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Rhenium complexes containing 1,1′-ferrocene dithiolato and diselenolato chelate ligands [1]

Max Herberhold *, Guo-Xin Jin, Wolfgang Milius

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

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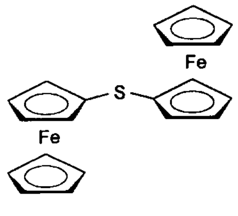
Abstract

The reactions of the rhenium(V) dihalides $TpRe(O)Cl_2$, $Cp^*Re(O)Cl_2$ and $Cp^*Re(N^tBu)Cl_2$ with the dilithium derivative of 1,1′-ferrocene dithiol and diselenol, respectively, have been used to prepare heterodimetallic complexes which contain both rhenium (in the center of a half-sandwich complex) and iron (in the sandwich cage). The six new complexes were characterized by IR, ^1H and ^{13}C NMR spectroscopy and by EI mass spectrometry. The molecular structure of $TpRe(O)[S_2fc]$ (**1a**) was determined by X-ray crystallography which revealed a long non-bonding distance (438.9 pm) between the two metals. (Abbreviations: Cp^* = η^5-pentamethylcyclopentadienyl, η^5-C_5Me_5; Tp = hydrido-tris(1-pyrazolyl)borate, $HB(C_3H_3N_2)_3$; Tp^* = hydrido-tris(3,5-dimethyl-1-pyrazolyl) borate, $HB(C_3H(Me_2)N_2)_3$; fc = 1,1′-ferrocenylene, $Fe(C_5H_4\text{-})_2$; ^tBu = tert-butyl, C_4H_9-.)

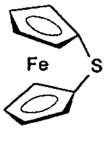
Keywords: Rhenium; Iron; Ferrocenophanes; Heterodimetallic complexes; X-ray diffraction

1. Introduction

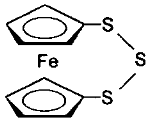
A number of ferrocene derivatives with sulfur as the only heteroelement have been described [1,2]. The prototype, diferrocenyl sulfane, SFc_2, was first reported in 1961 by M.D. Rausch [3]. Cycles such as 1-thia-[1]ferrocenophane, fc[S] [4], and 1,2,3-trithia-[3]ferrocenophane, $fc[S_3]$ [5–8], have attracted interest as potential precursors for polymers containing both ferrocene units and sulfur [9].



SFc_2



fc[S]



$fc[S_3]$

Although 1,2-dithia-[2]ferrocenophane, $fc[S_2]$, has not been characterized as a monomeric species so far [8], the dianion 1,1′-ferrocene dithiolate, fcS_2^{2-}, is a versatile chelate ligand by which transition metals can be brought close to the sandwich iron. A series of complexes containing a metal complex fragment in the central bridge position of 1,3-dichalcogena-2-metalla-[3]ferrocenophanes has been studied by X-ray crystallography (Table 1). With the exception of the palladium and platinum-triphenylphosphane complexes, $fc[S_2M(PPh_3)]$ (M = Pd, Pt), the dimetallic compounds show long metal–metal distances which clearly exclude the possibility of bonding interactions between the sandwich iron and the transition metal (M) at the center of the triatomic EME bridge.

In the present paper, we describe the first 1,3-dichalcogena-2-metalla-[3]ferrocenophanes containing rhenium in the bridge.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

The dilithium salts of 1,1′-ferrocene dithiol and 1,1′-ferrocene diselenol, $fc(SLi)_2$ and $fc(SeLi)_2$, react with

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* Corresponding author.

[1] Dedicated to Professor Marvin D. Rausch on the occasion of his 65th birthday.

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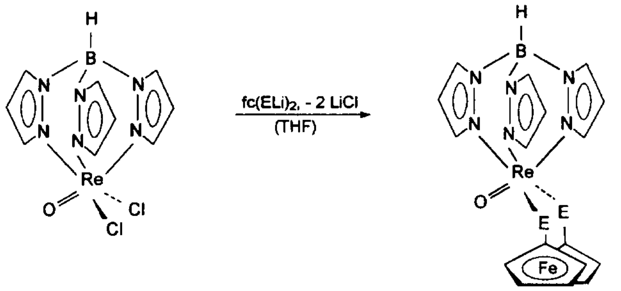
the dichlororhenium complex, TpRe(O)Cl_2, in THF solution to give the heterodimetallic products **1a** and **1b** in which the dianionic ligand fcE_2^{2-} (E = S, Se) has replaced two chloro ligands. The products **1a** and **1b** may be considered as 1,3-dichalcogena-[2]ferrocenophanes with rhenium from the 14-electron fragment [TpRe(O)] occupying the center of the bent triatomic bridge.

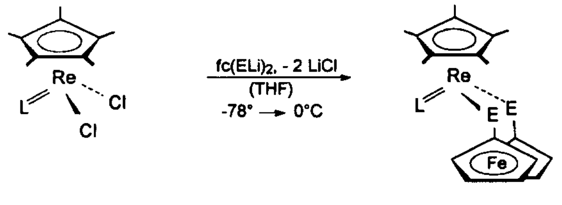


TpRe(O)Cl_2

1a: TpRe(O)[S_2fc]
1b: TpRe(O)[Se_2fc]

The green complexes **1a** and **1b** are air-stable in the solid state. Diagnostic IR absorptions are ν(B–H) around 2500 cm^{-1} and ν(Re=O) around 950 cm^{-1}. The ^1H and ^{13}C NMR solution spectra are consistent with the presence of a mirror plane which contains the metals Fe and Re and the oxo ligand and bisects the Tp and fcE_2 ligands. Two of the three 1-pyrazolyl rings of the tripodal Tp ligand are equivalent. The molecular geometry of **1a** in the solid state has been determined by an X-ray crystal structure analysis.

Similar to TpRe(O)Cl_2, the half-sandwich pentamethylcyclopentadienyl complexes Cp*Re(L)Cl_2 (L = O, N^tBu) may be used to incorporate a dianionic 1,1′-ferrocene dichalcogenate unit, fcE_2 (E = S, Se), into the coordination sphere of rhenium.



Cp*(L)Cl_2
L = O or N^tBu

2a : Cp*Re(O)[S_2fc]
2b : Cp*Re(O)[Se_2fc]

3a : Cp*Re(N^tBu)[S_2fc]
3b : Cp*Re(N^tBu)[Se_2fc]

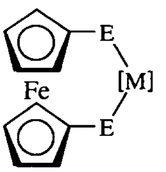
The IR spectra of **2a**, **2b**, **3a** and **3b** contain the strong band of the ν(CH_3) vibration of the Cp* ring ligand near 1380 cm^{-1} and either the intensive oxo absorption ν(Re=O) above 900 cm^{-1} or the strong tert-butylimido bands at 1360 and 1253 cm^{-1} which are typical of the terminal two-electron ligand L.

The ν(Re=O) frequency may be used to estimate the charge transfer from the voluminous Tp and Cp* ligands to the metal rhenium (Table 2). Apparently, the Cp* ring induces a higher charge density at Re than the tripod ligand Tp, both in the 1,1′-ferrocene dichalcogenate complexes **1a** and **1b** or **2a** and **2b** and in the comparable tetrachalcogenido complexes **1c** and **1d** or **2c** and **2d**.

In the ^1H NMR spectra (in $CDCl_3$ solution) of all complexes **1a,b–3a,b**, the 1,1′-ferrocene dichalcogenate ligand shows the pattern of a $[ABCD]_2$ spin system with four non-equivalent ring protons, and five cyclopentadienyl carbon signals are observed in the ^{13}C NMR spectra. The complexes are rigid at room temperature on the NMR time-scale.

Attempts to attach two 1,1′-ferrocene dichalcogenate ligands to rhenium by using Cp*$ReCl_4$ [20] as the educt were not successful, although the synthesis of a salt (PPh_4)[Re(O)(S_2fc)$_2$] has been reported [21] starting from ReOCl_3(PPh_3)$_2$ and fc(SH)$_2$. The reaction of

Table 1
Interatomic distances, d(Fe ··· M), in 1,3-dichalcogena-2-metalla-[3]ferrocenophanes

	E	[M]	d(Fe ··· M)	Ref.
	Se	V(O)Cp*	401.4(2)	[10]
	S	Mo(NO)Tp*	414.7(2)	[11]
	S	Re(O)Tp (**1a**)	438.9	[a]
	Se	$FeCl_2$	387	[12]
	S	Ru(CO)(C_6Me_6)	434.9	[13]
	S	Os(NO)Cp*	431.1	[17]
	S	Rh(PMe_3)Cp*	430.4(1)	[14]
	S	Pd(PPh_3)	287.8(1)	[15]
	S	Pt(PPh_3)	293.5(2)	[16]

[a] This work.

Table 2
IR frequency (cm^{-1}) of the terminal rhenium–oxo vibration

1a	TpRe(O)[S_2fc]	953	**1c**	TpRe(O)[S_4]	932	[17]
1b	TpRe(O)[Se_2fc]	946	**1d**	TpRe(O)[Se_4]	928	[17]
2a	Cp*Re(O)[S_2fc]	913	**2c**	Cp*Re(O)[S_4]	904	[18,19]
2b	Cp*Re(O)[Se_2fc]	931	**2d**	Cp*Re(O)[Se_4]	907	[19]

Cp*$ReCl_4$ with two equivalents of fc$(ELi)_2$ (E = S, Se) in THF solution and subsequent chromatography over silica gave Cp*Re(O)[E_2fc] (**2a**, **2b**); the analogous reaction of Cp*$ReCl_4$ with four equivalents of PhELi (E = S, Se) in THF produced Cp*Re(O)$(EPh)_2$ in high yields [22] after the final chromatography over silica by which the oxo ligand is introduced.

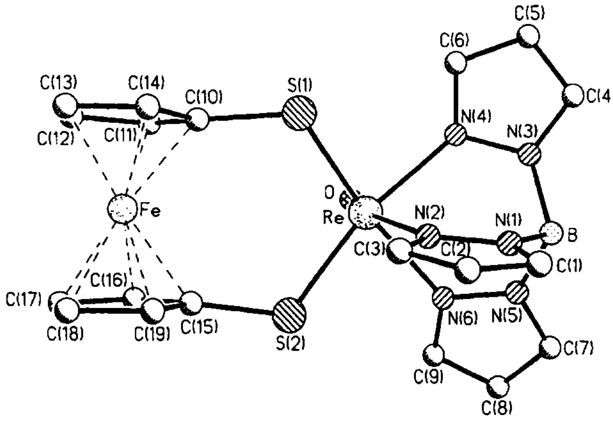


Fig. 1. Molecular structure of TpRe(O)[S_2fc] (**1a**).

2.2. Molecular structure of TpRe(O)[S_2fc] (1a)

The molecular geometry of **1a** is presented in Fig. 1, and some relevant interatomic distances and angles are collected in Table 3 [28].

To a first approximation, the molecule **1a** is bisected by a plane which includes the atoms Fe, Re, O and B, although it is not a symmetry plane in the solid state. The coordination geometry around rhenium(V) (d^2) corresponds to that of a distorted octahedron, one face of which is occupied by the tripodal Tp ligand. The Re-N(2) bond length (opposite to the oxo ligand) is significantly enlarged (227.1(3) pm) compared with the two other Re–N bonds (215.3(3) and 215.1(3) pm). The [TpRe(O)S_2] part of TpRe(O)[S_2fc] (**1a**) is similar to the corresponding part in TpRe(O)S_4 [17]; the rhenium–oxo bond length (168.8(3) pm in **1a**, 170.2(3) pm in TpRe(O)S_4 [17]) is found in the expected range for terminal oxo ligands in mononuclear [Cp*Re(O)] complexes (167–171 pm, cf. Ref. [29]).

The 1,1'-ferrocene dithiolate moiety in **1a** contains two almost exactly planar cyclopentadienyl rings which are inclined to each other at the rhenium side (distance C(10)···C(15) 319.1 pm, distance between the ring centers 327.8 pm, distance between the midpoints of the C(12)–C(13) and C(17)–C(18) bonds 334.3 pm). The sulfur atoms bend outwards from their respective cyclopentadienyl ring planes by 8.5° (S(1)) and 10.1° (S(2)). The cyclopentadienyl rings deviate significantly from the expected eclipsed conformation (dihedral angle S(1)–C(10)– Fe/S(2)–C(15)–Fe 9.7°).

Table 3
Selected interatomic distances and angles for TpRe(O)[S_2fc] (**1a**)

Bond lengths (pm)		Bond angles (°)	
Re–S(1)	231.6(1)	S(1)–Re–S(2)	101.4(1)
Re–S(2)	230.9(1)	S(1)–Re–O	103.7(1)
Re–O	168.8(3)	S(2)–Re–O	104.5(1)
Re–N(2)	227.1(3)	S(1)–Re–N(2)	88.0(1)
Re–N(4)	215.3(3)	S(1)–Re–N(4)	82.9(1)
Re–N(6)	215.1(3)	S(1)–Re–N(6)	163.9(1)
B–N(1)	152.6(5)	S(2)–Re–N(2)	85.7(1)
B–N(3)	154.9(4)	S(2)–Re–N(4)	162.0(1)
B–N(5)	155.2(5)	S(2)–Re–N(6)	82.5(1)
N(1)–N(2)	136.2(5)	N(2)–Re–O	162.3(1)
N(3)–N(4)	136.4(5)	N(4)–Re–O	91.2(1)
N(5)–N(6)	136.0(5)	N(6)–Re–O	90.3(1)
		N(2)–Re–N(4)	76.9(1)
S(1)–C(10)	175.7(4)	N(2)–Re–N(6)	82.5(1)
S(2)–C(15)	176.7(4)	N(4)–Re–N(6)	88.9(1)
S(1)···S(2)	357.8		
Re···B	334.3	Re–S(1)–C(10)	119.0(1)
Re···Fe	438.9	Re–S(2)–C(15)	120.9(1)
Fe···Centre (C(10)–C(14))	163.9	B···Re···Fe	146.0
Fe···Centre' (C(15)–C(19))	164.9	Centre···Fe···Centre'	175.8

The distance between the two transition metals Re and Fe (438.9 pm) is remarkably long.

3. Experimental details

All syntheses and manipulations were routinely carried out under a stream of argon from which traces of water and oxygen had been removed by molecular sieve and BTS catalyst, respectively. The silica (Merck Kieselgel 60) used for column chromatography had been activated at 600 °C overnight and then stored under argon. The parent half-sandwich complexes TpRe(O)Cl_2 [23], Cp* Re(E)Cl_2 (E = O [20,24], N^{t}Bu [25]) and the dilithium ferrocene dichalcogenates $Fe(C_5H_4\text{-}ELi)_2 \cdot 2THF$ (E = S, Se) [26] were prepared according to established literature procedures.

3.1. Instrumentation

The following instruments were used: IR, Perkin Elmer 983 G; ^1H and ^{13}C NMR (in $CDCl_3$ solution), Bruker ARX 250 and AC 300; EI-MS, Varian MAT 8500 (70 eV).

3.2. Synthesis and characterization

3.2.1. TpRe(O)[E_2fc] (E = S (1a), Se (1b))

A light-blue THF solution (20 ml) of TpRe(O)Cl_2 (0.22 g, 0.45 mmol) was combined with an orange THF solution (60 ml) of fc$(ELi)_2$ (0.45 mmol). The mixture was stirred for 16 h (overnight) whereupon the original orange–red color changed from green and brown to dark green. The solvent was removed under reduced pressure and the residue purified by column chromatography over silica. Elution with CH_2Cl_2/hexane (5:1) gave a dark green zone from which a dark green powder was obtained. Recrystallization from $CHCl_3$/hexane mixtures at −25 °C. According to the ^1H and ^{13}C NMR spectra, the recrystallized samples did not contain by-products.

1a: Prismatic green crystals which did not melt up to 250 °C. Yield 0.20 g (66.7%). IR (CsI pellet): ν(B–H) 2497 cm^{-1}, ν(Re=O) 953 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.42 (d, 2H), 8.02 (d, 1H), 7.84 (d, 2H), 7.34 (d, 1H), 6.43 (t, 2H), 6.03 (t, ^{1}H) [Tp]; δ = 4.76 (m, 2H), 4.70 (m, 2H), 4.24 (m, 4H) [fc]. ^{13}C NMR ($CDCl_3$): δ = 146.0, 144.5, 137.7, 133.6, 107.6, 105.9 [Tp]; δ 107.9 (C^1, sulfur-bound carbon), 77.2, 75.7, 74.5, 69.4 [fc]. EI-MS: *m/e* 664 (M^+, 100%), 596 (M^+–$C_3H_4N_2$, 22%), 528 (M^+–$2C_3H_4N_2$, 28%).

1b: Dark-brown crystals, m.p. > 250 °C). Yield 0.72 g (72.4%), starting from 0.73 g TpRe(O)Cl_2 (1.50 mmol). IR (CsI): ν(B–H) 2516 cm^{-1}, ν(R=O) 946 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.55 (d, 2H), 8.04 (d, 1H), 7.85 (d, 2H), 7.32 (d, 1H), 6.45 (t, 2H) 6.00 (t, 1H) [Tp]; δ = 4.72 (m, 2H), 4.58 (m, 2H), 4.30 (m, 4H) [fc]. ^{13}C NMR ($CDCl_3$): δ = 148.6, 145.6, 138.0, 133.6, 107.9, 106.0 [Tp]; δ = 95.4 (C^1), 77.3, 74.5, 70, 4, 70.0 [fc]. EI-MS: *m/e* 758 (M^+, 100%), 690 (M^+–$C_3H_4N_2$, 20%) 622 (M^+–$2(C_3H_4N_2)$, 28%).

3.2.2. Cp Re(O) [E_2fc] (E = S (2a), Se (2b))*

A green solution of 0.25 g (0.61 mmol) Cp* Re(O)Cl_2 in 30 ml of THF was slowly added to an orange solution of 0.61 mmol fc$(ELi)_2$ in 60 ml of THF at −78 °C. The reaction mixture was then allowed to warm up to room temperature and kept stirring for 2 h. The color of the solution turned red–brown. The solvent was evaporated and the residue worked up by column chromatography on silica. A red–brown zone was eluted with CH_2Cl_2/THF (5:1) which contained **2a** or **2b**, respectively. The products were recrystallized from CH_2Cl_2/toluene/pentane mixtures at −25 °C to give pure samples, as judged from the ^1H and ^{13}C NMR data.

2a: Dark-brown crystals, m.p. 205–206 °C. Yield 0.19 g (53.0%). IR (CsI): δ(Cp*) 1377 cm^{-1}, ν(Re=O) 913 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.68, 4.19, 4.08 and 4.04 (each m, 2H) [fc]; δ = 2.02 (s, 15H) [Cp*]. ^{13}C NMR ($CDCl_3$): δ = 101.9 (C^1), 75.85/75.62, 69.86/69.78 [fc], δ = 109.8 and 10.7 [Cp*]. EI-MS: *m/e* 586 (M^+, 100%), 554 (M^+–S, 5%), 490 (M^+–C_5H_4S, 34%), 472 (34%), 451 (M^+–Cp*, 15%).

2b: Dark red–brown powder which is almost insoluble in organic solvents, m.p. 236–238 °C. Yield 0.11 g (44.1%) starting from 0.15 g (0.37 mmol) Cp* Re(O)Cl_2. IR (CsI): δ (Cp*) 1376 cm^{-1}, ν(Re=O) 931 cm^{-1}. ^1H NMR ($CDCl_3$), δ = 1.70 (s, 15H) [Cp*]. ^{13}C NMR ($CDCl_3$): δ = 105.0 and 11.3 [Cp*]; only the Cp* signals could be identified owing to the low solubility. EI-MS: *m/e* 680 (M^+, 100%), 600 (M^+–Se, 18%), 545 (M^+–Cp*, 44%), 518 (M^+–C_5H_4Se–H_2O, 50%).

3.2.3. Cp Re(N^{t}Bu)[E_2fc] (E = S, (3a), Se (3b))*

A blue solution of Cp* Re(N^{t}Bu)Cl_2 (0.14 g, 0.30 mmol) and an orange solution of fc$(ELi)_2$ (0.30 mmol), each in 30 ml THF, were combined at −78 °C. The mixture was allowed to warm up to room temperature and then stirred for additional 3 h. Work-up by column chromatography over silica gave a red–brown zone from which the product was obtained as a brown powder.

3a: Yield 0.08 g (41.4%). IR (CsI): δ(Cp*) 1379 cm^{-1}, δ(t}Bu) 1359 and 1253 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.26, 4.17, 4.14 and 3.84 (each m, 2H) [fc]; 2.12 (s, 15H) [Cp*], 1.47 (s, 9H) [^{t}Bu]. ^{13}C NMR ($CDCl_3$): δ = 105.1 (C^1), 75.53/75.05, 68.89/68.63 [fc]; 108.2 (C_5Me_5) and 12.9 ($C_5\mathit{Me}_5$); 70.1 (CMe$_3$) and 26.6 (CMe_3). EI-MS: *m/e* 641 (M^+, 89%), 584 (M^+–

Table 4
Atomic coordinates (×10^5) and equivalent isotropic displacement coefficients (pm^2) of TpRe(O)[S_2fc] (**1a**)

	x	*y*	*z*	U_{eq} [a]
Re	2709(2)	33346(1)	22494(1)	154(1)
Fe	−23394(6)	15491(4)	43492(4)	201(2)
S(1)	16423(11)	31151(8)	39910(6)	237(3)
S(2)	−25294(11)	18880(7)	17221(6)	203(2)
O	−2433(35)	47183(21)	24959(20)	239(8)
B	26586(51)	30299(34)	4816(30)	220(12)
N(1)	22917(37)	18194(25)	8306(23)	206(9)
N(2)	13378(38)	17377(25)	15597(23)	209(9)
N(3)	37352(37)	40720(25)	15426(23)	202(9)
N(4)	30584(36)	42264(25)	24059(23)	202(9)
N(5)	7566(37)	32682(24)	−375(22)	192(9)
N(6)	−4915(36)	32363(23)	5168(21)	178(9)
C(1)	26797(47)	7317(31)	5163(31)	267(11)
C(2)	19718(51)	−747(32)	10611(33)	300(12)
C(3)	11575(49)	5848(31)	17019(30)	367(11)
C(4)	54408(49)	48129(33)	18522(31)	269(12)
C(5)	58878(51)	54803(35)	29237(32)	301(12)
C(6)	43721(48)	50780(31)	32475(28)	245(11)
C(7)	−419(50)	33794(30)	−10568(27)	238(11)
C(8)	−18187(51)	34319(31)	−11708(28)	247(11)
C(9)	−20526(46)	33389(29)	−1688(26)	211(10)
C(10)	2390(44)	26389(30)	47652(25)	204(10)
C(11)	−8973(53)	33050(33)	52106(31)	289(12)
C(12)	−15621(58)	26489(38)	59082(31)	349(13)
C(13)	−8357(54)	16029(38)	59233(29)	323(13)
C(14)	2949(49)	15930(34)	52228(29)	269(11)
C(15)	−33646(45)	12997(32)	27059(26)	225(10)
C(16)	−45249(50)	18132(42)	32385(31)	310(13)
C(17)	−51632(54)	9753(49)	38175(34)	409(16)
C(18)	−44145(59)	−475(43)	36446(32)	408(15)
C(19)	−33015(57)	1336(35)	29506(3)	323(12)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

C_4H_9, 26%), 489 (M^+-C_4H_9-C_5H_3S, 33%), 119 (Cp^*-CH_4)$^+$, 100%).

3b: Yield 0.10 g (38.1%) starting from 0.19 g (0.41 mmol) Cp^*Re(N^tBu)Cl_2. IR (CsI): δ(Cp^*) 1380 cm^{-1}, δ (N^tBu) 1359 and 1253 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.24, 3.99, 3.96 and 3.65 (each m, 2H) [fc]; 2.14 (s, 15H) [Cp^*]; 1.52 (s, 9H) [^{t}Bu]. ^{13}C NMR ($CDCl_3$): $\delta(C^1)$ not observed, δ = 76.23, 69.57/69.41 [fc]; 103.9 and 12.3 [Cp^*], 70.8 and 27.2 [^{t}Bu]. EI–MS: *m/e* 735 (M^+, 100%); 678 (M^+-C_4H_9, 12%), 534 (M^+-C_4H_9-SeC_5H_4, 90%).

3.3. X-Ray structure analysis of TpRe(O)[S_2fc] (1a)

Crystal data: $C_{19}H_{18}BN_6OS_2FeRe$, M = 663.4, triclinic, space group $P1$, $a = 779.8(2)$, $b = 1134.5(2)$, $c = 1304.5(2)$ pm, $\alpha = 100.74(2)°$, $\beta = 105.71(2)°$, $\gamma = 101.00(2)°$, $Z = 2$; dark red isometrically shaped crystal with dimensions 0.25 × 0.25 × 0.30 mm, μ(Mo Kα) = 6.640 mm^{-1}, $D_c = 2.087$ g cm^{-3}.

Data collection and processing: Siemens P4 diffractometer, ω-scan mode with scan width 1.10°, radiation Mo Kα ($\lambda = 71.073$ pm, graphite monochromator); $T = 173$ K, 9463 reflections collected in the range $3° \leqslant 2\theta \leqslant 55°$, 4744 unique and observed ($F_o \geqslant 0\sigma(F_o)$), absorption correction by DIFABS [27].

The atom positions are given in Table 4.

Structure solution and refinement: Patterson methods (Re, Fe) followed by difference Fourier syntheses, full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions, 281 refined parameters, $R = 0.0248$, $wR = 0.0236$, weighting scheme $w^{-1} = \sigma^2(F)$, max./min. residual electron density 2.01/− 1.34 e 10^{-6} pm^{-3}.

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