A-C6-H6B	109.5
C5-C6-H6C	109.5	H6A-C6-H6C	109.5
H6B-C6-H6C	109.5		

Torsion angles

Table S22. Torsion angles (°) for **2**.

Re1-S1-C1-C2	43.53(17)	S1-C1-C2-S2	-53.32(18)
C3-S2-C2-C1	155.43(15)	Re1-S2-C2-C1	39.84(15)
C2-S2-C3-C4	-149.09(16)	Re1-S2-C3-C4	-33.44(17)
S2-C3-C4-S3	54.48(18)	Re1-S3-C4-C3	-50.81(16)

Anisotropic displacement parameters

Table S23. Anisotropic atomic displacement parameters ($Å^2$) for **2**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	0.01308(3)	0.00980(3)	0.01459(4)	-0.00118(2)	0.00661(2)	-0.00081(2)
S1	0.01556(19)	0.01424(19)	0.0124(2)	-0.00012(15)	0.00474(16)	0.00346(15)
S2	0.01426(19)	0.01277(18)	0.0190(2)	0.00358(17)	0.00553(16)	0.00146(16)
S3	0.0183(2)	0.0171(2)	0.0237(2)	-0.00374(18)	0.01257(19)	-0.00158(17)
O1	0.0200(7)	0.0146(6)	0.0270(8)	-0.0030(6)	0.0088(6)	-0.0041(5)
C1	0.0190(9)	0.0227(9)	0.0122(8)	-0.0003(7)	0.0073(7)	0.0035(7)
C2	0.0183(9)	0.0213(9)	0.0131(8)	-0.0019(7)	0.0036(7)	0.0006(7)
C3	0.0134(8)	0.0191(9)	0.0281(11)	0.0008(8)	0.0043(8)	0.0013(7)
C4	0.0167(9)	0.0180(9)	0.0343(12)	-0.0045(8)	0.0107(9)	0.0014(7)
C5	0.0242(10)	0.0212(9)	0.0137(9)	-0.0014(7)	0.0061(8)	-0.0019(8)
C6	0.0221(10)	0.0288(11)	0.0200(10)	0.0003(9)	-0.0006(8)	-0.0057(9)

Hydrogen atom coordinates and isotropic atomic displacement parameters

Table S24. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **2**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1A	0.2335	0.4845	1.2128	0.021
H1B	0.1969	0.3971	1.2136	0.021
H2A	0.5224	0.4165	1.3388	0.021
H2B	0.5423	0.4657	1.1782	0.021
H3A	0.7942	0.3998	1.0767	0.024
H3B	0.8480	0.3237	1.1812	0.024
H4A	0.7421	0.2543	0.9293	0.027
H4B	0.8919	0.3142	0.8967	0.027
H5A	0.2570	0.4479	0.5912	0.023
H5B	0.2450	0.3706	0.4931	0.023
H6A	-0.0737	0.3554	0.5113	0.037
H6B	-0.0523	0.4306	0.4135	0.037
H6C	-0.0616	0.4329	0.6094	0.037

Crystal Structure Report for 3

Crystal description
A red-brown block-like specimen of $C_{10}H_{13}OReS_3$, approximate dimensions 0.233 mm x 0.359 mm x 0.428 mm, was used for the X-ray crystallographic analysis. Instrument description The X-ray intensity data were measured.
Data collection The total exposure time was 2.37 hours. Integration The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 68136 reflections to a maximum θ angle of 37.91° (0.58 Å resolution), of which 6680 were independent (average redundancy 10.200, completeness = 100.0%, R_{int} = 3.59%, R_{sig} = 1.97%) and 6168 (92.34%) were greater than $2\sigma(F^2)$. Unit cell The final cell constants of a = 8.2013(3) Å, b = 15.5245(5) Å, c = 9.8861(3) Å, β = 101.121(2)°, volume = 1235.07(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 479 reflections above 20 σ(I) with 4.972° < 2θ < 68.85°. Scaling Data were corrected for absorption effects using the numerical method (SADABS). The ratio of minimum to maximum apparent transmission was 0.268. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0960 and 0.1970.

Structure solution Structure refinement The final anisotropic full-matrix least-squares refinement on F^2 with 136 variables converged at R1 = 1.97%, for the observed data and wR2 = 4.26% for all data. The goodness-of-fit was 1.135. The largest peak in the final difference electron density synthesis was 2.002 $e^-/Å^3$ and the largest hole was -1.627 $e^-/Å^3$ with an RMS deviation of 0.150 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.321 g/cm^3 and F(000), 816 e^-. Structure Packing Sample and crystal data

Table S25. Sample and crystal data for **3**.

Identification code	rds234	
Chemical formula	$C_{10}H_{13}OReS_3$	
Formula weight	431.58	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.233 x 0.359 x 0.428 mm	
Crystal habit	red-brown block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.2013(3) Å	α = 90°
	b = 15.5245(5) Å	β = 101.121(2)°
	c = 9.8861(3) Å	γ = 90°
Volume	1235.07(7) $Å^3$	
Z	4	
Density (calculated)	2.321 g/cm^3	
Absorption coefficient	10.316 mm^{-1}	
F(000)	816	

Data collection and structure refinement

Table S26. Data collection and structure refinement for **3**.

Theta range for data collection	2.48 to 37.91°
Index ranges	-14<=h<=11, -26<=k<=26, -17<=l<=16
Reflections collected	68136
Independent reflections	6680 [R(int) = 0.0359]
Coverage of independent reflections	100.0%
Absorption correction	numerical
Max. and min. transmission	0.1970 and 0.0960
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6680 / 0 / 136
Goodness-of-fit on F^2	1.135
Δ/σ_{max}	0.001
Final R indices	6168 data; I>2σ(I) R1 = 0.0197, wR2 = 0.0419
	all data R1 = 0.0229, wR2 = 0.0426
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0151P)^2+1.5071P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.002 and -1.627 eÅ^{-3}
R.M.S. deviation from mean	0.150 eÅ^{-3}

Atomic coordinates and equivalent isotropic displacement parameters

Table S27. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for 3.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Re1	0.79012(2)	0.06356(2)	0.13499(2)	0.00888(2)
S1	0.61063(6)	0.16906(3)	0.17269(5)	0.01358(7)
S2	0.61404(5)	0.97177(3)	0.22927(5)	0.01159(7)
S3	0.99709(6)	0.00054(3)	0.29225(5)	0.01263(7)
O1	0.7781(2)	0.03556(10)	0.96888(14)	0.0172(3)
C1	0.4245(2)	0.11570(12)	0.2102(2)	0.0178(3)
C2	0.4712(2)	0.03849(13)	0.3032(2)	0.0172(3)
C3	0.7368(2)	0.91711(13)	0.3783(2)	0.0156(3)
C4	0.9072(2)	0.90166(12)	0.3470(2)	0.0154(3)
C5	0.9574(2)	0.16815(11)	0.15494(17)	0.0111(3)
C6	0.0078(2)	0.21551(12)	0.27657(18)	0.0134(3)
C7	0.1174(2)	0.28431(12)	0.2838(2)	0.0161(3)
C8	0.1794(2)	0.30866(12)	0.1682(2)	0.0182(3)
C9	0.1312(3)	0.26324(13)	0.0463(2)	0.0183(3)
C10	0.0223(2)	0.19376(13)	0.03893(19)	0.0158(3)

Bond lengths

Table S28. Bond lengths (Å) for **3**.

Re1-O1	1.6831(14)	Re1-C5	2.1101(17)
Re1-S1	2.2803(4)	Re1-S3	2.2886(5)
Re1-S2	2.3461(4)	S1-C1	1.836(2)
S2-C2	1.819(2)	S2-C3	1.825(2)
S3-C4	1.8296(19)	C1-C2	1.514(3)
C1-H1A	0.99	C1-H1B	0.99
C2-H2A	0.99	C2-H2B	0.99
C3-C4	1.508(3)	C3-H3A	0.99
C3-H3B	0.99	C4-H4A	0.99
C4-H4B	0.99	C5-C6	1.402(2)
C5-C10	1.411(2)	C6-C7	1.389(3)
C6-H6	0.95	C7-C8	1.390(3)
C7-H7	0.95	C8-C9	1.386(3)
C8-H8	0.95	C9-C10	1.393(3)
C9-H9	0.95	C10-H10	0.95

Bond angles

Table S29. Bond angles (°) for **3**.

O1-Re1-C5	101.81(7)	O1-Re1-S1	115.26(5)
C5-Re1-S1	81.99(5)	O1-Re1-S3	116.66(5)
C5-Re1-S3	83.21(5)	S1-Re1-S3	127.852(17)
O1-Re1-S2	107.82(5)	C5-Re1-S2	150.36(5)
S1-Re1-S2	84.555(16)	S3-Re1-S2	84.443(16)
C1-S1-Re1	107.28(6)	C2-S2-C3	103.78(10)
C2-S2-Re1	107.88(6)	C3-S2-Re1	108.50(6)
C4-S3-Re1	105.75(6)	C2-C1-S1	110.91(13)
C2-C1-H1A	109.5	S1-C1-H1A	109.5
C2-C1-H1B	109.5	S1-C1-H1B	109.5
H1A-C1-H1B	108.0	C1-C2-S2	108.31(14)
C1-C2-H2A	110.0	S2-C2-H2A	110.0
C1-C2-H2B	110.0	S2-C2-H2B	110.0
H2A-C2-H2B	108.4	C4-C3-S2	107.28(13)
C4-C3-H3A	110.3	S2-C3-H3A	110.3
C4-C3-H3B	110.3	S2-C3-H3B	110.3
H3A-C3-H3B	108.5	C3-C4-S3	111.69(13)
C3-C4-H4A	109.3	S3-C4-H4A	109.3
C3-C4-H4B	109.3	S3-C4-H4B	109.3
H4A-C4-H4B	107.9	C6-C5-C10	117.01(16)
C6-C5-Re1	124.23(12)	C10-C5-Re1	118.75(13)
C7-C6-C5	121.88(17)	C7-C6-H6	119.1
C5-C6-H6	119.1	C6-C7-C8	120.19(18)
C6-C7-H7	119.9	C8-C7-H7	119.9
C9-C8-C7	119.20(18)	C9-C8-H8	120.4
C7-C8-H8	120.4	C8-C9-C10	120.80(18)
C8-C9-H9	119.6	C10-C9-H9	119.6
C9-C10-C5	120.92(18)	C9-C10-H10	119.5
C5-C10-H10	119.5		

Torsion angles

Table S30. Torsion angles (°) for **3**.

Re1-S1-C1-C2	41.20(16)	S1-C1-C2-S2	-50.74(17)
C3-S2-C2-C1	152.61(14)	Re1-S2-C2-C1	37.63(15)
C2-S2-C3-C4	-149.18(14)	Re1-S2-C3-C4	-34.64(15)
S2-C3-C4-S3	51.87(16)	Re1-S3-C4-C3	-45.71(15)
C10-C5-C6-C7	-0.4(3)	Re1-C5-C6-C7	-179.51(14)
C5-C6-C7-C8	0.6(3)	C6-C7-C8-C9	-0.3(3)
C7-C8-C9-C10	-0.2(3)	C8-C9-C10-C5	0.4(3)
C6-C5-C10-C9	-0.1(3)	Re1-C5-C10-C9	179.04(15)

Anisotropic displacement parameters

Table S31. Anisotropic atomic displacement parameters (Å^2) for **3**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	0.00975(3)	0.00811(3)	0.00848(3)	-0.00053(2)	0.00104(2)	-0.00032(2)
S1	0.01303(18)	0.00925(16)	0.01833(19)	-0.00049(14)	0.00271(15)	0.00123(13)
S2	0.00985(17)	0.01018(16)	0.01446(17)	0.00003(13)	0.00161(14)	-0.00098(13)
S3	0.00929(17)	0.01324(17)	0.01508(18)	0.00274(14)	0.00164(14)	0.00063(13)
O1	0.0221(7)	0.0178(6)	0.0114(5)	-0.0023(5)	0.0023(5)	-0.0018(5)
C1	0.0096(7)	0.0150(7)	0.0285(10)	-0.0020(7)	0.0029(7)	0.0015(6)
C2	0.0132(8)	0.0153(7)	0.0247(9)	-0.0006(7)	0.0075(7)	-0.0004(6)
C3	0.0135(8)	0.0176(7)	0.0156(8)	0.0050(6)	0.0023(6)	-0.0013(6)
C4	0.0144(8)	0.0121(7)	0.0196(8)	0.0042(6)	0.0033(6)	0.0022(6)
C5	0.0110(7)	0.0111(6)	0.0112(6)	0.0009(5)	0.0026(5)	-0.0010(5)
C6	0.0138(7)	0.0131(7)	0.0132(7)	-0.0008(5)	0.0026(6)	-0.0023(6)
C7	0.0126(8)	0.0127(7)	0.0220(8)	-0.0037(6)	0.0007(6)	-0.0007(6)
C8	0.0120(7)	0.0123(7)	0.0306(10)	0.0026(7)	0.0049(7)	-0.0010(6)
C9	0.0150(8)	0.0192(8)	0.0218(9)	0.0068(7)	0.0062(7)	-0.0005(6)
C10	0.0159(8)	0.0184(8)	0.0140(7)	0.0021(6)	0.0050(6)	-0.0011(6)

Hydrogen atom coordinates and isotropic atomic displacement parameters

Table S32. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **3**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1A	0.3604	0.1571	0.2555	0.021
H1B	0.3530	0.0968	0.1229	0.021
H2A	0.3705	0.0051	0.3105	0.021
H2B	0.5248	0.0577	0.3967	0.021
H3A	0.7447	-0.0467	0.4618	0.019
H3B	0.6841	-0.1383	0.3947	0.019
H4A	0.8995	-0.1421	0.2733	0.018
H4B	0.9812	-0.1212	0.4303	0.018
H6	0.9658	0.2001	0.3563	0.016
H7	1.1501	0.3148	0.3680	0.019
H8	1.2540	0.3559	0.1727	0.022
H9	1.1729	0.2797	-0.0331	0.022
H10	0.9913	0.1632	-0.0454	0.019

Crystal Structure Report for 7

Crystal description
A red-brown block-like specimen of $C_7H_{13}O_2ReS_3$, approximate dimensions 0.241 mm x 0.256 mm x 0.275 mm, was used for the X-ray crystallographic analysis. Instrument description The X-ray intensity data were measured.
Data collection The total exposure time was 2.28 hours. Integration The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59081 reflections to a maximum θ angle of 35.17° (0.62 Å resolution), of which 10204 were independent (average redundancy 5.790, completeness = 99.6%, R_{int} = 3.20%, R_{sig} = 2.29%) and 9209 (90.25%) were greater than $2\sigma(F^2)$. Unit cell The final cell constants of a = 10.6520(4) Å, b = 14.5211(6) Å, c = 14.9039(6) Å, β = 94.2600(10)°, volume = 2298.95(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 616 reflections above 20 σ(I) with 5.591° < 2θ < 67.67°. Scaling Data were corrected for absorption effects using the numerical method (SADABS). The ratio of minimum to maximum apparent transmission was 0.533. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5986 and 0.7469.

Structure solution The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 8 for the formula unit, $C_7H_{13}O_2ReS_3$. Structure refinement The final anisotropic full-matrix least-squares refinement on F^2 with 237 variables converged at R1 = 2.02%, for the observed data and wR2 = 4.06% for all data. The goodness-of-fit was 1.074. The largest peak in the final difference electron density synthesis was 1.387 $e^-/Å^3$ and the largest hole was -0.922 $e^-/Å^3$ with an RMS deviation of 0.143 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.378 g/cm^3 and F(000), 1552 e^-. Structure Packing Sample and crystal data

Table S33. Sample and crystal data for **7**.

Identification code	rds293
Chemical formula	$C_7H_{13}O_2ReS_3$
Formula weight	411.55 g/mol
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal size	0.241 x 0.256 x 0.275 mm
Crystal habit	red-brown block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 10.6520(4) Å α = 90°
	b = 14.5211(6) Å β = 94.2600(10)°
	c = 14.9039(6) Å γ = 90°
Volume	2298.95(16) $Å^3$
Z	8
Density (calculated)	2.378 g/cm^3
Absorption coefficient	11.083 mm^{-1}
F(000)	1552

Data collection and structure refinement

Table S34. Data collection and structure refinement for **7**.

Theta range for data collection	1.92 to 35.17°
Index ranges	-16<=h<=17, -23<=k<=23, -24<=l<=24
Reflections collected	59081
Independent reflections	10204 [R(int) = 0.0320]
Coverage of independent reflections	99.6%
Absorption correction	numerical
Max. and min. transmission	0.7469 and 0.5986
Structure solution technique	direct methods
Structure solution program	XT (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	10204 / 0 / 237
Goodness-of-fit on F^2	1.074
Δ/σ_{max}	0.002
Final R indices	9209 data; I>2σ(I) R1 = 0.0202, wR2 = 0.0397
	all data R1 = 0.0245, wR2 = 0.0406
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0144P)^2+1.8390P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.387 and -0.922 eÅ^{-3}
R.M.S. deviation from mean	0.143 eÅ^{-3}

Atomic coordinates and equivalent isotropic displacement parameters

Table S35. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **7**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Re1	0.42183(2)	0.51220(2)	0.14977(2)	0.01234(2)
S1	0.49125(5)	0.51688(4)	0.29900(4)	0.01804(10)
S2	0.24072(5)	0.58386(3)	0.19825(4)	0.01486(9)
S3	0.28183(5)	0.41378(4)	0.07662(4)	0.01606(9)
O1	0.49098(15)	0.58704(11)	0.08195(11)	0.0194(3)
O2	0.51337(16)	0.32011(11)	0.17803(13)	0.0238(4)
C1	0.3861(2)	0.59602(16)	0.35365(16)	0.0209(4)
C2	0.2508(2)	0.57975(15)	0.32053(16)	0.0190(4)
C3	0.1063(2)	0.51164(15)	0.16494(16)	0.0180(4)
C4	0.1281(2)	0.47029(16)	0.07487(16)	0.0195(4)
C5	0.5395(2)	0.39607(15)	0.15143(15)	0.0159(4)
C6	0.6696(2)	0.41487(16)	0.11758(16)	0.0197(4)
C7	0.7296(2)	0.32956(18)	0.0811(2)	0.0287(5)
Re2	0.08106(2)	0.27078(2)	0.38930(2)	0.01227(2)
S4	0.00307(5)	0.27048(4)	0.24217(4)	0.01684(9)
S5	0.25611(5)	0.19785(4)	0.33238(4)	0.01659(10)
S6	0.23015(6)	0.36288(4)	0.46285(4)	0.02044(11)
O3	0.00768(16)	0.19707(11)	0.45641(11)	0.0199(3)
O4	0.99680(17)	0.46174(12)	0.35339(14)	0.0277(4)
C8	0.0984(2)	0.18874(16)	0.18233(16)	0.0223(4)
C9	0.2366(2)	0.20054(16)	0.21016(17)	0.0216(4)
C10	0.3913(2)	0.27181(16)	0.35885(18)	0.0223(5)
C11	0.3826(2)	0.30654(18)	0.45328(18)	0.0251(5)
C12	0.9746(2)	0.39251(16)	0.39366(16)	0.0192(4)
C13	0.8594(2)	0.38595(18)	0.44774(19)	0.0279(5)
C14	0.7475(3)	0.3489(3)	0.3912(2)	0.0409(7)

Bond lengths

Table S36. Bond lengths (Å) for **7**.

Re1-O1	1.6899(15)	Re1-C5	2.100(2)
Re1-S3	2.2832(5)	Re1-S1	2.2922(6)
Re1-S2	2.3524(5)	S1-C1	1.837(2)
S2-C3	1.814(2)	S2-C2	1.819(2)
S3-C4	1.830(2)	O2-C5	1.212(3)
C1-C2	1.508(3)	C1-H1A	0.99
C1-H1B	0.99	C2-H2A	0.99
C2-H2B	0.99	C3-C4	1.504(3)
C3-H3A	0.99	C3-H3B	0.99
C4-H4A	0.99	C4-H4B	0.99
C5-C6	1.534(3)	C6-C7	1.513(3)
C6-H6A	0.99	C6-H6B	0.99
C7-H7A	0.98	C7-H7B	0.98
C7-H7C	0.98	Re2-O3	1.6951(15)
Re2-C12	2.104(2)	Re2-S4	2.2864(6)
Re2-S6	2.2920(6)	Re2-S5	2.3565(5)
S4-C8	1.836(2)	S5-C10	1.816(2)
S5-C9	1.818(3)	S6-C11	1.833(3)
O4-C12	1.203(3)	C8-C9	1.509(4)
C8-H8A	0.99	C8-H8B	0.99
C9-H9A	0.99	C9-H9B	0.99
C10-C11	1.504(4)	C10-H10A	0.99
C10-H10B	0.99	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.520(3)
C13-C14	1.507(4)	C13-H13A	0.99
C13-H13B	0.99	C14-H14A	0.98
C14-H14B	0.98	C14-H14C	0.98

Bond angles

Table S37. Bond angles (°) for **7**.

O1-Re1-C5	103.72(8)	O1-Re1-S3	114.53(6)
C5-Re1-S3	82.60(6)	O1-Re1-S1	115.96(6)
C5-Re1-S1	82.13(6)	S3-Re1-S1	129.35(2)
O1-Re1-S2	107.64(6)	C5-Re1-S2	148.64(6)
S3-Re1-S2	84.380(19)	S1-Re1-S2	84.36(2)
C1-S1-Re1	106.59(8)	C3-S2-C2	103.99(11)
C3-S2-Re1	107.99(7)	C2-S2-Re1	107.74(8)
C4-S3-Re1	106.15(7)	C2-C1-S1	110.88(15)
C2-C1-H1A	109.5	S1-C1-H1A	109.5
C2-C1-H1B	109.5	S1-C1-H1B	109.5
H1A-C1-H1B	108.1	C1-C2-S2	107.86(16)
C1-C2-H2A	110.1	S2-C2-H2A	110.1
C1-C2-H2B	110.1	S2-C2-H2B	110.1
H2A-C2-H2B	108.4	C4-C3-S2	107.69(15)
C4-C3-H3A	110.2	S2-C3-H3A	110.2
C4-C3-H3B	110.2	S2-C3-H3B	110.2
H3A-C3-H3B	108.5	C3-C4-S3	111.33(16)
C3-C4-H4A	109.4	S3-C4-H4A	109.4
C3-C4-H4B	109.4	S3-C4-H4B	109.4
H4A-C4-H4B	108.0	O2-C5-C6	120.32(19)
O2-C5-Re1	125.69(16)	C6-C5-Re1	113.96(14)
C7-C6-C5	112.85(19)	C7-C6-H6A	109.0
C5-C6-H6A	109.0	C7-C6-H6B	109.0
C5-C6-H6B	109.0	H6A-C6-H6B	107.8
C6-C7-H7A	109.5	C6-C7-H7B	109.5
H7A-C7-H7B	109.5	C6-C7-H7C	109.5
H7A-C7-H7C	109.5	H7B-C7-H7C	109.5
O3-Re2-C12	103.83(8)	O3-Re2-S4	114.46(6)
C12-Re2-S4	82.70(7)	O3-Re2-S6	114.82(6)
C12-Re2-S6	81.43(7)	S4-Re2-S6	130.49(2)
O3-Re2-S5	109.91(6)	C12-Re2-S5	146.26(6)
S4-Re2-S5	83.96(2)	S6-Re2-S5	84.01(2)
C8-S4-Re2	107.00(8)	C10-S5-C9	103.57(12)
C10-S5-Re2	106.97(8)	C9-S5-Re2	108.44(8)
C11-S6-Re2	106.78(9)	C9-C8-S4	110.89(16)
C9-C8-H8A	109.5	S4-C8-H8A	109.5
C9-C8-H8B	109.5	S4-C8-H8B	109.5
H8A-C8-H8B	108.0	C8-C9-S5	108.04(16)
C8-C9-H9A	110.1	S5-C9-H9A	110.1
C8-C9-H9B	110.1	S5-C9-H9B	110.1
H9A-C9-H9B	108.4	C11-C10-S5	107.37(16)
C11-C10-H10A	110.2	S5-C10-H10A	110.2
C11-C10-H10B	110.2	S5-C10-H10B	110.2

H10A-C10-H10B	108.5	C10-C11-S6	109.80(17)
C10-C11-H11A	109.7	S6-C11-H11A	109.7
C10-C11-H11B	109.7	S6-C11-H11B	109.7
H11A-C11-H11B	108.2	O4-C12-C13	120.9(2)
O4-C12-Re2	124.06(17)	C13-C12-Re2	114.96(16)
C14-C13-C12	111.2(2)	C14-C13-H13A	109.4
C12-C13-H13A	109.4	C14-C13-H13B	109.4
C12-C13-H13B	109.4	H13A-C13-H13B	108.0
C13-C14-H14A	109.5	C13-C14-H14B	109.5
H14A-C14-H14B	109.5	C13-C14-H14C	109.5
H14A-C14-H14C	109.5	H14B-C14-H14C	109.5

Torsion angles

Table S38. Torsion angles (°) for **7**.

Re1-S1-C1-C2	42.90(18)	S1-C1-C2-S2	-52.55(19)
C3-S2-C2-C1	152.92(15)	Re1-S2-C2-C1	38.47(16)
C2-S2-C3-C4	-150.70(16)	Re1-S2-C3-C4	-36.43(16)
S2-C3-C4-S3	52.33(18)	Re1-S3-C4-C3	-44.49(17)
O2-C5-C6-C7	26.8(3)	Re1-C5-C6-C7	-154.93(18)
Re2-S4-C8-C9	-43.73(18)	S4-C8-C9-S5	51.18(19)
C10-S5-C9-C8	-149.41(16)	Re2-S5-C9-C8	-36.02(17)
C9-S5-C10-C11	156.30(16)	Re2-S5-C10-C11	41.86(17)
S5-C10-C11-S6	-55.16(19)	Re2-S6-C11-C10	43.61(18)
O4-C12-C13-C14	90.8(3)	Re2-C12-C13-C14	-85.6(3)

Anisotropic displacement parameters

Table S39. Anisotropic atomic displacement parameters ($Å^2$) for **7**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	0.01247(3)	0.01016(3)	0.01458(4)	0.00076(3)	0.00218(3)	-0.00139(2)
S1	0.0178(2)	0.0178(2)	0.0180(2)	-0.00194(19)	-0.00207(19)	-0.00040(18)
S2	0.0154(2)	0.01055(19)	0.0187(2)	0.00015(17)	0.00244(18)	-0.00006(16)
S3	0.0171(2)	0.0142(2)	0.0169(2)	-0.00257(18)	0.00142(18)	-0.00169(17)
O1	0.0195(7)	0.0159(7)	0.0233(8)	0.0032(6)	0.0051(6)	-0.0033(6)
O2	0.0218(8)	0.0167(7)	0.0343(10)	0.0041(7)	0.0107(7)	0.0023(6)
C1	0.0225(11)	0.0200(10)	0.0202(11)	-0.0065(8)	0.0008(8)	-0.0029(8)
C2	0.0219(10)	0.0166(9)	0.0191(10)	-0.0039(8)	0.0058(8)	-0.0018(8)
C3	0.0139(9)	0.0167(9)	0.0234(11)	0.0001(8)	0.0010(8)	-0.0010(7)
C4	0.0173(10)	0.0190(10)	0.0213(11)	0.0004(8)	-0.0038(8)	-0.0006(8)
C5	0.0154(9)	0.0163(9)	0.0163(9)	0.0004(7)	0.0033(7)	0.0003(7)
C6	0.0165(9)	0.0208(10)	0.0222(11)	0.0041(8)	0.0051(8)	0.0004(8)
C7	0.0220(12)	0.0237(11)	0.0416(16)	0.0057(11)	0.0112(11)	0.0071(9)
Re2	0.01379(4)	0.01183(3)	0.01153(3)	0.00171(3)	0.00327(3)	-0.00084(2)
S4	0.0169(2)	0.0194(2)	0.0141(2)	0.00052(18)	0.00069(18)	0.00027(18)
S5	0.0154(2)	0.0128(2)	0.0219(3)	0.00435(18)	0.00389(19)	0.00124(17)
S6	0.0234(3)	0.0216(3)	0.0164(2)	-0.0016(2)	0.0015(2)	-0.0067(2)
O3	0.0222(8)	0.0207(7)	0.0177(8)	0.0050(6)	0.0062(6)	-0.0029(6)
O4	0.0280(9)	0.0181(8)	0.0384(11)	0.0039(7)	0.0125(8)	0.0028(7)
C8	0.0287(12)	0.0206(10)	0.0181(10)	-0.0049(8)	0.0057(9)	-0.0038(9)
C9	0.0238(11)	0.0184(10)	0.0240(11)	-0.0005(8)	0.0113(9)	0.0033(8)
C10	0.0135(9)	0.0207(10)	0.0330(13)	0.0056(9)	0.0038(9)	-0.0012(8)
C11	0.0183(10)	0.0294(12)	0.0267(12)	0.0078(10)	-0.0043(9)	-0.0061(9)
C12	0.0175(10)	0.0193(10)	0.0217(11)	0.0028(8)	0.0080(8)	0.0021(8)
C13	0.0291(13)	0.0243(11)	0.0327(14)	-0.0042(10)	0.0186(11)	0.0023(9)
C14	0.0217(13)	0.060(2)	0.0421(18)	-0.0007(15)	0.0077(12)	0.0040(13)

Hydrogen atom coordinates and isotropic atomic displacement parameters

Table S40. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **7**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1A	0.3961	0.5869	0.4196	0.025
H1B	0.4096	0.6604	0.3407	0.025
H2A	0.1963	0.6278	0.3444	0.023
H2B	0.2225	0.5189	0.3412	0.023
H3A	0.0975	0.4624	0.2100	0.022
H3B	0.0282	0.5488	0.1606	0.022
H4A	0.1234	0.5193	0.0286	0.023
H4B	0.0612	0.4248	0.0584	0.023
H6A	0.6612	0.4621	0.0697	0.024
H6B	0.7256	0.4400	0.1677	0.024
H7A	0.7405	0.2831	0.1287	0.043
H7B	0.8118	0.3455	0.0600	0.043
H7C	0.6752	0.3049	0.0308	0.043
H8A	0.0724	0.1250	0.1956	0.027
H8B	0.0838	0.1988	0.1167	0.027
H9A	0.2671	0.2600	0.1876	0.026
H9B	0.2857	0.1503	0.1847	0.026
H10A	0.4703	0.2368	0.3545	0.027
H10B	0.3906	0.3241	0.3162	0.027
H11A	0.4515	0.3509	0.4686	0.03
H11B	0.3919	0.2545	0.4961	0.03
H13A	-0.1218	0.3450	0.5002	0.033
H13B	-0.1610	0.4478	0.4706	0.033
H14A	-0.2691	0.3879	0.3380	0.061
H14B	-0.3264	0.3487	0.4266	0.061
H14C	-0.2348	0.2859	0.3722	0.061

Crystal Structure Report for 9

Crystal description
A brown plate-like specimen of $C_{12}H_{16}O_4Re_2S_6$, approximate dimensions 0.041 mm x 0.143 mm x 0.246 mm, was used for the X-ray crystallographic analysis. Instrument description The X-ray intensity data were measured.
Data collection The total exposure time was 9.26 hours. Integration The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 68912 reflections to a maximum θ angle of 36.41° (0.60 Å resolution), of which 9359 were independent (average redundancy 7.363, completeness = 99.9%, R_{int} = 4.19%, R_{sig} = 2.79%) and 7930 (84.73%) were greater than $2\sigma(F^2)$. Unit cell The final cell constants of a = 11.6120(5) Å, b = 8.9891(4) Å, c = 19.1466(9) Å, β = 106.025(2)°, volume = 1920.89(15) $Å^3$, are based upon the refinement of the XYZ-centroids of 321 reflections above 20 σ(I) with 5.040° < 2θ < 62.46°. Scaling Data were corrected for absorption effects using the numerical method (SADABS). The ratio of minimum to maximum apparent transmission was 0.279. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.1390 and 0.6120.

Structure solution Structure refinement The final anisotropic full-matrix least-squares refinement on F^2 with 217 variables converged at R1 = 2.30%, for the observed data and wR2 = 4.72% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 2.556 $e^-/Å^3$ and the largest hole was -1.041 $e^-/Å^3$ with an RMS deviation of 0.205 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.728 g/cm^3 and F(000), 1464 e^-.

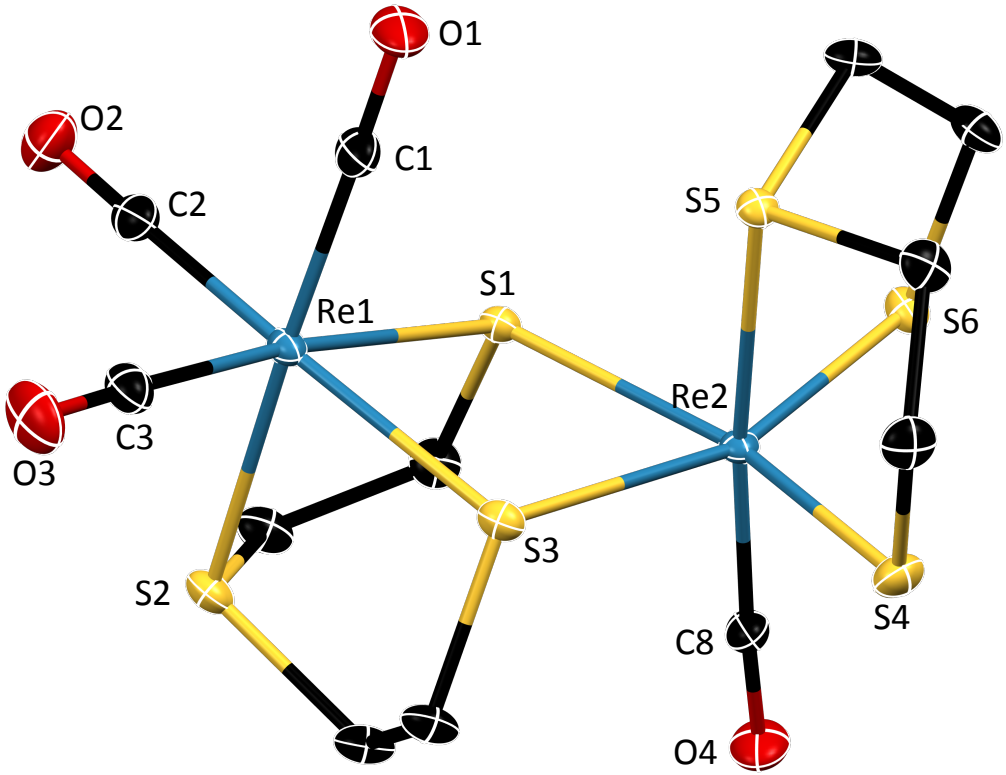

Figure S1. Thermal ellipsoid plot (50% ellipsoids) for **9**.

Structure Packing Sample and Crystal Data.

Table S41. Sample and crystal data for **9**.

Identification code	rds306
Chemical formula	$C_{12}H_{16}O_4Re_2S_6$
Formula weight	789.01 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.041 x 0.143 x 0.246 mm
Crystal habit	brown plate
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 11.6120(5) Å α = 90°
	b = 8.9891(4) Å β = 106.025(2)°
	c = 19.1466(9) Å γ = 90°
Volume	1920.89(15) $Å^3$
Z	4
Density (calculated)	2.728 g/cm^3
Absorption coefficient	13.258 mm^{-1}
F(000)	1464

Data collection and structure refinement

Table S42. Data collection and structure refinement for **9**.

Theta range for data collection	2.21 to 36.41°
Index ranges	-19<=h<=17, -15<=k<=15, -31<=l<=30
Reflections collected	68912
Independent reflections	9359 [R(int) = 0.0419]
Coverage of independent reflections	99.9%
Absorption correction	numerical
Max. and min. transmission	0.6120 and 0.1390
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	9359 / 0 / 217
Goodness-of-fit on F^2	1.046
Δ/σ_{max}	0.002
Final R indices	7930 data; I>2σ(I) R1 = 0.0230, wR2 = 0.0447
	all data R1 = 0.0328, wR2 = 0.0472
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0205P)^2+0.9555P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.556 and -1.041 eÅ^{-3}
R.M.S. deviation from mean	0.205 eÅ^{-3}

Atomic coordinates and equivalent isotropic displacement parameters

Table S43. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **9**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Re1	0.40157(2)	0.20622(2)	0.07629(2)	0.01129(2)
Re2	0.14219(2)	0.25216(2)	0.16299(2)	0.00999(2)
S1	0.18632(5)	0.27260(6)	0.04122(3)	0.01118(10)
S2	0.43046(6)	0.47597(7)	0.07798(4)	0.01498(11)
S3	0.36795(5)	0.24367(6)	0.19691(3)	0.01248(10)
S4	0.15889(6)	0.23001(7)	0.28316(4)	0.01750(12)
S5	0.16060(5)	0.97892(6)	0.16232(3)	0.01151(10)
S6	0.94542(5)	0.22031(6)	0.10279(4)	0.01415(11)
O1	0.34451(19)	0.8718(2)	0.06762(13)	0.0278(5)
O2	0.40416(19)	0.1928(2)	0.91559(12)	0.0261(4)
O3	0.67263(18)	0.1498(3)	0.13533(13)	0.0308(5)
O4	0.09870(19)	0.5839(2)	0.17452(12)	0.0248(4)
C1	0.3675(2)	0.9970(3)	0.07271(16)	0.0180(5)
C2	0.4055(2)	0.1968(3)	0.97589(15)	0.0179(5)
C3	0.5708(2)	0.1691(3)	0.11261(15)	0.0189(5)
C4	0.1814(2)	0.4691(3)	0.01352(14)	0.0156(4)
C5	0.2987(2)	0.5313(3)	0.00650(14)	0.0174(5)
C6	0.3960(2)	0.5430(3)	0.16014(14)	0.0176(5)
C7	0.4295(2)	0.4293(3)	0.22140(14)	0.0178(5)
C8	0.1177(2)	0.4582(3)	0.16926(14)	0.0158(4)
C9	0.2021(2)	0.0375(3)	0.30701(14)	0.0185(5)
C10	0.1357(2)	0.9299(3)	0.24934(13)	0.0173(5)
C11	0.0199(2)	0.9231(3)	0.09910(14)	0.0159(4)
C12	0.9154(2)	0.0205(3)	0.10240(15)	0.0168(5)

Bond lengths

Table S44. Bond lengths (Å) for **9**.

Re1-C1	1.919(3)	Re1-C3
Re1-C2	1.937(3)	Re1-S2
Re1-S3	2.4691(6)	Re1-S1
Re2-C8	1.883(2)	Re2-S4
Re2-S6	2.2753(6)	Re2-S5
Re2-S3	2.5219(6)	Re2-S1
S1-C4	1.841(2)	S2-C5
S2-C6	1.829(3)	S3-C7
S4-C9	1.825(3)	S5-C11
S5-C10	1.822(2)	S6-C12
O1-C1	1.155(3)	O2-C2
O3-C3	1.155(3)	O4-C8
C4-C5	1.512(4)	C4-H4A
C4-H4B	0.99	C5-H5A
C5-H5B	0.99	C6-C7
C6-H6A	0.99	C6-H6B
C7-H7A	0.99	C7-H7B
C9-C10	1.509(4)	C9-H9A
C9-H9B	0.99	C10-H10A
C10-H10B	0.99	C11-C12
C11-H11A	0.99	C11-H11B
C12-H12A	0.99	C12-H12B

Bond angles

Table S45. Bond angles (°) for **9**.

C1-Re1-C3	91.31(11)	C1-Re1-C2	89.01(11)
C3-Re1-C2	92.86(11)	C1-Re1-S2	176.14(8)
C3-Re1-S2	92.55(8)	C2-Re1-S2	90.90(8)
C1-Re1-S3	94.75(8)	C3-Re1-S3	95.45(8)
C2-Re1-S3	170.79(8)	S2-Re1-S3	84.78(2)
C1-Re1-S1	92.51(8)	C3-Re1-S1	173.65(8)
C2-Re1-S1	92.28(8)	S2-Re1-S1	83.64(2)
S3-Re1-S1	79.18(2)	C8-Re2-S4	89.65(8)
C8-Re2-S6	90.45(8)	S4-Re2-S6	107.22(2)
C8-Re2-S5	174.33(8)	S4-Re2-S5	86.24(2)
S6-Re2-S5	87.04(2)	C8-Re2-S3	100.24(8)
S4-Re2-S3	86.81(2)	S6-Re2-S3	162.50(2)
S5-Re2-S3	83.440(19)	C8-Re2-S1	93.43(8)
S4-Re2-S1	164.02(2)	S6-Re2-S1	88.44(2)
S5-Re2-S1	91.584(18)	S3-Re2-S1	77.22(2)
C4-S1-Re1	104.95(8)	C4-S1-Re2	109.72(8)
Re1-S1-Re2	100.30(2)	C5-S2-C6	102.65(12)
C5-S2-Re1	100.21(8)	C6-S2-Re1	106.03(8)
C7-S3-Re1	102.31(9)	C7-S3-Re2	110.13(9)
Re1-S3-Re2	100.65(2)	C9-S4-Re2	106.16(9)
C11-S5-C10	101.67(12)	C11-S5-Re2	102.43(8)
C10-S5-Re2	101.55(8)	C12-S6-Re2	106.82(8)
O1-C1-Re1	177.2(3)	O2-C2-Re1	177.9(2)
O3-C3-Re1	178.4(3)	C5-C4-S1	115.04(17)
C5-C4-H4A	108.5	S1-C4-H4A	108.5
C5-C4-H4B	108.5	S1-C4-H4B	108.5
H4A-C4-H4B	107.5	C4-C5-S2	115.06(18)
C4-C5-H5A	108.5	S2-C5-H5A	108.5
C4-C5-H5B	108.5	S2-C5-H5B	108.5
H5A-C5-H5B	107.5	C7-C6-S2	111.78(18)
C7-C6-H6A	109.3	S2-C6-H6A	109.3
C7-C6-H6B	109.3	S2-C6-H6B	109.3
H6A-C6-H6B	107.9	C6-C7-S3	114.65(17)
C6-C7-H7A	108.6	S3-C7-H7A	108.6
C6-C7-H7B	108.6	S3-C7-H7B	108.6
H7A-C7-H7B	107.6	O4-C8-Re2	177.0(2)
C10-C9-S4	112.01(18)	C10-C9-H9A	109.2
S4-C9-H9A	109.2	C10-C9-H9B	109.2
S4-C9-H9B	109.2	H9A-C9-H9B	107.9
C9-C10-S5	109.66(17)	C9-C10-H10A	109.7
S5-C10-H10A	109.7	C9-C10-H10B	109.7
S5-C10-H10B	109.7	H10A-C10-H10B	108.2
C12-C11-S5	113.42(17)	C12-C11-H11A	108.9

S5-C11-H11A	108.9	C12-C11-H11B	108.9
S5-C11-H11B	108.9	H11A-C11-H11B	107.7
C11-C12-S6	114.47(17)	C11-C12-H12A	108.6
S6-C12-H12A	108.6	C11-C12-H12B	108.6
S6-C12-H12B	108.6	H12A-C12-H12B	107.6

Torsion angles

Table S46. Torsion angles (°) for **9**.

Re1-S1-C4-C5	9.7(2)	Re2-S1-C4-C5	116.67(18)
S1-C4-C5-S2	-41.9(3)	C6-S2-C5-C4	-58.4(2)
Re1-S2-C5-C4	50.8(2)	C5-S2-C6-C7	137.21(18)
Re1-S2-C6-C7	32.5(2)	S2-C6-C7-S3	-52.5(2)
Re1-S3-C7-C6	43.4(2)	Re2-S3-C7-C6	-62.9(2)
Re2-S4-C9-C10	-40.7(2)	S4-C9-C10-S5	56.5(2)
C11-S5-C10-C9	-147.82(18)	Re2-S5-C10-C9	-42.36(19)
C10-S5-C11-C12	69.8(2)	Re2-S5-C11-C12	-34.97(19)
S5-C11-C12-S6	46.6(2)	Re2-S6-C12-C11	-32.9(2)

Anisotropic displacement parameters

Table S47. Anisotropic atomic displacement parameters ($Å^2$) for **9**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	0.00943(4)	0.00856(4)	0.01592(4)	-0.00054(3)	0.00356(3)	0.00006(3)
Re2	0.01110(4)	0.00665(4)	0.01230(4)	-0.00030(3)	0.00336(3)	0.00051(3)
S1	0.0105(2)	0.0104(2)	0.0118(2)	-0.00053(18)	0.00167(19)	-0.00086(17)
S2	0.0138(3)	0.0116(2)	0.0183(3)	0.0009(2)	0.0025(2)	-0.0036(2)
S3	0.0115(2)	0.0107(2)	0.0133(3)	0.00083(19)	0.00009(19)	0.00033(18)
S4	0.0217(3)	0.0177(3)	0.0139(3)	-0.0034(2)	0.0062(2)	0.0008(2)
S5	0.0126(2)	0.0086(2)	0.0132(3)	0.00147(18)	0.0034(2)	0.00116(18)
S6	0.0113(3)	0.0106(2)	0.0201(3)	0.0030(2)	0.0036(2)	0.00146(19)
O1	0.0297(11)	0.0119(8)	0.0470(14)	-0.0055(9)	0.0189(10)	-0.0020(8)
O2	0.0252(11)	0.0322(11)	0.0228(11)	-0.0034(9)	0.0096(9)	0.0034(8)
O3	0.0128(9)	0.0309(11)	0.0471(14)	0.0035(10)	0.0057(9)	0.0028(8)
O4	0.0316(11)	0.0101(8)	0.0368(12)	-0.0017(8)	0.0163(10)	0.0031(7)
C1	0.0151(11)	0.0154(11)	0.0254(13)	-0.0013(9)	0.0086(10)	0.0019(8)
C2	0.0145(11)	0.0160(11)	0.0238(13)	-0.0034(9)	0.0061(9)	0.0011(9)
C3	0.0168(12)	0.0149(10)	0.0259(13)	0.0002(10)	0.0071(10)	-0.0009(9)
C4	0.0180(11)	0.0125(10)	0.0153(11)	0.0048(8)	0.0030(9)	0.0027(8)
C5	0.0199(12)	0.0138(10)	0.0160(12)	0.0029(9)	0.0007(9)	-0.0018(9)
C6	0.0215(12)	0.0115(10)	0.0168(12)	-0.0023(9)	0.0003(9)	-0.0024(9)
C7	0.0194(12)	0.0151(11)	0.0155(12)	-0.0028(9)	-0.0007(9)	-0.0046(9)
C8	0.0154(11)	0.0129(10)	0.0208(12)	-0.0024(9)	0.0079(9)	0.0003(8)
C9	0.0221(13)	0.0204(12)	0.0117(11)	0.0023(9)	0.0024(9)	0.0008(9)
C10	0.0212(12)	0.0162(11)	0.0137(11)	0.0053(9)	0.0036(9)	-0.0007(9)
C11	0.0195(12)	0.0101(9)	0.0156(11)	-0.0015(8)	0.0009(9)	-0.0013(8)
C12	0.0141(11)	0.0116(10)	0.0226(13)	0.0018(9)	0.0016(9)	-0.0025(8)

Hydrogen atom coordinates and isotropic atomic displacement parameters

Table S48. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **9**.

	x/a	**y/b**	**z/c**	**U(eq)**
H4A	0.1203	0.4802	-0.0338	0.019
H4B	0.1551	0.5296	0.0495	0.019
H5A	0.2936	0.6412	0.0059	0.021
H5B	0.3094	0.4993	-0.0408	0.021
H6A	0.4403	0.6366	0.1763	0.021
H6B	0.3093	0.5650	0.1489	0.021
H7A	0.4015	0.4661	0.2626	0.021
H7B	0.5179	0.4217	0.2383	0.021
H9A	0.2893	0.0264	0.3138	0.022
H9B	0.1854	0.0128	0.3537	0.022
H10A	0.0490	-0.0665	0.2454	0.021
H10B	0.1645	-0.1726	0.2629	0.021
H11A	0.0286	-0.0741	0.0491	0.019
H11B	0.0022	-0.1808	0.1097	0.019
H12A	-0.1083	-0.0048	0.1468	0.02
H12B	-0.1534	-0.0026	0.0601	0.02

ADDITIONAL EXPERIMENTAL DATA

[(SSS)Re(O)CH_3], 1. An alternative to the original synthesis by Shan and coworkers (*Inorg. Chem.* **2003,** *42*, 2362-2367) was utilized for the synthesis of **1**. Methyl trioxorhenium (111 mg, 0.447 mmol) and triphenylphosphine (117 mg, 0.447 mmol) was added to a 25.0 mL scintillation vial and dissolved in a minimal amount of methylene chloride. 2, 2'-Thiodiethanethiol (58 μL, 0.45 mmol) was added via syringe to the reaction mixture. The mixture was left to stand for 24 h undisturbed. The resulting red crystals were filtered and washed with diethyl ether (~10mL) to afford **1** in a 52% yield (90.3 mg, 0.244 mmol).

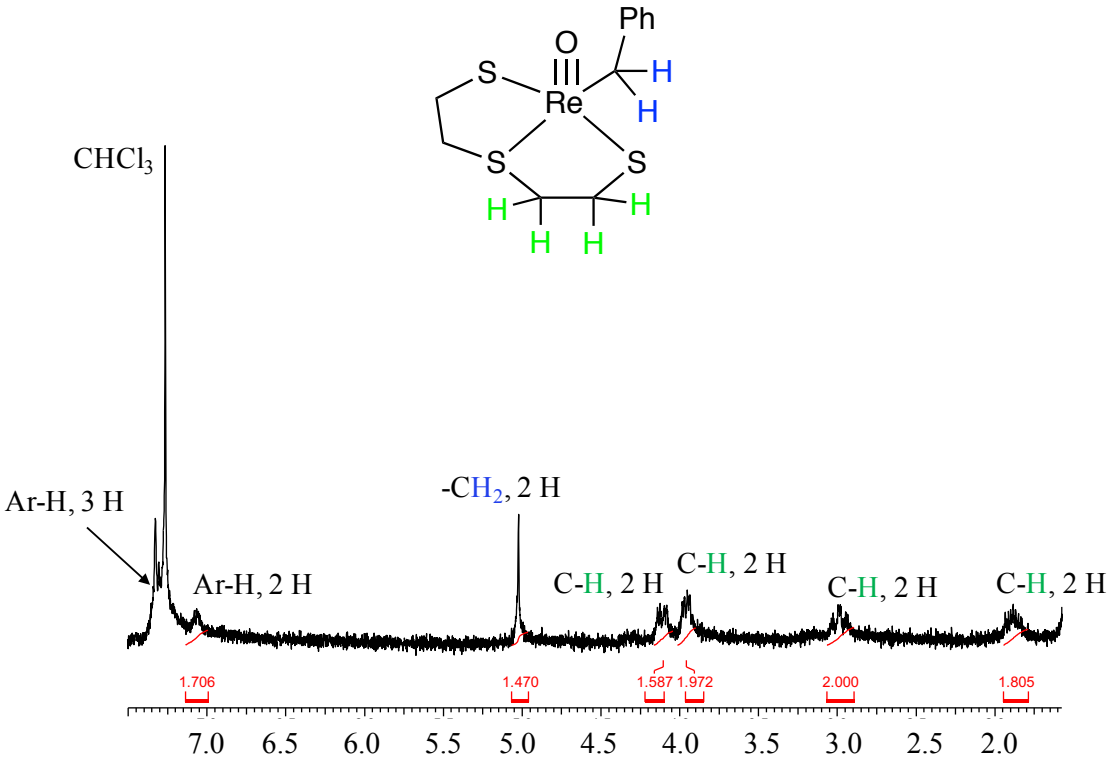

Figure S2. ^{1}H NMR spectrum of **4** in $CDCl_3$.

Full Gaussian09 Citation

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