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C–S Bond Cleavage during Reactions between *N*,*N*-Diethylthiocarbamoyliminothianes and $[M\mathrm{OCl}_4]^-$ Complexes (*M* = Re, Tc)

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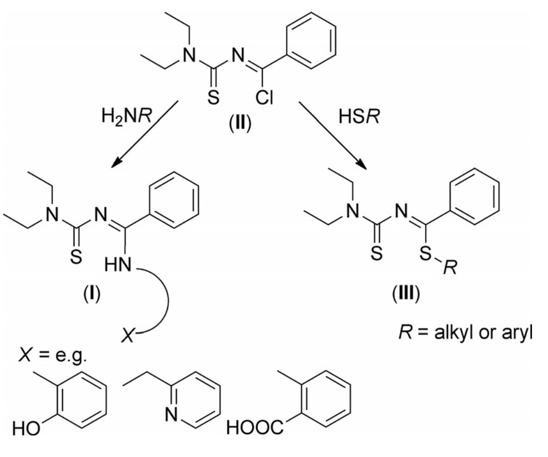
In Memory of Professor Kurt Dehnicke

Keywords: Rhenium; Technetium; Tridentate benzamidines; Oxo complexes; Structure analysis

Abstract. $[M\mathrm{OCl}_4]^-$ complexes (M = Re, Tc) react with thianes derived from *N*-[(diethylamino)(thiocarbonyl)]benzamidoyl chloride and 2-mercaptophenol (HL^1) and 2-mercaptoaniline (HL^2) under C–S bond cleavage and formation of oxorhenium(V) and oxotechnetium(V) complexes with the resulting decomposition products 2-mercaptophenol and *N*-[(dialkylamino)thiocarbonyl]-*N′*-2-mercaptophenyl)benzamidine ($\mathrm{H_2L^{2a}}$), respectively. The products, $(\mathrm{NBu_4})[\mathrm{ReO(S,O\text{-}C_6H_4)_2}]$, $[\mathrm{ReOCl(L^{2a})}]$ and $[\mathrm{TcO(L^{2a})}]$ were obtained in good yields and isolated in crystalline form. Single-crystal X-ray studies reveal square-pyramidal coordination environments with apical oxo ligands for all three product complexes under study.

Introduction

Rhenium and technetium complexes with bi- and tridentate [*N*-[(dialkylamino)(thiocarbonyl)]benzamidines (**I**) are extensively studied and a number of oxo, nitrido and carbonyl complexes with such chelators were structurally characterised.[1–11] The ligands can readily be prepared by reactions of the corresponding benzimidoyl chlorides (**II**) with functionalised primary amines.[12,13] They allow a variety of modifications in the periphery of their chelating system, which tune their properties and also give access to amino acid derivatives and bioconjugation.[8] Some complexes of the new ligands, preferably derivatives of thiosemicarbazides, reveal promising cytotoxic properties against human MCF-7 breast cancer cells.[9]

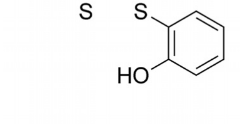


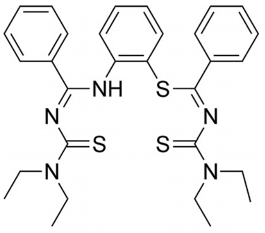
Surprisingly less is known about the coordination behaviour of related thianes (**III**), which can be synthesised by reactions of **II** with thiols. Some basic reports about such ligands are given in an early paper[14] and the thesis of *Köhler*,[15] and some coordination chemistry together with the structures of bi- and tetranuclear silver complexes were described.[16]

In this paper, we report about the synthesis of two new thiane derivatives of **II** and their reactions with $(\mathrm{NBu_4})[M\mathrm{OCl_4}]$ (M = Re, Tc) complexes, which resulted in unexpected C–S bond cleavage, which can finally be used for the synthesis of complexes with novel ligands such as $(\mathrm{L^{2a}})^{2-}$.

Results and Discussion

The proligands HL^1 and HL^2 can readily be prepared by reactions of **II** with one equivalent of 2-mercaptophenol or 0.5 equivalents of 2-aminothiophenol, respectively. The compounds are obtained as pale yellow solids in medium yields. The products were fully characterised by elemental analyses, IR and NMR spectroscopy.


HL¹


HL²

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Additionally, X-ray structure analysis was performed for a single crystal of HL^1. The molecular structure of the compound is depicted in Figure 1. Selected bond lengths and angles are summarised in Table 1. The structural determination shows an almost located C–N double bond between the atoms C4 and N3, whereas the bond between N3 and C2 of 1.399(3) Å can be assigned to a single bond. This situation is in contrast to the bonding features in dialkylaminothiocarbonylbenzamidines, where also in the pro-ligands an extended delocalisation of π-electron density between all carbon and nitrogen atoms is found.[2–13] The solid-state structure of HL^1 shows a distorted *Z* configuration concerning the sulfur atoms, which is stabilised by hydrogen bonds between O30 and the sulfur atoms.

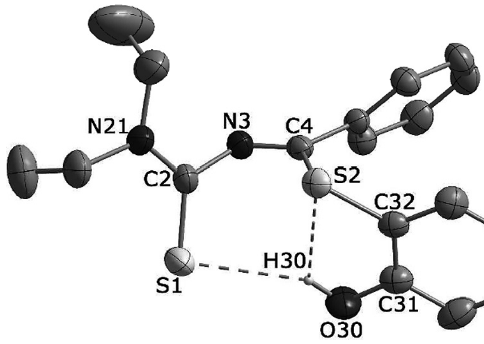


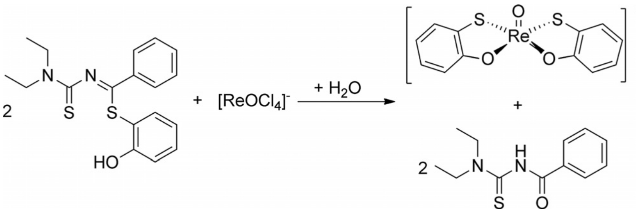
Figure 1. Ellipsoid representation[17] of the molecular structure of HL^1. Hydrogen atoms on carbon atoms are omitted for clarity. Thermal ellipsoids represent 50 % probability.

Table 1. Selected bond lengths /Å and angles /° in HL^1.

S1–C2	1.679(3)	C2–N3	1.399(3)	
C2–N21	1.326(3)	N3–C4	1.272(3)	
C4–S2	1.781(2)	S2–C32	1.768(2)	
S1–C2–N3	118.3(2)	C2–N3–C4	123.4(2)	
N3–C4–S2	121.9(2)	C4–S2–C32	101.83(9)	
Hydrogen bonds				
	d(D–H)	*d*(A···H)	*d*(D···A)	D–H···A
O30–H30.S1	0.82	2.61	3.359(3)	151.7
O30–H30.S2	0.82	2.57	3.059(2)	120.0

HL^1 reacts with equimolar amounts of $(NBu_4)[ReOCl_4]$ to give a greenish-brown solution, from which green crystals of $(NBu_4)[ReO(S,O\text{-}C_6H_4)_2]$ were isolated upon concentration. The formation of the mercaptophenolato chelate is unexpected and can be understood as the result of a hydrolytic decomposition of HL^1 under the influence of the rhenium complex as is given in Scheme 1. The yield of the chelate is expectedly low for the 1:1 reaction, but can be increased to about 80 per cent when two equivalents of HL^1 are used. No complex formation could be observed with the released benzoylthiourea, which also is known to be a suitable chelating ligand for $\{ReO\}^{3+}$ and $\{TcO\}^{3+}$ atoms.[18]

The rhenium atom in $(NBu_4)[ReO(S,O\text{-}C_6H_4)_2]$ is five-coordinate and the Re=O stretch is found at 961 cm^{-1}, which is in the normal range for square-pyramidal oxo and nitrido complexes of rhenium(V) and technetium(V).[19,20] Figure 2 depicts an ellipsoid representation of the complex anion, and selected bond lengths and angles are contained in Table 2. The two mercaptophenolato ligands are arranged in *cis* coordination in the basal plane of a square pyramid, the apex of which is formed by the oxo ligand. The rhenium atom is situated by 0.712(1) Å above the basal plane. Such an arrangement is common for five-coordinate oxo-, nitrido and phenylimidorhenium(V) complexes and is explained by the steric requirements of the multiply bonded oxygen and nitrogen atoms, and has also been found in corresponding complexes with maleonitrildithiolato, ethane-1,2-dithiolato or toluene-3,4-dithiolato ligands.[19–21]



Scheme 1.

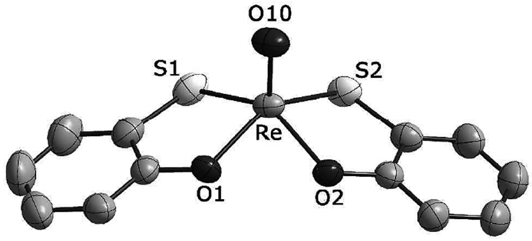
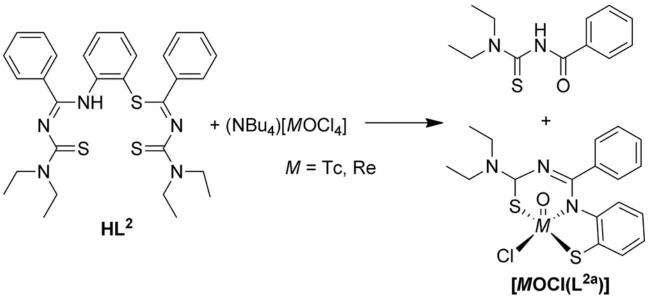


Figure 2. Ellipsoid representation[17] of the complex anion of $(NBu_4)[ReO(S,O\text{-}C_6H_4)_2]$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50 % probability.

Table 2. Selected bond lengths /Å and angles /° in $(NBu_4)[ReO(S,O\text{-}C_6H_4)_2]$.

Re–O10	1.676(3)	Re–O1	1.977(3)
Re–O2	1.998(3)	Re–S1	2.284(2)
Re–S2	1.781(2)		
O10–Re–O1	108.7(2)	O10–Re–O2	110.8(2)
O10–Re–S1	109.5(2)	O10–Re–S2	109.2(1)
O1–Re–O2	79.5(1)	O1–Re–S1	83.0(1)
O1–Re–S2	141.9(1)	O2–Re–S1	139.4(1)
O2–Re–S2	82.8(1)	S1–Re–S2	89.06(5)

The facile cleavage of the C4–S2 bond during the reaction of HL^1 with $[ReOCl_4]^-$ is unexpected and seems to be metal-induced, since even prolonged heating of HL^1 in aqueous methanol gave no evidence for the formation of mercaptophenol and/or *N*,*N*-diethyl-*N*′-benzoylthiourea. Most probable, the reaction begins with a tridentate coordination of the metal on the S,S,O-donor set of HL^1, and the hydrolytic cleavage of the C–S bond is a consequence of the decrease of electron density at the central carbon atom upon coordination, which makes it more sensitive against a nucleophilic attack. Despite the fact, that we could not finally prove this assumption by experimental data (e.g. by NMR spectroscopic data of intermediates), the observed type of bond cleavage can be used for the synthesis of metal complexes with ligands, which are not easily accessible by conventional synthetic procedures (cf. Scheme 2).



Scheme 2.

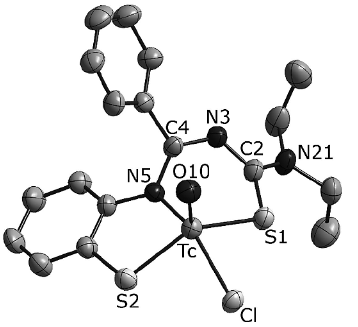


Figure 3. Ellipsoid representation[17] of the molecular structure of [TcOCl(L^{2a})]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50 % probability.

Thus, a corresponding C–S bond cleavage in HL^2 can be applied for the synthesis of metal complexes with the ligand {L^{2a}}$^–$, the direct synthesis of which causes problems due to the parallel attack of benzimidoyl chlorides to the amine and mercapto sites of 1,2-aminobenzenethiol. The reaction of HL^2 with (NBu$_4$)[ReOCl$_4$], however, yields the oxorhenium(V) complex [ReOCl(L^{2a})] in good yields as red crystals. A similar reaction with (NBu$_4$)[TcOCl$_4$] gives the analogous technetium complex.

Both compounds are readily soluble in organic solvents such as dichloromethane or chloroform and stable on air in the solid state as well as in solutions. Infrared bands at 949 (Tc complex) and 976 cm$^{–1}$ (Re compound) confirm the presence of terminal oxo ligands. The ratios between the aliphatic and the aromatic protons in the ^{1}H NMR spectra strongly suggest that the ligand HL^2 is no more intact and a similar C–S bond cleavage as shown in Scheme 1 for HL^1, also occurs during the reactions of HL^2 with [*M*OCl$_4$]$^–$ (*M* = Tc, Re) complexes. An alternative approach to [ReOCl(L^{2a})] is given with a reaction starting from [ReOCl$_3$(PPh$_3$)$_2$]. The sparingly soluble starting material rapidly dissolves during the reaction with HL^2 in boiling dichloromethane. From the resulting red solution, [ReOCl(L^{2a})] precipitates upon cooling and concentration.

Both the technetium and the rhenium complexes crystallise in the monoclinic space group $P2_1/c$ with each two crystallographically independent [*M*OCl(L^{2a})] molecules in the asymmetric units. An ellipsoid representation of the molecular structure of the technetium complex is shown in Figure 3. The structure of the rhenium compound is virtually identical and therefore no extra Figure is given. Selected bond lengths and angles of both compounds are compared in Table 3. The atomic labelling scheme of Figure 3 is also applied for the rhenium complex.

The complexes are five-coordinate with the donor atoms of the tridentate ligand together with the chloro ligands forming the basal planes of distorted square pyramids. The domination of this coordination polyhedron over a trigonal pyramid is indicated by τ values between 0.23 and 0.32 for the four independent molecules of the [MOCl(L^{2a})] complexes, where values of 0 and 1 would be expected for idealised C_{4v} and D_{3h} geometries, respectively.[22] Expectedly, the metal atoms are placed above the basal planes: the corresponding distances are 0.733(2) Å for the technetium complex and 0.700(2) Å for [ReOCl(L^{2a})] (values given for one of the two independent species each). This common structural feature of monooxo complexes is addressed during the discussion of the structure of the [ReO(S,O-C$_6$H$_4$)$_2$]$^–$ anion (vide supra).

The Re–O10 and Tc–O10 distances of 1.657(5) and 1.680(6) Å are within the expected range of rhenium or technetium–oxygen double bonds.[18] The six-membered chelate rings are strongly distorted for both complexes, with main deviations of 0.458(4) Å ([TcOCl(L^{2a})]) and 0.454(4) Å ([ReOCl(L^{2a})]) from the mean least-square planes each for the nitrogen atoms N5. Nevertheless, a considerable delocalisation of π-electron density is observed. This is indicated by the C–S and C–N bond lengths inside the chelate rings, which are all in the range between carbon–sulfur and carbon–nitrogen single and double bonds. This bond length equalisation is even extended to the C2–N21 bonds, which are significantly shorter than expected for single bonds.

The latter fact is also reflected in the NMR spectra of the chelates, where a rotational barrier around the C2–N21 bonds is indicated by the splitting of the ethyl signals into two sets of resonances. This is in accordance with structurally related rhenium and technetium complexes with thiocarbamoylbenzamidinates such as with the oxygen-analogous ligand derived from 2-aminophenol.[6,23]

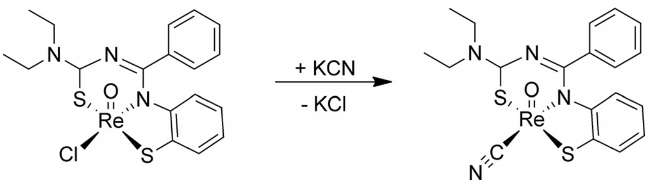
The chloro ligand in [ReOCl(L^{2a})] is only weakly bonded and can readily be replaced as is demonstrated by a metathesis reaction with CN$^–$. When the complex is treated with KCN in a mixture of methanol and CH$_2$Cl$_2$ at ambient temperature, a red powder of [ReO(CN)(L^{2a})] precipitates (Scheme 3). The product is readily soluble in dichloromethane or chloroform and yields large red crystals after recrystallisation from these solvents. The IR spectrum shows an absorption at 2208 cm$^{–1}$, which can be assigned to the ν_{CN} stretch. The Re=O band appears at 984 cm$^{–1}$.

Figure 4 shows the molecular structure of [ReO(CN)(L^{2a})]. Selected bond lengths and angles are compared to the values of [ReOCl(L^{2a})] and [TcOCl(L^{2a})] in Table 3. It is obvious that all main structural features of the chloro complexes also apply for the cyano compound. The complex has a distorted square-pyramidal coordination sphere (τ = 0.25) with the oxo ligand at the apex of the pyramid. The six membered chelate ring show similar deviations from planarity as discussed for the chloro complexes (here with a maximum deviation for N5 of 0.454(4) Å).

Table 3. Selected bond lengths /Å and angles /° in [*M*O*X*(L^{2a})] complexes (*M* = Re, Tc; *X* = Cl, CN). The atomic labelling scheme of Figure 3 is also applied for [ReOCl(L^{2a})].

	[TcOCl(L^{2a})]$^{a)}$	[ReOCl(L^{2a})]$^{a)}$	[ReO(CN)(L^{2a})]
M–O10	1.657(5)	1.662(5)	1.681(6)
	1.640(5)	1.680(6)	
M–Cl/C40	2.410(2)	2.365(2)	2.086(7)
	2.398(2)	2.374(2)	
M–S1	2.326(2)	2.313(2)	2.313(2)
	2.318(2)	2.312(2)	
M–S2	2.258(2)	2.278(2)	2.277(2)
	2.267(2)	2.272(2)	
M–N5	2.006(5)	2.018(5)	2.025(5)
	2.016(5)	2.010(6)	
S1–C2	1.745(8)	1.761(8)	1.754(8)
	1.742(7)	1.756(9)	
C2–N3	1.356(9)	1.347(9)	1.34(1)
	1.356(8)	1.34(1)	
N3–C4	1.310(9)	1.30(1)	1.308(9)
	1.307(8)	1.287(9)	
C4–N5	1.371(9)	1.371(9)	1.376(8)
	1.374(8)	1.387(9)	
C2–N21	1.329(9)	1.33(1)	1.32(1)
	1.321(9)	1.33(1)	
O10–*M*–Cl/C40	105.6(2)	104.6(2)	103.8(3)
	106.0(2)	104.4(2)	
O10–*M*–S1	115.9(2)	111.8(2)	114.1(2)
	112.8(2)	114.6(2)	
O10–*M*–S2	111.8(2)	111.4(2)	111.9(2)
	111.5(2)	111.4(2)	
O10–*M*–N5	102.9(3)	104.9(3)	107.7(2)
	104.3(2)	103.8(3)	
Cl/C40–*M*–S1	81.32(6)	82.71(7)	80.6(2)
	82.72(6)	81.99(7)	
Cl/C40–*M*–S2	83.88(7)	83.70(7)	83.5(2)
	82.97(7)	84.20(7)	
Cl/C40–*M*–N5	151.3(2)	150.3(2)	148.3(3)
	149.4(2)	151.6(2)	
S1–*M*–S2	132.19(7)	136.62(7)	133.61(8)
	135.59(7)	133.68(8)	
S1–*M*–N5	89.2(2)	89.9(2)	89.7(2)
	89.3(2)	89.5(2)	
S2–*M*–N5	82.7(2)	82.1(2)	81.7(2)
	82.3(2)	82.3(2)	
M–S1–C2	105.1(2)	106.8(3)	106.8(3)
	107.0(2)	105.6(2)	
S1–C2–N3	122.0(5)	123.1(6)	121.8(6)
	122.8(5)	121.1(6)	
C2–N3–C4	122.7(6)	124.8(7)	125.7(6)
	125.0(6)	124.2(7)	
N3–C4–N5	123.2(6)	127.1(7)	124.2(6)
	125.8(5)	123.1(7)	
C4–N5–*M*	115.9(4)	113.1(4)	114.4(4)
	112.9(4)	114.4(5)	

a) Values for two crystallographically independent molecules.



Scheme 3.

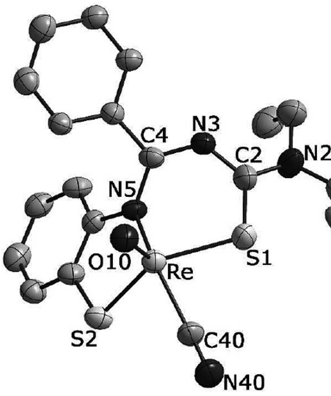


Figure 4. Ellipsoid representation[17] of the molecular structure of [ReO(CN)(L^{2a})]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50 % probability.

Conclusions

N,*N*-Diethylthiocarbonylbenzimidoyl chloride readily reacts with functionalised thiophenols such as 2-mercaptophenol or 2-mercaptoaniline with formation of the corresponding thianes. The formed C–S bonds however do not resist reactions with common technetium and rhenium complexes such as (NBu$_4$)[MOCl$_4$] or [ReOCl$_3$(PPh$_3$)$_2$] and undergo a defined cleavage. The resulting building blocks can be used as chelating ligands as is demonstrated for 2-mercaptophenol and a tridentate S,N,S-ligand, which is formed from HL^2. For nuclear medical labelling procedures or anticancer drugs with technetium and rhenium atoms, the thianes, however, are most probably not suitable due to their low stability.

Experimental Section

Materials and Measurements

All reagents used in this study were reagent grade and used without further purification. Solvents were dried and used freshly distilled unless otherwise stated. (NBu$_4$)[ReOCl$_4$],[24] (NBu$_4$)[TcOCl$_4$],[25] and [ReOCl$_3$(PPh$_3$)$_2$][26] were prepared by standard procedures

Infrared spectra were recorded from KBr pellets with a Shimadzu FT instrument in the range 400–4000 cm^{-1}. Elemental analyses were determined using a Heraeus vario EL elemental analyser. The technetium content was determined by liquid scintillation measurements. NMR spectra were taken at 25 °C with a JEOL 400 MHz multinuclear spectrometer.

Radiation Precautions

^{99}Tc is a weak β$^-$-emitter. All manipulations with this isotope were performed in a laboratory approved for the handling of radioactive materials. Normal glassware provides adequate protection against the low-energy β$^-$ emission of the technetium compounds. Secondary X-rays (bremsstrahlung) play an important role only when larger amounts of ^{99}Tc are used.

Synthesis of HL^1

2-Mercaptophenol (0.22 mL, 3 mmol) was dissolved in dry acetone (20 mL) and triethylamine (0.35 mL, 2.5 mmol) was added. After addition of **II** (605 mg, 2.5 mmol), the mixture was stirred for 4 h at room temperature. During this period, colourless (NHEt$_3$)Cl precipitated, which was filtered off. The solvent was removed in vacuo and the residue was redissolved in dry THF and filtered off from a small amount of an insoluble solid. Concentration of the solution and addition of ethyl ether gave a yellow solid. Yield: 430 mg, 50 %. Elemental analysis. Calcd. for $C_{18}H_{20}N_2OS_2$: C, 62.76; H, 5.85; N, 8.13; S, 18.61 %. Found: C, 62.47; H, 5.29; N, 8.02; S, 18.42 %. **IR:** 3267 (s); 3059 (w); 2974 (w); 2928 (w); 1609 (s); 1504 (s); 1312 (m); 1288 (s); 1219 (s); 1146 (m); 1099 (m); 922 (m) 837 (m); 752 (s); 698 (m); 582 (w) cm^{-1}. **^{1}H NMR** (DMSO): δ = 1.18 (t, 3 H, CH$_3$); 1.23 (t, 3 H, CH$_3$); 3.60 (q, 2 H, CH$_2$); 3.84 (q, 2 H, CH$_2$); 6.66–7.48 (m, 9 H, CH$_{arom.}$); 10.14 ppm (s, 1 H, OH).

Synthesis of HL^2

2-Aminothiophenol (0.38 mL, 5 mmol) was dissolved in dry THF (20 mL) and triethylamine (1.4 mL, 10 mmol) was added. After addition of **II** (2.4 g, 10 mmol), the mixture was stirred for 4 h at room temperature. During this period, colourless (NHEt$_3$)Cl precipitated, which was filtered off. The solvent was removed in vacuo remaining a yellow oil, which was suspended in ethyl ether (10 mL) and stored at –20 °C for 18 h. The resulting yellow solid was carefully washed with ethyl ether and dried in vacuo. Yield: 1.07 g, 40 %. Elemental analysis. Calcd. for $C_{30}H_{35}N_5S_3$: C, 64.13; H, 6.28; N, 12.47; S, 17.12 %. Found: C, 63.87; H, 6.04; N, 12.21; S, 16.49 %. **IR:** 2982 (m); 2932 (m); 1647 (s); 1508 (s); 1431 (m); 1354 (w); 1277 (m); 1215 (w); 1076 (w); 907 (w); 764 (m); 687 (m) cm^{-1}. **^{1}H NMR** (DMSO): δ = 1.12 (t, 3 H, CH$_3$); 1.16 (t, 3 H, CH$_3$); 1.25 (t, 3 H, CH$_3$); 1.30 (t, 3 H, CH$_3$); 3.44 (m, 4 H, CH$_2$); 3.93 (m, 4 H, CH$_2$); 7.52–8.22 (m, 9 H, CH$_{arom.}$); 10.06 ppm (s, 1 H, NH).

Reaction between (NBu$_4$)[ReOCl]$_4$ and HL^1, Synthesis of (NBu$_4$)[ReO(O,S-C$_6$H$_4$)$_2$]

(NBu$_4$)[ReOCl$_4$] (59 mg, 0.1 mmol) was dissolved in methanol (1.5 mL) and HL^1 (33 mg, 0.1 mmol) was added. After stirring for 1 h, CH$_2$Cl$_2$ (2 mL) was added and the mixture was kept for 24 h. Green crystals deposited during this period. They were filtered off and washed with ethyl ether. Yield: 27 mg, 40 %. The yield could be improved by using a 1:2 ratio between the rhenium precursor and HL^1. Elemental analysis. Calcd. for $C_{28}H_{44}NO_3ReS_3$: C, 48.53; H, 6.40; N, 2.02; S, 9.25 %. Found: C, 48.27; H, 6.33; N, 2.49; S, 8.54 %. **IR:** 3059 (w); 2962 (m); 2870 (m); 1570 (w); 1481 (m); 1450 (s); 1377 (w); 1219 (s); 1115 (w); 1022 (w); 961 (s); 841 (m); 756 (s); 687 (m); 656 (m) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 0.86 (m, 12 H, CH$_3$); 1.24 (m, 16 H, NCH$_2$); 1.55 (m, 8 H, CH$_2$); 6.70–7.55 ppm (m, 8 H, CH$_{arom.}$).

Synthesis of [TcOCl(L^{2a})]

(NBu$_4$)[TcOCl$_4$] (50 mg, 0.1 mmol) was dissolved in methanol (4 mL). HL^2 (54 mg, 0.1 mmol) was added and the resulting mixture was stirred for 1 h at room temperature. A red precipitate deposited during this time, which was collected and washed with a minimum amount of cold methanol. The product was dissolved in CH$_2$Cl$_2$ (3 mL) and overlayered with methanol (7 mL). Red crystals were formed during the slow diffusion of methanol into the CH$_2$Cl$_2$ solution of the product. Yield: 39 mg (80 %). Elemental analysis. Calcd. for $C_{18}H_{19}ClN_3OTcS_2$: Tc, 20.07 %. Found: Tc, 18.79 %. **IR:** 2974 (w); 1539 (s); 1458 (m); 1443 (m); 1335 (m) 1308 (m); 1223 (m); 949 (m); 748 (m) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 1.35 (dd, 6 H, CH$_3$); 3.72 (m, 2 H, CH$_2$); 4.03 (m, 1 H, CH$_2$); 4.28 (m, 1 H, CH$_2$); 6.68–7.54 ppm (m, 9 H, CH$_{arom.}$).

Synthesis of [ReOCl(L^{2a})]

a) (NBu$_4$)[ReOCl$_4$] (59 mg, 0.1 mmol) was dissolved in methanol (2 mL). HL^2 (54 mg, 0.1 mmol) was added and the resulting mixture was stirred for 1 h at room temperature. A red precipitate deposited during this time, which was collected and washed with a minimum amount of cold methanol. The product was dissolved in CH$_2$Cl$_2$ (2 mL) and overlayered with methanol (3 mL). Red crystals were formed during the slow diffusion of methanol into the CH$_2$Cl$_2$ solution of the product. Yield: 50 mg (86 %).

Table 4. Crystal data and refinement results.

	HL^1	(NBu$_4$)[ReO(S,O-C$_6$H$_4$)$_2$]	[TcOCl(L^{2a})]	[ReOCl(L^{2a})]	[ReO(CN)(L^{2a})]
Formula	$C_{18}H_{20}N_2OS_2$	$C_{28}H_{44}NO_3S_2Re$	$C_{18}H_{19}ClN_3OS_2Tc$	$C_{18}H_{19}ClN_3OS_2Re$	$C_{19}H_{19}N_4OS_2Re_2$
M$_w$	344.48	693.00	491.71	579.01	569.70
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
a /Å	6.837(1)	8.656(1)	19.265(1)	19.284(1)	11.132(1)
b /Å	15.256(1)	9.532(1)	12.876(1)	12.870(1)	13.198(1)
c /Å	17.070(1)	20.387(1)	17.070(1)	17.074(1)	13.619(1)
α /°	90	78.81(1)	90	90	90
β /°	90	85.25(1)	109.50(1)	109.33(1)	93.94(1)
γ /°	90	64.42(1)	90	90	90
V /Å^3	1780.5(3)	1488.4(3)	3991.4(4)	3998.6(4)	1996.2(3)
Space group	$P2_1cn$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	4	2	8	8	4
$D_{calcd.}$/g·cm^{-3}	1.285	1.546	1.637	1.924	1.896
μ /mm^{-1}	0.304	4.250	1.077	6.433	6.313
No. of reflections	7213	15548	44414	39681	14503
No. of independent	4057	7949	10792	10757	5361
No. parameters	198	317	470	470	245
*R*1/*wR*2	0.0494 / 0.1469	0.0395 / 0.0979	0.0671 / 0.1616	0.0542 / 0.1342	0.0560 / 0.1331
GOF	0.898	0.873	0.918	0.921	1.106
Flack parameter	0.02(10)	–	–	–	–
CCDC deposit	CCDC-837172	CCDC-837173	CCDC-837174	CCDC-837175	CCDC-837176

b) [ReOCl$_3$(PPh$_3$)$_2$] (79 mg, 0.1 mmol) was suspended in CH$_2$Cl$_2$ (5 mL) and HL^2 (54 mg, 0.1 mmol) was added whilst stirring. After a stirring period of 1 h, a clear red solution was formed, which was reduced in volume giving a red precipitate of [ReOCl(L^{2a})]. Yield: 37 mg (64 %).

Elemental analysis. Calcd. for C$_{18}$H$_{19}$ClN$_3$OReS$_2$: C, 37.26; H, 3.47; N, 7.24; S, 11.05 %. Found: C, 38.72; H, 2.04; N, 7.10; S, 10.98 %. **IR:** 2974 (w); 1539 (s); 1458 (m); 1335 (m); 1312 (m); 1223 (m); 976 (m); 748 (m) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 1.35 (dd, 6 H, CH$_3$); 3.65 (m, 1 H, CH$_2$); 3.68 (m, 1 H, CH$_2$); 4.14 (m, 1 H, CH$_2$); 4.49 (m, 1 H, CH$_2$); 6.70–7.69 ppm (m, 9 H, CH$_{arom.}$).

Synthesis of [ReO(CN)(L^{2a})]

[ReOCl(L^{2a})] (30 mg, 0.05 mmol) was added to a suspension of KCN (10 mg, 0.115 mmol) in a mixture of methanol (2 mL) and CH$_2$Cl$_2$ (1 mL). The mixture was stirred at room temperature for 1 h. The resulting red precipitate was filtered off, subsequently washed with water, methanol and ethyl ether, and recrystallised from a CH$_2$Cl$_2$/methanol mixture. Yield: 24 mg (88 %). Elemental analysis. Calcd. for C$_{19}$H$_{19}$N$_4$OReS$_2$: C, 39.98; H, 3.53; N, 9.82; S, 11.24 %. Found: C, 39.63; H, 2.97; N, 8.70; S, 11.18 %. **IR:** 2208 (s), 1701 (m); 1543 (s); 1458 (m); 1339 (w); 1223 (m); 984 (m); 752 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.15 (dd, 6 H, CH$_3$); 3.59 (m, 1 H, CH$_2$); 3.79 (m, 1 H, CH$_2$); 3.98 (m, 1 H, CH$_2$); 4.28 (m, 1 H, CH$_2$); 7.19–8.07 ppm (m, 9 H, CH$_{arom.}$).

X-ray Crystallography

The X-ray diffraction data were collected with a STOE IPDS diffractometer with Mo-K_α radiation. The structures were solved by the Patterson method using SHELXS-97.[27] Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97.[27] The positions of hydrogen atoms were calculated for idealised positions and treated with the "riding model" option of SHELXL-97. Crystal data and more details of the data collections and refinements are contained in Table 4. Additional information on the structure determinations have been deposited at the Cambridge Crystallographic Data Centre.

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