4 Experimental Section

4.1 Starting Materials

All chemicals and reagents were purchased from commercial sources (Acros Organics, Fluka, Sigma-Aldrich, Alfa Aesar, Merck).
All solvents were used as received (pure for synthesis) unless otherwise stated.
The technetium and rhenium precursors were synthesized as described in the cited references:
$(NBu_4)[ReOCl_4]$ [111]
$[ReOCl_3(PPh_3)_2]$ [112]
$[Re(NPh)Br_3(PPh_3)_2]$ [113]
$[ReCl_3(PPh_3)_2(NCMe)]$ [114]
$[ReNCl_2(PPh_3)_2]$ [115]
$(NBu_4)[TcOCl_4]$ [116]
$[TcNCl_2(PPh_3)_2]$ [117]

4.2 Analytical Methods

All IR spectra were measured from KBr pellets on a *Shimadzu-FTIR 8300* spectrometer.
The ^{1}H, ^{31}P, ^{13}C NMR spectra were recorded on a *JEOL-400MHz* nuclear magnetic resonance spectrometer (*Lambda*- software).
Cyclic voltammetric studies were performed in acetonitrile solutions, containing $(NBu_4)(PF_6)$ (0.1 M) as supporting electrolyte, using a *Gamry PCI4-300* potentiostat board and *PHE200* software.
The technetium content was measured by a *Beckman* LS6500 liquid scintillation counter.
Carbon, hydrogen, nitrogen and sulfur contents were measured by a *Heraeus* (Vario EL) elemental analyzer.
The ESI-TOF mass spectra were measured on an Agilent 6210 ESI-TOF, Agilent Technologies, Santa Clara, CA, USA. Solvent flow rate was adjusted to 4 μL/min. Spray voltage was set to 4 kV. Drying gas flow rate was set to 15 psi (1 bar). All other parameters were adjusted for a maximum abundance of the relative $[M+H]^+$ peaks.
The FAB mass spectra were measured on a CH-5, Varian MAT, Bremen. Glycol, m-nitrotoluene or nitrobenzyl alcohol was used as matrix.

4.3 Syntheses

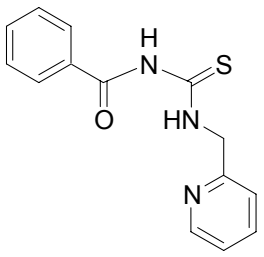
4.3.1 Aroylthioureas and their Complexes

4.3.1.1 N,N-Dialkylbenzoylthioureas (HR^1R^2btu)

The syntheses of the HR^1R^2btu [15] and $H_2phth(R^1R^2tu)_2$ [18] ligands were performed by standard procedures.

4.3.1.2 N-Picolylbenzoylthiourea ($H_2picbtu$)

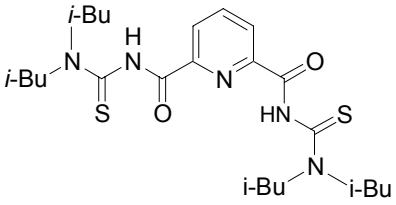
Benzoyl chloride (2.80 g, 20 mmol) was dissolved in 2 mL of dry acetone and NH_4SCN (1.52 g, 20 mmol) in 4 mL of dry acetone was added dropwise under stirring. After the addition was completed, the mixture was kept at 40 ^oC for 1h. The formed precipitate of NH_4Cl was filtered off. Picolylamine (2.16 g, 20 mmol) in 2 mL of dry acetone was slowly added to the resulting yellow solution, which then was stirred at room temperature for 3h. After reducing the volume of solvent to about 2 mL, the mixture was kept at 0 °C and the formed precipitate was filtered off, washed with cold MeOH and diethylether and dried in *vacuo*. Yield 62% (3.36 g).



Elemental analysis:
Calcd. for $C_{14}H_{13}N_3OS$: C, 61.97; H, 4.83; N, 15.49; S, 11.82%.
Found: C, 61.81; H, 4.47; N, 15.48; S, 11.79%.
IR (KBr, cm^{-1}): 3186 (s, br), 1666 (vs), 1551 (vs), 1496 (vs), 1431 (vs), 1365 (s), 1311 (m), 1250 (s), 1207 (s), 1172 (vs), 1122 (m), 1087 (w), 1049 (w), 1022 (w) 995 (w), 790 (s), 752 (vs), 710 (vs) 671 (s), 640 (m), 609 (m).
^1H NMR (400 MHz, DMSO-d_6, ppm): 4.94 (d, J = 4.8 Hz, 2H, py-CH_2), 7.32 (d, J = 7.2 Hz, 1H, py), 7.42 (d, J = 7.9 Hz, 1H, py), 7.51 (t, J = 7.7 Hz, 2H, Ph), 7.63 (t, J = 7.5 Hz, 1H, Ph), 7.80 (t, J_1 = 7.7, 1H, py), 7.95 (d, J = 7.2 Hz, 2H, Ph), 8.57 (d, J = 4.5 Hz, 1H, py), 11.48 (s, 1H, CONH), 11.67 (t, J = 4.8 Hz, 1H, CH_2-NH).
^{13}C NMR (400 MHz, DMSO-d_6, ppm): 49.89 (CH_2), 121.75, 122.57, 128.41, 128.62, 132.27, 132.97, 136.93, 148.97, 155.42 (Ph + py), 168.08 (C=S), 180.28 (C=O).

4.3.1.3 2,6-Dipicolinoyl-bis(N,N-diisobutylthiourea) [H_2dpic(*i*-Bu_2btu)$_2$]

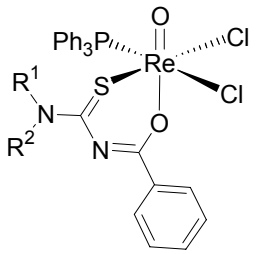
The synthesis of the H_2dpic(*i*-Bu_2btu)$_2$ ligand was adopted from the literature [19], except that N,N-diisobutylthiourea was used. Yield 72%.



Elemental analysis:
Calcd. for $C_{14}H_{20}N_2OS$: C, 59.14; H, 8.14; N, 13.79; S, 12.63%.
Found: C, 59.59; H, 8.04; N, 13.53; S, 12.81%.
IR (KBr, cm^{-1}): 3248 (m), 2959 (s), 2870 (m), 1701 (vs), 1689 (vs), 1527 (vs), 1461 (s), 1419 (s), 1388 (m), 1261 (m), 1222 (m), 1172 (m), 1138 (m), 1081 (m), 999 (w), 740 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.84 (d, J = 6.1 Hz, 12H, Me), 0.99 (d, J = 6.2 Hz, 12H, Me), 2.06 (m, 2H, CH), 2.33 (m, 2H, CH), 3.37 (d, J = 7.1 Hz, 4H, CH_2), 3.79 (d, J = 7.2 Hz, 4H, CH_2), 8.05 (t, J = 7.8 Hz, 1H, py), 8.37 (d, J = 7.8 Hz, 2H, py), 10.12 (s, 2H, NH).

4.3.1.4 [$ReOCl_2(PPh_3)(R^1R^2btu)$] (1)

Solid [$ReOCl_3(PPh_3)_2$] (83 mg, 0.1 mmol) was added to a stirred solution of HR^1R^2btu (0.2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 15 min. This resulted in a complete dissolution of [$ReOCl_3(PPh_3)_2$] and the formation of a green solution. The solvent was removed under vacuum, and the residue was redissolved in 3 mL of acetone. The green-yellow solution slowly changed its color to orange-red. It contained a mixture of the complexes **1** and **6**.
In the case of HPh_2btu, large yellow-orange crystals of **1a** and red plates of **6a** (both types of X-ray quality) deposited together from this solution upon standing for 2 days and were separated mechanically.
Nitromethane (3 mL) was used for the crystallization of the *i*-Pr_2btu chelates **1d** and **6d**. Large yellow-green plates of **1d** deposited from such solutions upon standing overnight at room temperature, while small red crystals of **6d** were obtained by slow evaporation of the resulting filtrate in a refrigerator.
Yellow-green crystals of **1e** (the morphbtu- derivative) were isolated by slow evaporation of the acetone solution described above. All attempts to isolate the corresponding compound **6e** from the remaining solution in crystalline form failed, and only oily, impure products could be recovered.



Data for 1a (R^1 = R^2 = Ph). Yield: 26% (23 mg).

Elemental analysis:

Calcd. for $C_{38}H_{30}Cl_2N_2O_2PSRe$: C, 52.64; H, 3.48; N, 3.23; S, 3.69%.

Found: C, 51.70; H, 3.35; N, 3.41; S, 3.82%.

IR (KBr, cm^{-1}): 3055 (w), 1469 (vs), 1439 (s), 1415 (s), 1389 (vs), 1272 (w), 1095 (m), 976 (s), 748 (m), 694 (m), 529 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.3-8.1 (m, Ph).

^{31}P NMR (400 MHz, $CDCl_3$, ppm): -2.97 (s).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 126-137 (Ph), 172.01 (C=S), 191.23 (C=O).

FAB^+ MS (*m*/*z*): 948, 80%, $[M(NBA) - 2Cl]^+$; 866, 20%, $[M]^+$; 831, 5%, $[M - Cl]^+$.

Data for 1d (R^1 = R^2 = *i*-Pr). Yield: 55% (44 mg).

Elemental analysis:

Calcd. for $C_{32}H_{24}Cl_2N_2O_2PSRe$: C, 48.11; H, 4.26; N, 3.51; S, 4.01%.

Found: C, 48.02; H, 4.05; N, 3.36; S, 4.15%.

IR (KBr, cm^{-1}): 3055 (w), 2977 (w), 2933 (w), 1481 (vs), 1435 (vs), 1396 (s), 1373 (vs), 1307 (m), 1265 (m), 1145 (m), 1096 (s), 976 (s), 752 (s), 694 (vs), 509 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.11-1.39 (m, 12H, Me), 3.64-3.70 (m, 2H, CH), 7.33-7.66 (m, 20H, Ph).

^{31}P NMR (400 MHz, $CDCl_3$, ppm): -2.23 (s).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 19.26, 19.96 (CH_3), 67.75, 68.01 (CH), 127-134 (Ph), 170.27 (C=S), 190.43 (C=O).

FAB^+ MS (*m*/*z*): 881, 75%, $[M(NBA) - 2Cl]^+$; 764, 20%, $[M - Cl + H]^+$; 729, 12%, $[M - 2Cl + H]^+$; 466, 15%, $[ReO(i\text{-}Pr_2btu)]^+$.

Data for 1e (NR^1R^2 = morph). Yield: 54% (42 mg).

Elemental analysis:

Calcd. for $C_{30}H_{28}Cl_2N_2O_3PSRe$: C, 45.91; H, 3.57; N, 3.57; S, 4.08%.

Found: C, 46.00; H, 3.45; N, 3.47; S, 4.12%.

IR (KBr, cm^{-1}): 3055 (w), 2923 (w), 2862 (w), 1481 (vs), 972 (s), 748 (m), 694 (s), 528 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.9-4.9 (m, 8H, CH_2), 7.1-7.8 (m, 20H, Ph).

^{31}P NMR (400 MHz, $CDCl_3$, ppm):-5.23 (s).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 49.68, 51.41, 67.00, 67.48 (CH_2), 127-135 (Ph), 172.67 (C=S), 190.66 (C=O).

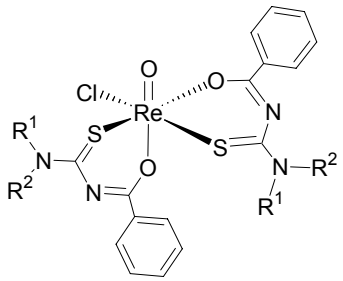
FAB^+ MS (*m*/*z*): 866, 80%, $[M(NBA) - 2Cl]^+$; 784, 12 %, $[M]^+$; 749, 5%, $[M - Cl]^+$.

4.3.1.5 [ReOCl(R^1R^2btu)$_2$] (2)

Method 1. HR^1R^2btu (0.22 mmol) in 3 mL of acetone was added to a stirred suspension of [$ReOCl_3(PPh_3)_2$] (83 mg, 0.1 mmol) in 3 mL of acetone. Three drops of Et_3N were added, and stirring was continued for 30 min at room temperature, whereupon the precursor complex completely dissolved and the color of the reaction mixture changed from yellow-green to deep green. After the mixture was cooled to 0 °C, a colorless precipitate of $Et_3N{\cdot}HCl$ was filtered off, and the solvent was removed under reduced pressure. Released PPh_3, excess ligand and small amounts of other, unidentified compounds were removed by washing the resulting residue with 2 mL of cold acetone, and the product remained as an analytically pure, green powder. The separation of the complex can alternatively be done by column chromatography. For this, the crude reaction mixture is loaded onto a silica gel column. The first, yellow fraction of triphenylphosphine and unidentified compounds is eluted with *n*-hexane/acetone (1/1), while the second green fraction containing the complex is eluted with acetone.

Method 2. A solution of (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) in MeOH (2 mL) was added dropwise while stirring to a solution of 0.22 mmol of the ligand dissolved in 3 mL of MeOH. The color of the solution immediately turned to deep green, and a green precipitate deposited within 30 min. The green powder was filtered off, washed with cold methanol, and recrystallized from dichloromethane/acetone.

Data for 2a (R^1 = R^2 = Ph)



Yield: 45% for method 1; 78% (70 mg) for method 2.

Elemental analysis:

Calcd. for $C_{40}H_{30}ClN_4O_3S_2Re$: C, 53.35; H, 3.33; N, 6.22; S, 7.11%.

Found: C, 53.01; H, 3.10; N, 6.14; S, 7.01%.

IR (KBr, cm^{-1}): 3040 (w), 1485 (vs), 1450 (vs), 1427 (vs), 1380 (vs), 1261 (m), 1172 (m), 1107 (w), 1072 (w), 975 (s), 871 (w), 798 (w), 756 (m), 698 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.3-8.0 (m, Ph).

^{13}C NMR (400 MHz, CDCl3, ppm): 126-144 (Ph), 174.13 (C=S), 176.04 (C=S), 186.40 (C=O), 194.14 (C=O).

FAB$^+$ MS (*m*/*z*): 865, 10%, $[M - Cl]^+$.

Data for 2b (R^1 = Ph, R^2 = Me)

Yield: 44% (34 mg) for method 1; 93% (72 mg) for method 2.

Elemental analysis:

Found: C, 46.33; H, 2.95; N, 7.21; S, 8.41%.

Calcd. for $C_{30}H_{26}ClN_4O_3S_2Re$: C, 46.41; H, 3.36; N, 7.22; S, 8.25%.

IR (KBr, cm^{-1}): 3035 (w), 1473 (vs), 1423 (vs), 1377 (vs), 1269 (m), 1172 (w), 1103 (m), 1072 (w), 984 (s), 898 (m), 798 (w), 698 (s), 547 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 3.87, 3.91, 3.94, 3.96, 3.98, 4.02, 4.13 (7 singlets, 6H, CH_3), 7.1-8.5 (m, 20H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 42.24 (CH_3), 42.76 (CH_3), 126-144 (Ph), 173.53 (C=S), 175.40 (C=S), 185.73 (C=O), 194.11 (C=O).

FAB^+ MS (*m*/*z*): 741, 20%, $[M - Cl]^+$.

Data for 2c ($R^1 = R^2$ = Et)

Yield: 30% (21 mg) for method 1; 91% (64 mg) for method 2.

Elemental analysis:

Found: C, 40.31; H,4.19; N, 7.56; S, 8.81%.

Calcd. for $C_{24}H_{30}ClN_4O_3S_2Re$: C, 40.70; H, 4.24; N, 7.91; S, 9.04%.

IR (KBr, cm^{-1}): 3055 (w), 2977 (w), 2931 (w), 2870 (w), 1496 (vs), 1419 (vs), 1358 (vs), 1250 (m), 1173 (w), 1141 (m), 1072 (m), 980 (s), 887 (w), 825 (w), 794 (w), 702 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.27-1.31 (m, 6H, CH_3), 1.39-1.46 (m, 6H, CH_3), 3.78-3.84 (m, 3H, CH_2), 3.93-3.99 (m, 2H, CH_2), 4.17-4.30 (m, 3H, CH_2), 6.92 (t, 2H, J = 7.8 Hz, Ph, *m*-H), 7.36-7.45 (m, 6H, Ph), 8.36 (d, 2H, J = 7.4 Hz, Ph, *o*-H).

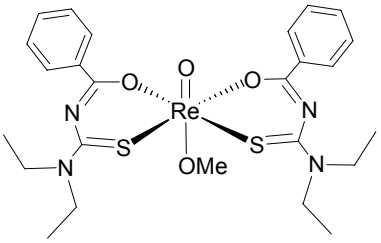
^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.13, 13.47, 13.59 and 13.67 (CH_3), 46.79, 47.06, 47.56, and 47.84 (CH_2), 127.49, 128.13, 129.44, 131.38, 131.79, 132.98, 134.40 and 134.94 (Ph), 171.63 (C=S), 174.04 (C=S), 183.06 (C=O), 190.80 (C=O).

4.3.1.6 [ReO(OMe)(Et_2btu)$_2$] (3c)

Method 1. HEt_2btu (52 mg, 0.22 mmol) dissolved in 3 mL of MeOH was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in MeOH (2 mL). The color of the solution immediately turned to deep green. After the addition of three drops of Et_3N and heating, the color of the reaction mixture turned to red and a purple precipitate began to deposit. The mixture was refluxed for 30 min and then cooled to 0 °C. The product was filtered off, washed with cold MeOH, and recrystallized from CH_2Cl_2/MeOH. **3c** can also be synthesized from $[ReOCl_3(PPh_3)_2]$ applying the same reaction conditions.

Method 2. 2c (71 mg, 0.1 mmol) was suspended in 3 mL of MeOH, and three drops of Et_3N were added. The mixture was heated on reflux for 15 min, whereupon its color changed from green to red. After the mixture was cooled to 0 °C, a purple precipitate of **6c** was filtered off, washed with MeOH, and dried under vacuum. Yield: 84% (59 mg) for method 1; 90% (63 mg) for method 2.

Elemental analysis:



Calcd. for $C_{25}H_{33}N_4O_4S_2Re$: C, 42.70; H, 4.69; N, 7.96; S, 9.10%.

Found: C, 42.67; H, 4.68; N, 8.03; S, 9.23%.

IR (KBr, cm^{-1}): 3053 (w), 2977 (m), 2931 (m), 2808 (m), 1512 (vs), 1500 (vs), 1419 (vs), 1350 (s), 1305 (m), 1249 (m), 1203 (m), 1172 (m), 1138 (m), 1091 (s), 941 (s), 887 (m), 713 (s), 671 (m), 493 (m).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.34 (t, J = 7.2 Hz, 6H, CH_3), 1.28 (t, J = 7.2 Hz, 6H, CH_3), 3.17 (s, 3H, OCH_3), 3.79-4.01 (m, 8H, CH_2), 7.40-7.46 (m, 6H, Ph, *m*-H and *p*-H), 8.41 (d, J = 6.5 Hz, 4H, Ph, *o*-H).

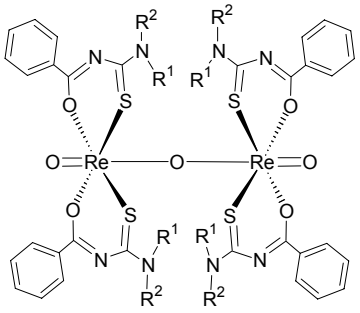
^{13}C NMR (400 MHz, $CDCl_3$, ppm): 12.96, 13.19 (CH_3), 46.38, 47.44 (CH_2), 57.37 (OCH_3), 127.98, 130.23, 131.96 and 136.96 (Ph), 172.65 (C=S), 180.32 (C=O).

FAB^+ MS (*m*/*z*): 674, 80%, $[M - OMe + H]^+$; 470, 35%, $[M - Et_2btu + H]^+$; 454, 30%, $[ReO_2(Et_2btu)]^+$; 438, 10%, $[ReO(Et_2btu)]^+$.

4.3.1.7 [{ReO(Et$_2$btu)$_2$}$_2$O] 4c.

Compound **3c** (35 mg, 0.05 mmol) was dissolved in 5 mL of hot MeCN. The mixture was refluxed for 5 min and then slowly cooled to 0 °C. The product precipitated as small green microcrystals. Single crystals of X-ray quality were obtained by slow evaporation of a solution of **4c** in CH_2Cl_2/MeCN. Yield 91% (31 mg).

Elemental analysis:



Calcd. for $C_{48}H_{60}N_8O_7S_4Re_2$: C, 42.30; H, 4.41; N, 8.23; S, 9.41%.

Found: C, 42.12; H, 4.42; N, 8.30; S, 9.43%.

IR (KBr, cm^{-1}): 3054 (w), 2977 (w), 2924 (w), 2870 (w), 1497 (vs), 1423 (vs), 1354 (s), 1250 (m), 1204 (m), 1168 (w), 1138 (m), 1076 (w), 953 (w), 934 (w), 891 (m), 725 (s), 665 (s), 547 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.27 (t, J = 7.1 Hz, 6H, CH_3), 1.28 (t, J = 7.1 Hz, 6H, CH_3), 3.13 (q, J = 6.8 Hz, 2H, CH_2), 3.73-3.81 (m, 6H, CH_2), 7.33 (t, J = 7.5 Hz, 4H, Ph, *m*-H), 7.42 (t, J = 7.3 Hz, 2H, Ph, *p*-H), 8.25 (d, J = 7.4 Hz, 4H, Ph, *o*-H).

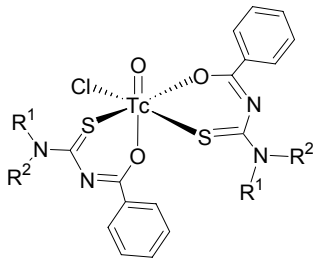
^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.20, 13.36 (CH_3), 45.74, 47.25 (CH_2), 127.47, 130.65, 131.33 and 138.10 (Ph), 172.16 (C=S), 182.12 (C=O).

FAB$^+$ MS (*m*/*z*): 1363, 5%, $[M + H]^+$; 690, 30%, $[ReO_2(Et_2btu)_2 + H]^+$; 673, 70%, $[ReO(Et_2btu)_2]^+$; 454, 35%, $[ReO_2(Et_2btu)]^+$.

4.3.1.8 [TcOCl(R^1R^2btu)$_2$] (5).

The technetium complexes **5** were prepared from $(NBu_4)[TcOCl_4]$ by the procedure described above as method 2 for their rhenium analogues **2**.

Data for 5a (R^1 = R^2 = Ph): Yield: 70% (57 mg).



Elemental analysis:

Calcd. for $C_{40}H_{30}ClN_4O_3S_2Tc$: Tc, 12.2%. Found: 12.0%.

IR (KBr, cm^{-1}): 3058 (w), 1501 (s), 1485 (vs), 1450 (vs), 1429 (vs), 1389 (vs), 1261 (s), 1172 (m), 1107 (m), 1072 (w), 1022 (w), 956 (s), 871 (w), 798 (m), 756 (m), 698 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.06-7.09 (m, Ph).

Data for 5b (R^1 = Ph, R^2 = Me): Yield: 74% (51 mg).

Elemental analysis:

Calcd. for $C_{30}H_{26}ClN_4O_3S_2Tc$: Tc, 14.37%. Found: 14.1%.

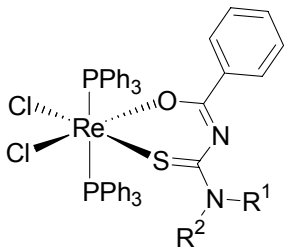
IR (KBr, cm^{-1}): 3050 (w), 1473 (vs), 1423 (vs), 1381 (vs), 1269 (m), 1174 (w), 1107 (w), 1072 (w), 1022 (w), 964 (s), 898 (m), 795 (w), 698 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.8-4.1 (br, 6H, CH_3), 7.1-8.0 (m, 20H, Ph).

4.3.1.9 [$ReCl_2(PPh_3)_2$(R^1R^2btu)] (6)

The syntheses of compounds **6** were discussed together with those of compound **1** in Section 4.3.1.5.

Data for 6a (R^1 = R^2 = Ph): Yield: 41% (46 mg).



Elemental analysis:

Calcd. for $C_{56}H_{45}Cl_2N_2OP_2SRe$: C, 60.42; H, 4.05; N, 2.52; S, 2.88%.

Found: C, 59.13; H, 4.01; N, 2.39; S, 3.04%.

IR (KBr, cm^{-1}): 3059 (m), 1481 (s), 1465 (s), 1434 (vs), 1365 (vs), 1261 (m), 1091 (m), 1026 (w), 744 (m), 694 (vs), 513 (vs).

FAB^+ MS (*m*/*z*): 850, 5%, $[M - PPh_3]^+$; 553, 10%, $[Re(Ph_2btu)Cl]^+$.

Data for 6d (R^1 = R^2 = *i*-Pr): Yield: 18% (19 mg)

Elemental analysis:

Calcd. for $C_{50}H_{49}Cl_2N_2OP_2SRe$: C, 57.46; H, 4.69; N, 2.68; S, 3.06%.

Found: C, 57.03; H, 4.31; N, 2.82; S, 3.34%.

IR (KBr, cm^{-1}): 3055 (m), 2970 (w), 2927 (w), 1477 (s), 1458 (s), 1434 (vs), 1400 (s), 1373 (s), 1338 (s), 1261 (m), 1195 (w), 1149 (m), 1091 (m), 1026 (w), 744 (m), 694 (vs), 516 (vs).

FAB^+ MS (*m*/*z*): 1044, $[M]^+$; 1009, $[M - Cl]^+$; 782, $[M - PPh_3]^+$; 747, $[M - Cl - PPh_3]^+$; 712, $[Re(i\text{-}Pr_2btu)(PPh_3)]^+$; 450, $[Re(i\text{-}Pr_2btu)]^+$.

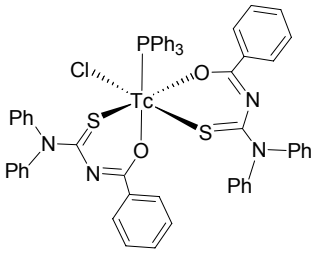
4.3.1.10 $[TcCl(PPh_3)(Ph_2btu)_2]$ (7a)

Compound **5a** (40 mg, 0.05 mmol) was dissolved in 5 mL of CH_2Cl_2, and PPh_3 (26 mg, 0.1 mmol) was added. The solution was stirred at room temperature for 3 h. During this time, the color of the solution changed from yellow-brown to deep red. The volume of the solvent was reduced to 2 mL and 1 mL of MeOH was added. The resulting solution was slowly evaporated at room temperature resulting in big red crystals of **7a**, which were suitable for X-ray diffraction. Yield: 64% (35 mg).

Elemental analysis:

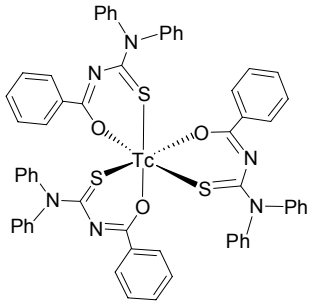
Calcd. for $C_{58}H_{45}ClN_4O_2PS_2Tc$: Tc, 9.3%. Found: 9.5%.

IR (KBr, cm^{-1}): 3055 (w), 1488 (vs), 1435 (vs), 1384 (vs), 1311 (vs), 1176 (s), 1118 (m), 1011 (w), 748 (m), 693 (s).



4.3.1.11 [Tc(Ph$_2$btu)$_3$] (8a)

HPh$_2$btu (33 mg, 0.1 mmol) and PPh$_3$ (26 mg, 0.1 mmol) were added to a solution of **5a** (40 mg, 0.05 mmol) in 5 mL of CHCl$_3$, and the mixture was stirred at room temperature for 3 hours. The color changed from yellow to deep red, and an almost black solid was obtained after removal of the solvent in vacuum. The residue was re-dissolved in a CH$_2$Cl$_2$/MeOH mixture (1/1) and dark red crystals were deposited after slow evaporation of the solvent. Yield: 75% (42 mg).

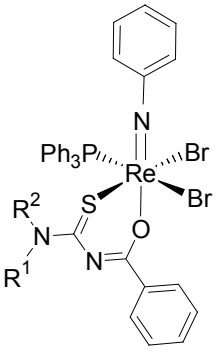


Elemental analysis:
Calcd. for $C_{61}H_{49}N_6O_4S_3Tc$: Tc, 8.80%. Found: 7.8%.
IR (KBr, cm^{-1}): 3050 (w), 1479 (vs), 1419 (vs), 1366 (vs), 1257 (s), 1172 (w), 1111 (w), 1072 (w), 1026 (w), 756 (m), 698 (s).

4.3.1.12 [Re(NPh)Br$_2$(PPh$_3$)(R^{1}R^{2}btu)] (**9**).

Solid HR^{1}R^{2}btu (0.15 mmol) was added to a stirred suspension of [Re(NPh)Br$_3$(PPh$_3$)$_2$] (104 mg, 0.1 mmol) in 5 mL of CH$_2$Cl$_2$. The temperature of the mixture was kept at 30 ^{o}C for 1h. During this time, the precursor complex completely dissolved and a clear yellow-green solution was obtained. The solvent was removed under vacuum to dryness and the residue was recrystallized from 3 mL of acetone.

Data for 9a (R^1 = R^2 = Ph): Yield: 70% (72 mg).



Elemental analysis:
Calcd. for $C_{44}H_{35}Br_2N_3OPSRe$: C, 51.25; H, 3.40; N, 4.08; S, 3.11%.
Found: C, 51.21; H, 3.08; N, 3.78; S, 3.08%.
IR (KBr, cm^{-1}): 3055 (w), 1481 (s), 1431 (vs), 1400 (vs), 1257 (w), 1173 (w), 1091 (m), 1072 (w), 1026 (m), 999 (w), 759 (m), 694 (s), 528 (s).
^{1}H NMR (400 MHz, CDCl$_3$, ppm): 7.0-7.5 (m, 35H, Ph).
^{31}P NMR (400 MHz, CDCl$_3$, ppm): 1.06 (s);
^{13}C NMR (400 MHz, CDCl$_3$, ppm): 121-134 (Ph), 158.26 (Re=N-$\underline{C}_{Ph}$), 173.11 (C=S), 191.77 (C=O).
FAB$^+$ MS (m/z): 1032, [M +H]$^+$, 950, [M – Br]$^+$, 941, [M – PhN]$^+$.

Data for 9e (R^1, R^2 = Morph): Yield: 66% (61 mg).

Elemental analysis:

Calcd. for $C_{36}H_{33}Br_2N_3OPSRe$: C, 45.56; H, 3.48; N, 4.43; S, 3.37%.

Found: C, 45.70; H, 3.41; N, 4.32; S, 3.41%.

IR (KBr, cm^{-1}): 3051 (w), 2862 (w), 1508 (s), 1485 (s), 1435 (s), 1396 (vs), 1261 (m), 1211 (m), 1176 (w), 1091 (m), 1064 (w), 1026 (m), 995 (w), 750 (w), 694 (s), 524 (s).

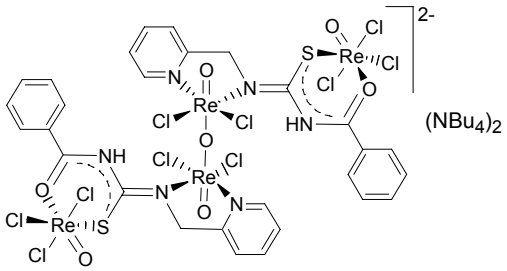
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.8-4.0 (m, 5H, CH_2), 4.14 (m, 1H, CH_2), 4.77 (m, 2H, CH_2), 7.1-7.7 .(m, 25H, Ph).

^{31}P NMR (400 MHz, $CDCl_3$, ppm): 1.88 (s).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 48.79, 51.16 (CH_2-N), 66.51, 67.38 (CH_2-O), 121-134 (Ph), 172.24 (C=S), 189.33 (C=O).

4.3.1.13 $(NBu_4)_2[\{Re_2O_2Cl_5(Hpicbtu)_2\}O]$ (10)

A solution of Hpicbtu (27 mg, 0.1 mmol) in 3 mL of acetone was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 2 mL of acetone. The color of the solution immediately turned to deep green. The resulting mixture was stored at room temperature overnight, whereupon large green crystals deposited. When the mixture is stirred at room temperature for 1h, the product quantitatively precipitates as a micro-crystalline solid. Yield: 93% (52 mg).



Elemental analysis:

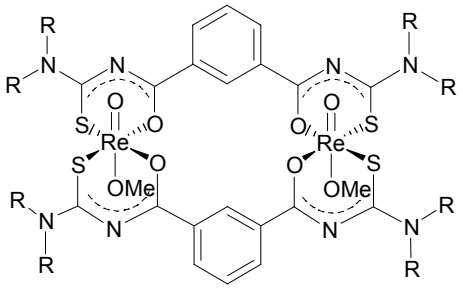
Calcd. for $C_{60}H_{96}Cl_{10}N_8O_7Re_4S_2$: C, 32.68; H, 4.39; N, 5.08; S, 2.91%.

Found: C, 31.98; H, 4.09; N, 5.18; S, 3.01%.

IR (KBr, cm^{-1}): 3291 (m), 3055 (w), 2957 (s), 2924 (s), 2867 (m), 1635 (vs), 1543 (vs), 1466 (m), 1412 (m), 1304 (s), 1226 (m), 1153 (w), 1045 (w), 991 (s), 779 (s), 729 (s), 691 (s).

4.3.1.14 $[ReO(OMe)\{phth(R_2tu_2)\}]_2$ (11)

A mixture of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol), $H_2phth(R_2tu_2)$ (0.1 mmol) and 3 drops of Et_3N in MeOH (3 mL) was heated under reflux for 30 min. Afer cooling to 0 °C, the formed red prepicitate was filtered off, washed with cold MeOH, and recrystallized from CH_2Cl_2/MeOH.



Data for 11a (R = Et): Yield 81%

Elemental analysis:

Calcd. for $C_{38}H_{54}N_8O_8Re_2S_4$: C, 36.44; H, 4.43; N, 8.95; S, 10.24%.

Found: C, 36.75; H, 4.28; N, 8.83; S, 10.02%.

IR (KBr, cm^{-1}): 2978 (m), 2935 (w), 2870 (w), 1508 (vs), 1431 (s), 1354 (s), 1257 (m), 1195 (m), 1076 (m), 945 (m), 725 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): (two series of resonances with ratio about 1.0 / 0.8) 1.36 (m, 24H, Me), 3.23 / 3.24 (s, 6H, OMe), 3.95 (m, br, 16H, CH_2), 7.43 (m, 2H, Ph), 8.43 / 8.45 (d, 4H, Ph), 9.82 / 9.90 (s, 2H, Ph).

Data for 11b (R = *i*-Bu): Yield 86%.

Elemental analysis:

Calcd. for $C_{54}H_{86}N_8O_8Re_2S_4$: C, 43.94; H, 5.87; N, 7.59; S, 8.69%.

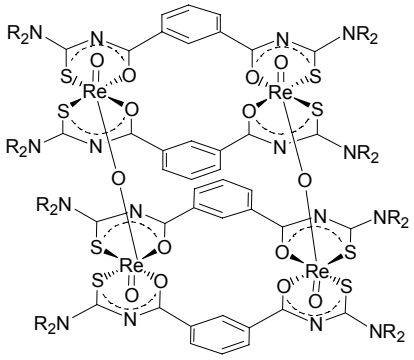
Found: C, 43.91; H, 5.69; N, 7.64; S, 8.58%.

IR (KBr, cm^{-1}): 2959 (m), 2931 (m), 2870 (w), 2808 (w), 1519 (vs), 1420 (s), 1354 (s), 1234 (m), 1149 (m), 1099 (m), 941 (m), 729 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) (two series with ratio: 1.0 / 0.8): 0.90 (t, 12H, Me), 1.06 (t, 12H, Me), 2.11 (m, 2H, CH), 2.46 (m, 2H, CH), 3.22 / 3.29 (s, 6H, OMe), 3.75 (m, br, 16H, CH_2), 7.42 (m, 2H, Ph), 8.43 / 8.45 (d, 4H, Ph), 9.87 / 9.90 (s, 2H, Ph).

4.3.1.15 $\{[ReO\{phth(R_2tu)_2\}]_4\}O_2$ (12) and $\{[ReO\{phth(R_2tu)_2\}]_2O\}_n$ (12^n)

Freshly prepared compound **11** (0.02 mmol) was disolved in CH_2Cl_2 (1 mL) and 1 mL of MeCN was added. Slow evaporation of the resulting solution gives a mixture of green crystals of **12** and green fine powder of $\mathbf{12^n}$.



Data for 12a (R = Et): Yield 72%

Elemental analysis:

Calcd. for $C_{72}H_{96}N_{16}O_{14}Re_4S_8$: C, 35.87;

H, 4.01; N, 9.30; S, 10.64%.

Found: C, 35.70; H, 4.11; N, 9.13; S, 10.48%.

IR (KBr, cm^{-1}): 2974 (w), 2931 (w), 1508 (s), 1423 (vs),

1353 (s), 1257 (m), 1195 (m), 1134 (m), 1080 (m), 949 (w), 914 (w), 725 (s), 683 (s), 652 (s).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.37 (m, 48H, Me), 3.0-4.5 (m, 32H, CH_2), 7.04 (t, 4H, Ph), 8.00 (d, 8H, Ph), 9.45 (s, 4H, Ph).

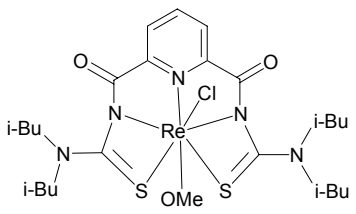
Data for 12b (R = *i*-Bu): Yield 80%.
Elemental analysis:
Calcd. for $C_{104}H_{160}N_{16}O_{14}Re_4S8$: C, 43.68; H, 5.64; N, 7.84; S, 8.97%.
Found: C, 43.72; H, 5.60; N, 7.69; S, 8.77%.
IR (KBr, cm^{-1}): 295 (m), 2866 (w), 1519 (s), 1492 (m), 1419 (vs), 1353 (m), 1234 (w), 1141 (w), 1095 (w), 937 (w), 729 (m), 694 (s), 663 (m).

Data for 12^{n}a (R = Et): Yield 28%
Elemental analysis:
Calcd. for $(C_{36}H_{48}N_8O_7Re_2S_4)_n$: C, 35.87; H, 4.01; N, 9.30; S, 10.64%.
Found: C, 35.72; H, 4.19; N, 9.44; S, 10.68%.
IR (KBr, cm^{-1}): 2970 (w), 2924 (w), 2850 (w), 1504 (s), 1427 (vs), 1354 (s), 1254 (m), 1195 (m), 1134 (m), 1076 (m), 910 (w), 725 (s), 655 (s).

4.3.1.16 [Re(OMe)Cl{dpic(*i*-Bu$_2$tu)$_2$}] (13)

Hdpic(*i*-Bu$_2$tu)$_2$ (51 mg, 0.1 mmol) was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in MeOH (3 mL). The color of the solution immediately turned to dark green. After the addition of three drops of Et_3N and heating, the color of the reaction mixture turned to dark black. The sovent was removed under vacumm and the residue was extracted with ethylacetate (10 mL). The organic phase was washed with water and dried over $MgSO_4$ and then slowly evaporated to give black crystals.

Elemental analysis:
Calcd. for $C_{26}H_{42}ClN_5O_3ReS_2$: C, 41.17; H, 5.58; N, 9.23;
S, 8.46%.
Found: C, 41.32; H, 5.47; N, 9.54; S, 8.60%.
IR (KBr, cm^{-1}): 2957 (m), 2924 (m), 2870 (w), 1654 (s), 1543 (s), 1438 (m), 1384 (m), 1330 (w), 1292 (m), 1153 (m), 1057 (m), 910 (w), 806 (w), 744 (w).

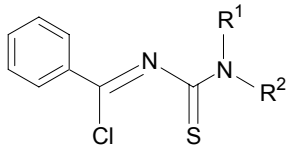


4.3.2 Tridentate Benzamidine Ligands and their Complexes

4.3.2.1 N-[(Dialkylamino)(thiocarbonyl)]benzimidoyl chlorides (R^1R^2bzm-Cl)

The syntheses of Et_2bzm-Cl ($R^1 = R^2 = Et$) and morphbzm-Cl (NR^1R^2 = morph) followed the standard procedure of Beyer et al. [54]. This procedure was slightly modified for the synthesis of benzimidoyl chlorides such as PhMebzm-Cl. The reactions of the corresponding nickel(II) bisbenzoylthiourea complexes with $SOCl_2$ were done in warm CH_2Cl_2 until pure green suspensions were obtained (about 1 hour). The solvents were evaporated to dryness and then residues were extracted with hot CCl_4. Pure benzimidoyl chlorides were directly obtained by evaporation of CCl_4.

Data for PhMebzm-Cl (R^1 = Ph, R^2 = Me): Yield: 39%.

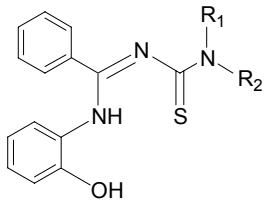


Elemental analysis:
Calcd. for $C_{15}H_{13}ClN_2S$: C, 62.38; H, 4.54; N, 9.70; S, 11.10%.
Found: C, 62.59; H, 4.35; N, 9.62; S, 11.01%.
IR (KBr, cm^{-1}): 3047 (w), 2935 (w), 1651 (s), 1582 (m), 1443 (m), 1373 (m), 1280 (m), 1149 (m), 1103 (m), 1064 (w), 903 (s), 841 (m), 771 (s), 694 (s), 640 (m), 547 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.21 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.3 Hz, 3H, CH_3), 3.69 (q, *J* = 7.2 Hz, 2H, CH_2), 3.87 (q, *J* = 7.1 Hz, 2H, CH_2), 6.60 (t, *J* = 6.9 Hz, 1H, PhOH), 6.86 (d, *J* = 6.7 Hz, 1H, PhOH), 6.89 (t, *J* = 6.4 Hz, 1H, PhOH), 7.04 (d, *J* = 7.5 Hz, 1H, PhOH), 7.24 (t, *J* = 7.5 Hz, 2H, Ph), 7.33 (t, *J* = 7.4 Hz, 1H, Ph), 7.43 (d, *J* = 7.2 Hz, 2H, Ph).

4.3.2.2 N'-(2-Hydroxyphenyl)benzamidines, H_2L^1

Compound R^1R^2bzm-Cl (5 mmol) was dissolved in 10 mL of dry acetone and slowly added to a stirred mixture of 2-aminophenol (545 mg, 5 mmol) and NEt_3 (1.51 g, 15 mmol) in 10 mL of dry acetone. The mixture was stirred for 2 hours at 40 °C and then cooled to 0 °C. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off and the filtrate was evaporated under reduced pressure. The resulting residue was re-dissolved in 4 mL MeOH. Diethylether (10 mL) was added and the mixture was stored at -20 °C. The pale yellow solid of H_2L^1, which deposited from this solution over a period of two days, was filtered off, washed with diethylether and dried under vacuum.

Data for H_2L^{1a} ($R^1 = R^2 = Et$): Yield: 78% (1.275 g).



Elemental analysis:

Calcd. for $C_{18}H_{21}N_3OS$: C, 66.06; H, 6.42; N, 12.84; S, 9.79%.

Found: C, 65.80; H, 6.40; N, 13.22; S, 9.02%.

IR (KBr, cm^{-1}): 3420 (m), 2975 (w), 2930(w), 1620 (vs), 1595 (s), 1535 (s), 1495 (s), 1455 (s), 1425 (s), 1360 (m), 1325 (s), 1250 (s), 1230 (s), 1140 (m), 1080 (s), 1040 (w), 950 (w), 925 (w), 900 (m), 855 (m), 790 (w), 770 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.21 (t, J = 7.1 Hz, 3H, CH_3), 1.32 (t, J = 7.3 Hz, 3H, CH_3), 3.69 (q, J = 7.2 Hz, 2H, CH_2), 3.87 (q, J = 7.1 Hz, 2H, CH_2), 6.60 (t, J = 6.9 Hz, 1H, PhOH), 6.86 (d, J = 6.7 Hz, 1H, PhOH), 6.89 (t, J = 6.4 Hz, 1H, PhOH), 7.04 (d, J = 7.5 Hz, 1H, PhOH), 7.24 (t, J = 7.5 Hz, 2H, Ph), 7.33 (t, J = 7.4 Hz, 1H, Ph), 7.43 (d, J = 7.2 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 12.01, 13.45 (CH_3), 46.01, 46.17 (CH_2), 116.89, 120.00, 126.27, 126.94, 127.60, 128.24, 128.54, 128.90, 130.67 and 134.53 (Ph + PhOH), 149.36 (C=N), 187.06 (C=S).

Data for H_2L^{1b} (NR^1R^2 = Morph): Yield: 80% (1.364 g).

Elemental analysis:

Calcd. for $C_{18}H_{19}N_3O_2S$: C, 63.34; H, 5.61; N, 12.32; S, 9.38%.

Found: C, 60.60; H, 6.4; N, 12.67; S, 9.10%.

IR (KBr, cm^{-1}): 3367 (s), 3045 (s), 2945 (m), 2850 (m), 1612 (vs), 1585 (s), 1570 (s), 1535 (s), 1510 (s), 1475 (s), 1440 (s), 1355 (m), 1325 (s), 1290 (s), 1250 (m), 1235 (s), 1210 (s), 1105 (s), 1080 (m), 1025 (m), 945 (w), 925 (w), 900 (w), 860 (w), 800 (w), 775 (m), 645 (m), 580 (w).

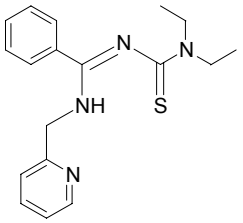
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.63 (t, J = 4.8 Hz, 2H, NCH_2), 3.69 (t, J = 4.7 Hz, 2H, NCH_2), 3.93 (t, J = 4.8 Hz, 2H, OCH_2), 4.14 (t, J = 4.8 Hz, 2H, OCH_2), 6.66 (t, J = 7.6 Hz, 1H, PhOH), 6.86 (d, J = 7.4 Hz, 1H, PhOH), 6.93 (t, J = 7.7 Hz, 1H, PhOH), 7.00 (d, J = 8.0 Hz, 1H, PhOH), 7.28 (t, J = 7.5 Hz, 2H, Ph), 7.37 (t, J = 7.4 Hz, 1H, Ph), 7.44 (d, J = 7.7 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 48.06, 48.70 (NCH_2), 65.99, 66.51 (OCH_2), 117.29, 120.50, 124.60, 127.00, 127.63, 128.40, 128.49, 128.92, 131.04 and 134.24 (Ph + PhOH), 149.45 (C=N), 187.57 (C=S).

EI MS (m/z): 341, 49%, $[M]^{+\cdot}$; 255, 30%, $[M\text{-Morph}]^{+\cdot}$; 233, 35%, $[M\text{-Ph(OH)NH}]^{+\cdot}$.

4.3.2.3 N'-Picolylbenzamidine, HL^2

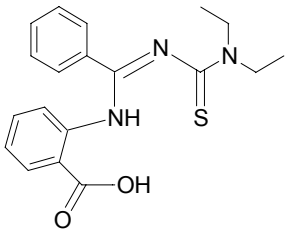
A solution of Et_2bzm-Cl (1.018 g, 4 mmol) in 10 mL of dry acetone was added dropwise to a mixture of 2-methylaminopyridine (436 mg, 4 mmol) and triethylamine (606 mg, 6 mmol) in 5 mL of dry acetone over a period of 5 min. The mixture was stirred for 2 h and then cooled to 0 °C. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off, and the solvent was removed under vacuum. Yield: 85% (1.108 g).



Elemental analysis:
Calcd. for $C_{18}H_{22}N_4S$: C, 66.26; H, 6.75; N, 17.18; S, 9.82%.
Found: C, 65.72; H, 6.58; N, 16.82; S, 9.05%.
IR (KBr, cm^{-1}): 3217 (s), 3065 (s), 2946 (m), 1608 (vs), 1582 (s), 1535 (s), 1482 (s), 1355 (m), 1292 (s), 1254 (m), 1112 (s), 1080 (m), 1025 (m), 946 (w), 925 (w), 779 (m), 687 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.18 (t, J = 7.0 Hz, 3H, CH_3), 1.25 (t, J = 7.0 Hz, 3H, CH_3), 3.64 (q, J = 7.0 Hz, 2H, CH_2), 3.93 (q, J = 7.0 Hz, 2H, CH_2), 4.73 (s, 2H, CH_2-Py), 7.21 (t, J = 6.1 Hz, 1H, py), 7.38-7.45 (m, 4H, Ph + py), 7.52 (d, J = 6.8 Hz, 2H, Ph), 7.70 (t, J = 7.5 Hz, 1H, py), 8.53 (d, J = 4.8 Hz, 1H, py).

4.3.2.4 N'-(2-Carboxyphenyl)benzamidine, H_2L^3

Compound H_2L^3 was synthesized by a procedure similar to the method described for H_2L^{1a}, except that 2-aminobenzoic acid was used instead of 2-aminophenol. Yield: 40% (711 mg).

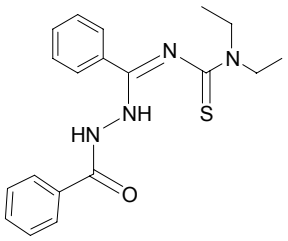


Elemental analysis:
Calcd. for $C_{19}H_{21}N_3O_2S$: C, 64.23; H, 5.92; N, 11.83; S, 9.01%.
Found: C, 64.61; H, 5.81; N, 11.73; S, 10.33%.
IR (KBr, cm^{-1}): 3163 (m), 2977 (w), 2931 (w), 1681 (vs), 1635 (s), 1604 (s), 1573 (m), 1496 (s), 1450 (s), 1380 (m), 1311 (s), 1249 (s), 1134 (s), 1080 (m), 1018 (s), 949 (m), 902 (m), 786 (s), 694 (s), 524 (w).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.2-1.4 (m, 6H, CH_3), 3.4-4.0 (m, 4H, CH_2), 5.78 (s, br, 1H, NH), 7.3-7.6 (m, 6H, Ph + PhCOOH), 7.63 (t, J = 8.1 Hz, 1H, PhCOOH), 7.78 (t, J = 7.2 Hz, 1H, PhCOOH), 8.25 (t, J = 8.0 Hz, 1H, PhCOOH).

4.3.2.5 N'-(Benzamido)benzamidines, H_2L^4

Et_2bzm-Cl (1.227g, 5 mmol) was dissolved in 10 mL of dry acetone and slowly added to a stirred mixture of benzoylhydrazine (680 mg, 5 mmol) and NEt_3 (1.51 g, 15 mmol) in 10 mL of dry acetone. The mixture was stirred for 4 h at room temperature. The formed precipitate of $NEt_3 \cdot HCl$ was filtered and the filtrate was evaporated under reduced pressure. The residue was re-dissolved in 10 mL of CH_2Cl_2 and extracted two times with brine solution (2 x 10 mL). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure to dryness. The residue was treated with diethylether (15 mL), filtered off and dried under vacuum. The resulting compound was used for the syntheses of the complexes without further purification. Yield: 56% (0.991 g).

Elemental analysis:

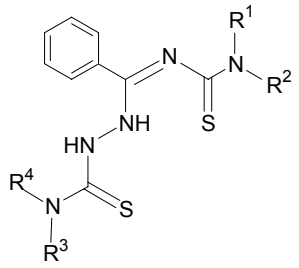


Calcd. for $C_{19}H_{22}N_4OS$: C, 64.38; H, 6.26; N, 15.81;S, 9.05%.
Found: C, 65.08; H, 6.42; N, 15.22; S, 9.00%.
IR (KBr, cm^{-1}): 3215 (m), 3163 (m), 3043 (m), 2978 (m), 2931 (m), 1659 (vs), 1547 (vs), 1508 (vs), 1477 (vs), 1265 (s), 1142 (m), 1072 (m), 1026 (m), 771 (m), 698 (s), 683 (s).
^1H NMR (400 MHz, $CDCl_3$, ppm): 0.92 (s, br, 3H, CH_3), 1.00 (s, br, 3H, CH_3), 3.40 (s, br, 2H, CH_2), 3.76 (s, br, 2H, CH_3), 7.36-7.48 (m, 6H, Ph), 7.77 (d, J = 7.2 Hz, 2H, Ph), 7.84 (d, J = 7.4 Hz, 2H, Ph).

4.3.2.6 Benzamidines Derived from 4,4-Dialkylthiosemicarbazide, H_2L^5

R_1R_2bzm-Cl (5 mmol) was dissolved in 10 mL of dry acetone and slowly added to a stirred mixture of 4,4-dialkylthiosemicarbazide (5 mmol) and NEt_3 (1.51 g, 15 mmol) in 10 mL of dry acetone. The mixture was stirred for 4 hours at room temperature. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was redissolved in 5 mL of CH_2Cl_2 and the obtained solution was extracted with brine solution (3 x 5 mL). After being dried with $MgSO_4$, the organic solvent was removed under vacuum. Diethylether (10 mL) was added and the mixture was stored at -20 °C for 1 day. The colourless solid of H_2L^5, which deposited from this solution, was filtered off, washed with diethylether and then recrystallized from a mixture of CH_2Cl_2/n-hexane.

Data for H_2L^{5a} ($R^1 = R^2 = Et$, $R^3 = R^4 = Me$): Yield: 75%.



Elemental analysis:

Calcd. for $C_{15}H_{23}N_5S_2$: C, 53.38; H, 6.87; N, 20.75; S, 19.00%.

Found: C, 53.80; H, 6.69; N, 21.02; S, 19.02%.

IR (ν in cm^{-1}): 3286 (m), 3031 (w), 2970 (w), 2931 (w), 1635 (vs), 1573 (m), 1496 (vs), 1427 (m), 1346 (s), 1307 (s), 1253 (s), 1137 (w), 1072 (w), 906 (m), 856 (m), 775 (m), 698 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.24 (t, J = 7.2 Hz, 3H, CH_3), 1.36 (t, J = 7.2 Hz, 3H, CH_3), 3.28 (s, 6H, NCH_3), 3.54 (q, J = 7.2 Hz, 2H, CH_2), 3.90 (q, J = 7.1 Hz, 2H, CH_2), 7.41-7.48 (m, 3H, Ph), 7.90 (d, J = 8.3 Hz, 2H, *o*-Ph), 9.50 (s, br, 2H, NH).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 12.32, 12.89 (CH_3), 44.90 (NCH_3), 46.25, 46.75 (NCH_2), 127.70, 128.70, 131.47 and 132.86(Ph), 148.96 (C=N), 179.73(C=S), 183.26 (C=S).

Data for H_2L^{5b} ($R^1 = R^2 = Et$, $R^3R^4 = -(CH_2)_4-$): Yield: 60% (1.089 g).

Elemental analysis:

Calcd. for $C_{17}H_{25}N_5S_2$: C, 56.17; H, 6.93; N, 19.26; S, 17.64%.

Found: C, 55.98; H, 6.77; N, 18.80; S, 17.46%.

IR (ν in cm^{-1}): 3143 (m), 2974 (w), 2927 (w), 1625 (vs), 1523 (vs), 1450 (m), 1411 (s), 1346 (s), 1315 (s), 1269 (s), 1188 (m), 1134 (w), 1072 (w), 902 (w), 840 (m), 775 (m), 694 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.06 (t, J = 6.6 Hz, 3H, CH_3), 1.19 (t, J = 6.6 Hz, 3H, CH_3), 1.91 (s, 2H, pyrolidine CH_2), 2.01 (s, 2H, pyrolidine CH_2), 3.47 (s, 2H, pyrolidine NCH_2), 3.53 (q, J = 6.6 Hz, 2H, NCH_2CH_3), 3.76 (s, 2H, pyrolidine NCH_2), 3.87 (q, J = 6.6 Hz, 2H, NCH_2CH_3), 7.37 - 7.47 (m, 3H, Ph), 7.86 (d, J = 8.0 Hz, 2H, o-Ph), 9.75 (s, br, 2H, NH).

ESI^+ MS (m/z): 386, 80%, $[M + Na]^+$; 402, 100%, $[M + K]^+$.

Data for H_2L^{5c} ($R^1 = R^2 = Et$, $R^3R^4 = -(CH_2)_5-$): Yield: 52% (0.989 g).

Elemental analysis:

Calcd. for $C_{18}H_{27}N_5S_2$: C, 57.26; H, 7.21; N, 18.55; S, 16.98%.

Found: C, 56.90; H, 7.24; N, 18.48; S, 16.99%.

IR (ν in cm^{-1}): 3194 (m), 3062 (w), 2923 (w), 2854 (w), 1628 (vs), 1577 (m), 1489 (vs), 1446 (m), 1342 (m), 1307 (m), 1249 (s), 906 (m), 848 (m), 779 (m), 694 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.07 (t, J = 6.5 Hz, 3H, CH_3), 1.21 (t, J = 6.6 Hz, 3H, CH_3), 1.65 (m, 6H, piperidine CH_2), 3.56 (q, J = 6.5 Hz, 2H, NCH_2CH_3), 3.80 (s, 4H, piperidine NCH_2), 3.86 (q, J = 6.5 Hz, 2H, NCH_2CH_3), 7.38 -7.48 (m, 3H, Ph), 7.84 (d, J =

8.5 Hz, 2H, o-Ph), 10.10 (s, br, 2H, NH).

ESI^+ MS (m/z): 378, 40%, $[M + H]^+$; 400, 100%, $[M + Na]^+$; 416, 55%, $[M + K]^+$.

Data for H_2L^{5d} ($R^1 = R^2 = Et$, $R^3R^4 = -(CH_2)_6-$): Yield: 60% (1.173 g).

Elemental analysis:

Calcd. for $C_{19}H_{29}N_5S_2$: C, 58.27; H, 7.46; N, 17.88; S, 16.38%.

Found: C, 59.12; H, 7.40; N, 17.19; S, 16.82%.

IR (ν in cm^{-1}): 3186 (m), 2977 (m), 2935 (m), 2873 (m), 1632 (vs), 1558 (s), 1434 (vs), 1353 (s), 1315 (s), 1253 (m), 1134 (m), 1091 (m), 918 (m), 848 (m), 776 (m), 697 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.05 (t, J = 7.1 Hz, 3H, CH_3), 1.27 (t, J = 7.1 Hz, 3H, CH_3), 1.52 (s, br, 4H, CH_2), 1.79 (s, br, 4H, CH_2), 3.56 q, J = 7.0 Hz, 2H, NCH_2), 3.64 N(s, 2H, azepine -CH_2), (q, J = 7.0 Hz, 2H, NCH_2), 3.93 (q, J = 7.1 Hz, 2H, NCH_2), 4.00 (s, 2H, azepine-CH_2), 7.41 - 7.51 (m, 3H, Ph), 7.89 (d, J = 7.0 Hz, 2H, o-Ph), 9.81 (s, br, 2H, NH).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 12.25, 12.87 (CH_3), 26.73 (CH_2), 28.04 (CH_2), 45.56, 46.25 (NCH_2), 58.20 (NCH_2), 127.64, 128.64, 131.39 and 132.81(Ph), 148.93 (C=N), 178.76 (C=S), 183.10 (C=S).

Data for H_2L^{5e} ($R^1 = R^2 = Et$, $R^3 = Me$, $R^4 = Ph$): Yield: 39% (0.781 g).

Elemental analysis:

Calcd. for $C_{20}H_{25}N_5S_2$: C, 60.12; H, 6.31; N, 17.53; S, 16.05%.

Found: C, 58.95; H, 6.13; N, 18.42; S, 15.95%.

IR (ν in cm^{-1}): 3310 (m), 3178 (m), 2974 (w), 2931 (w), 1628 (s), 1515 (s), 1492 (s), 1454 (m), 1346 (s), 1311 (m), 1269 (s), 1107 (w), 1072 w), 910 (w), 771 (m), 698 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.13 (t, J = 7.1 Hz, 3H, CH_3), 1.22 (t, J = 7.2 Hz, 3H, CH_3), 3.40 (m, 4H, NCH_2CH_3), 3.58 (s, 3H, NCH_3), 7.1-7.4 (m, 8H, Ph), 7.82 (d, J = 8.0 Hz, 2H, Ph).

ESI^+ MS (m/z): 400 $[M + H]^+$, 422 $[M + Na]^+$, 438 $[M + K]^+$.

Data for H_2L^{5f} (NR^1R^2 = morph, $R^3R^4 = -(CH_2)_6-$): Yield: 74% (1.498 g).

Elemental analysis:

Calcd. for $C_{19}H_{27}N_5OS_2$: C, 56.27; H, 6.71; N, 17.27; S, 15.81%.

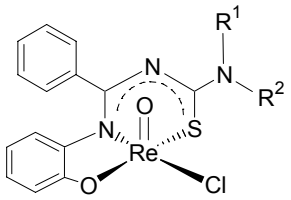
Found: C, 56.17; H, 6.59; N, 17.24; S, 15.90%.

IR (ν in cm^{-1}): 3201 (m), 2954 (w), 2934 (w), 1630 (s), 1520 (s), 1462 (m), 1341 (s), 1318 (m), 1264 (s), 1072 w), 905 (w), 772 (m), 698 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.51 (s, br, 4H, CH_2), 1.77 (s, br, 4H, CH_2), 3.4-4.1 (m, 12H, NCH_2), 7.32-7.47 (m, 3H, Ph), 7.85 (d, *J* = 7.8 Hz, 2H, *o*-Ph), 9.60 (s, br, 2H, NH).

4.3.2.7 [ReOCl(L^1)] (14)

H_2L^1 (0.11 mmol) dissolved in 3 mL of MeOH was added dropwise to a stirred solution of (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) in 2 mL of MeOH. The color of the solution immediately turned to deep red and a red precipitate deposited within 30 min. The red powder was filtered off, washed with cold methanol and recrystallized from CH_2Cl_2/MeOH.



Data for 14a (R^1 = R^2 = Et): Yield: 87% (49 mg).

Elemental analysis:

Calcd. for $C_{18}H_{19}ClN_3O_2SRe$: C, 38.33; H, 3.38; N, 7.46; S, 5.69%.

Found: C, 38.49; H, 3.41; N, 7.08; S, 5.63%.

IR (KBr, cm^{-1}): 3055 (w), 2980 (w), 2927 (w), 1527 (s), 1474 (s), 1444 (s), 1363 (s), 1355 (s), 1320 (m), 1250 (s), 991 (s), 855 (m), 770 (m), 697 (m), 592 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.34 (t, *J* = 7.6 Hz, 3H, CH_3), 1.38 (t, *J* = 7.6 Hz, 3H, CH_3), 3.80 (m, 1H, CH_2), 3.84 (m, 1H, CH_2), 4.21 (m, 1H, CH_2), 4.43 (m, 1H, CH_2), 6.5-6.6 (m, 2H, PhOH), 6.85 (t, *J* = 7.3 Hz, 1H, PhOH), 7.26 (d, *J* = 7.4 Hz, 1H, PhOH), 7.36 (t, *J* = 7.7 Hz, 2H, Ph), 7.49 (t, *J* = 7.4 Hz, 1H, Ph), 7.68 (d, *J* = 7.3 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.20, 13.32 (CH_3), 47.80, 48.57 (CH_2), 116.79, 117.69, 120.64, 124.55, 128.99, 130.63, 133.25 (Ph + PhOH), 145.12 (C_{PhOH}-N), 165.26, (C_{PhOH}-O), 165.18 (C=N), 173.98 (C=S).

ESI$^+$ MS (m/z): 560, 50%, $[M - Cl + MeOH]^+$; 528, 5%, $[M - Cl]^+$.

Data for 14b (R^1, R^2 = morph): Yield: 83% (48 mg).

Elemental analysis:

Calcd. for $C_{18}H_{17}ClN_3O_3SRe$: C, 37.45; H, 2.95; N, 7.28; S, 5.55%.

Found: C, 37.41; H, 2.83; N, 7.40; S, 5.39%.

IR (KBr, cm^{-1}): 3060 (w), 2965 (w), 2925 (w), 2860 (w), 1527 (s), 1475 (s), 1445 (s), 1365 (s), 1355 (s), 1320 (m), 1265 (s), 1240 (s), 1180 (w), 1155 (w), 1115 (m), 1065 (w), 1025 (m),

995 (s), 920 (w), 880 (m), 855 (m), 815 (m), 770 (m), 735 (m), 690 (m), 670 (m), 615 (w), 590 (w).

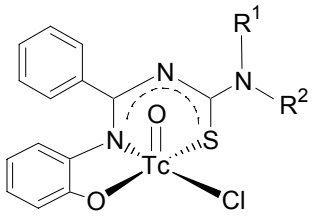
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.7-4.1 (m, 4H, NCH_2), 4.2-4.5 (m, 4H, OCH_2), 6.56 (t, *J* = 7.8 Hz, 1H, PhOH), 6.61 (d, *J* = 7.0 Hz, 1H, PhOH), 6.93 (t, *J* = 6.6 Hz, 1H, PhOH), 7.32 (d, *J* = 7.6 Hz, 1H, PhOH), 7.43 (t, *J* = 7.8 Hz, 2H, Ph), 7.55 (t, *J* = 7.4 Hz, 1H, Ph), 7.73 (d, *J* = 7.3 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 50.20, 50.41 (NCH_2), 66.53, 66.57 (OCH_2), 116.93, 117.95, 120.70, 124.98, 129.04, 130.77, 133.11, 133.56 (Ph + PhOH), 144.82 (C_{PhOH}-N), 166.48, (C_{PhOH}-O), 165.4 (C=N), 172.26 (C=S).

ESI^+ MS (m/z): 574, 100%, $[M - Cl + MeOH]^+$; 542, 5%, $[M - Cl]^+$.

4.3.2.8 [TcOCl(L^1)], (15)

The technetium complexes **15** were prepared from $(NBu_4)[TcOCl_4]$ by the procedure described previously for their rhenium analogue **14**.



Data for 15a ($R^1 = R^2 = Et$): Yield: 86% (41 mg).

Elemental analysis:

Calcd. for $C_{18}H_{19}ClN_3O_2STc$: Tc, 20.8%. Found: Tc: 19.9%.

IR (KBr, cm^{-1}): 3065 (w), 2980 (w), 2935 (w), 1524 (s), 1470 (s), 1445 (s), 1360 (s), 1315 (m), 1245 (s), 1210 (m), 1180 (m), 1140 (m), 1085 (m), 1025 (m), 972 (s), 920 (m), 845 (w), 815 (m), 775 (m), 745 (m), 715 (w), 690 (m), 670 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.42 (m, 6H, CH_3), 3.89 (m, 2H, CH_2), 4.12 (m, 1H, CH_2), 4.27 (m, 1H, CH_2), 6.5-6.6 (m, 2H, PhOH), 6.91 (t, *J* = 7.5 Hz, 1H, PhOH), 7.25 (d, *J* = 7.4 Hz, 1H, PhOH), 7.40 (t, *J* = 7.1 Hz, 2H, Ph), 7.54 (t, *J* = 7.3 Hz, 1H, Ph), 7.70 (d, *J* = 7.7 Hz, 2H, Ph).

Data for 15b (NR^1R^2 = morph): Yield: 88% (43 mg).

Elemental analysis:

Calcd. for $C_{18}H_{17}ClN_3O_3STc$: Tc, 20.2%. Found: Tc, 20.1%.

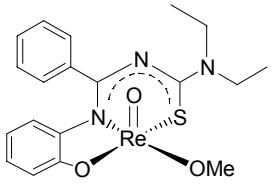
IR (KBr, cm^{-1}): 3051 (w), 2970 (w), 2916 (w), 2851 (w), 1520 (vs), 1470 (vs), 1439 (vs), 1352 (s), 1311 (m) 1265 (s), 1246 (vs), 1175 (w), 1115 (s), 1026 (s), 972 (s), 771 (m), 741 (m), 691 (m), 672 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.7-4.0 (m, 4H, NCH_2), 4.2-4.4 (m, 4H, OCH_2), 6.56 (t, *J* = 7.8 Hz, 1H, PhOH), 6.61 (d, *J* = 7.0 Hz, 1H, PhOH), 6.93 (t, *J* = 6.6 Hz, 1H, PhOH), 7.32 (d, *J* = 7.6 Hz, 1H, PhOH), 7.43 (t, *J* = 7.8 Hz, 2H, Ph), 7.55 (t, *J* = 7.4 Hz, 1H, Ph), 7.73 (d, *J* = 7.3 Hz, 2H, Ph).

4.3.2.9 [ReO(OMe)(L^{1a})], (16a)

Method 1. H_2L^{1a} (0.1 mmol) was dissolved in 5 mL of MeOH and $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was added to this solution. After adding 3 drops of Et_3N, the reaction mixture was refluxed for 30 min. The formed red precipitate was filtered off, washed with cold methanol and recrystallized from CH_2Cl_2/MeOH. Yield: 85% (47 mg).

Method 2. Compound **14a** (56 mg, 0.1 mmol) was suspended in 5 mL of MeOH and three drops of Et_3N were added. The reaction mixture was heated on reflux for 15 min. After being cooled down to room temperature, the red solid was filtered off, washed with cold MeOH and dried under vacumm. Yield: 90% (50 mg).



Elemental analysis:

Calcd. for $C_{19}H_{22}N_3O_3SRe$: C, 40.85; H, 3.97; N, 7.52; S, 5.74%.

Found: C, 40.71; H, 3.84; N, 7.52; S, 5.53%.

IR (KBr, cm^{-1}): 3060 (w), 2977 (w), 2866/w), 1535 (s), 1473 (s), 1447 (w), 1358 (s), 1319 (m), 1246 (s), 1142 (w), 1076 (w), 995 (s), 772 (m), 691 (s), 671 (m).

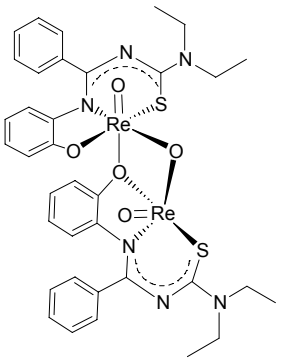
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.34 (m, 6H, CH_3), 3.31 (s, 3H, OMe) 3.82 (m, 2H, CH_2), 4.24 (m, 1H, CH_2), 4.40 (m, 1H, CH_2), 6.5-6.6 (m, 2H, PhOH), 6.84 (t, *J* = 7.6 Hz, 1H, PhOH), 7.29 (d, *J* = 7.5 Hz, 1H, PhOH), 7.37 (t, *J* = 7.4 Hz, 2H, Ph), 7.45 (t, *J* = 7.3 Hz, 1H, Ph), 7.67 (d, *J* = 7.3 Hz, 2H, Ph).

ESI^+ MS (m/z): 560 (100%, $[M + H]^+$), 582 (60, $[M + Na]^+$).

4.3.2.10 [{ReO(L^{1a})}$_2$O], (17a)

Compound **14a** (56 mg, 0.1 mmol) was dissolved in 3 mL of CH_2Cl_2 and one drop of Et_3N was added. The mixture was heated on reflux for 15 min. Then the solvent was removed under vacuum and the residue was crystallized from CH_2Cl_2 /n-hexane mixture to give dark red crystals. Yield 50%.

Elemental analysis:



Calcd. for $C_{36}H_{38}N_6O_5Re_2S_2$: C, 40.36; H, 3.58; N, 7.84; S, 5.99%.

Found: C, 40.02; H, 3.37; N, 7.68; S, 5.85%.

IR (KBr, cm^{-1}): 3055 (w), 2980(w), 2928 (w), 1516(s), 1484 (s), 1435 (m), 1342 (w), 1026 (m), 970 (s), 779(m), 691(w).

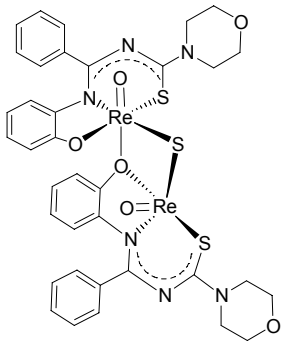
^1H NMR (400 MHz, $CDCl_3$, ppm): 1.39 (m, 6H, CH_3), 3.8-4.2 (m, 4H, CH_2), 6.29 (t, J = 7.1 Hz, 1H, PhOH), 6.42 (d, J = 7.2 Hz, 1H, PhOH), 6.65 (m, 2H, PhOH), 7.29 (t, J = 7.3 Hz, 2H, Ph), 7.34 (t, J = 7.4 Hz, 1H, Ph), 7.68 (d, J = 7.3 Hz, 2H, Ph).

ESI^+ MS (m/z): 1072.1387, 70%, $[M + H]^+$; 1095.1397, 100, $[M + Na]^+$; 1111.1123, 50%, $[M + K]^+$.

4.3.2.11 [{ReO(L^{1b})}$_2$O], (18b)

$Na_2S{\cdot}9H_2O$ (0.24 mg, 0.01 mmol) and one drop of Et_3N were added to a solution of compound **14b** (56 mg, 0.1 mmol) in CH_2Cl_2 (3mL). The mixture was heated on reflux for 30 minutes. After complete removal of solvent, the residue was crystallized from $CHCl_3$ to give dark red crystals. Yield 15%.

Elemental analysis:



Calcd. for $C_{36}H_{34}N_6O_6Re_2S_3$: C, 38.77; H, 3.07; N, 7.54; S, 8.63%.

Found: C, 38.49; H, 3.19; N, 7.44; S, 8.63%.

IR (KBr, cm^{-1}): 2954(w), 2916 (w), 2850 (w), 1542(s), 1523 (s), 1473 (s), 1438 (m), 1353 (w), 1245 (m), 1114 (w), 1022 (m), 972 (s), 752(m), 686(w).

^1H NMR (400 MHz, $CDCl_3$, ppm): 3.54 (m, 1H, NCH_2), 3.70 (m, 2H, NCH_2), 3.83 (m, 2H, NCH_2 + ONH_2), 4.21 (m, 1H, OCH_2), 4.28 (m, 1H, OCH_2), 4.45 (m, 1H, OCH_2), 6.30 (t, J = 7.4 Hz, 1H, PhOH), 6.45 (d, J = 7.2 Hz, 1H, PhOH), 6.61 (m, 2H, PhOH), 7.29 (t, J = 7.5 Hz, 2H, Ph), 7.37 (t, J = 7.4 Hz, 1H, Ph), 7.64 (d, J = 7.3 Hz, 2H, Ph).

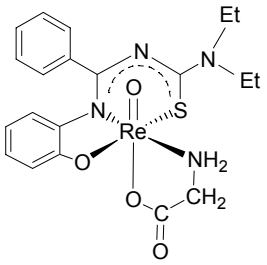
ESI^+ MS (m/z): 1116.0706, 60 %, $[M + H]^+$; 1139.0768, 100%, $[M + Na]^+$.

4.3.2.12 [ReO(L^{1a})(gly)], (19)

Method 1. HL^{1a} (33 mg, 0.1 mmol) in 3 mL of MeOH was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL of CH_2Cl_2. After stirring at room temperature for

15 min, solid glycine (8.2 mg, 0.11 mmol) and three drops of NEt_3 were added, and the mixture was heated under reflux for 3 hours. This resulted in a complete dissolution of glycine and the formation of a dark red solution. The solvent was removed under vacuum and the residue was washed with cold methanol and recrystallized from CH_2Cl_2/MeOH to yield big red crystals of **7** suitable for X-ray diffraction.

Method 2. Glycine (8.2 mg, 0.11 mmol), three drops of NEt_3 and **5a** (57 mg, 0.1 mmol) were heated under reflux in a CH_2Cl_2/MeOH mixture (1/1) (10 mL) for 3 h, whereupon glycine completely dissolved. The volume of the mixture was reduced to approximately 2 mL and the red solid, which precipitated upon cooling to room temperature, was filtered off, subsequently washed with cold MeOH, and dried in vacuum. Yield: 73% (44 mg) for method 1, 80% (48 mg) for method 2.



Elemental analysis:

Calcd. for $C_{20}H_{23}N_4O_4SRe$: C, 39.92; H, 3.83; N, 9.31; S, 5.32%.

Found: C, 40.61; H, 3.68; N, 10.09; S, 5.73%.

IR (KBr, cm^{-1}): 3425 (m), 3055 (w), 2984 (w), 2930 (w), 1651 (vs), 1543 (vs), 1480 (s), 1440 (s), 1374 (s), 1250 (s), 972 (s), 855 (m), 777 (m), 698 (m).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.25 - 1.31 (m, 6H, CH_3), 3.50 (m, 1H, CH_2), 3.86 (m, 2H, CH_2), 3.9-4.1 (m, $1H_{\alpha\text{-}CH2}$ + $2H_{CH2}$), 5.87 (bs, 1H, NH_2), 6.28 (t, J = 7.0 Hz, 1H, PhOH), 6.36 (d, J = 6.8 Hz,1H, PhOH), 6.85 (bs, $1H_{PhOH}$ + $1H_{NH2}$), 6.95 (d, J = 7.7 Hz, 1H, PhOH), 7.30 (t, J = 7.3 Hz, 2H, Ph), 7.35 (t, J = 7.2 Hz, 1H, Ph), 7.57 (d, J = 6.9 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.41 (CH_3), 47.42, 47.81 (CH_2), 61.91 (α-CH_2, glycine), 116.98, 118.92, 120.83, 125.24, 128.40, 130.55, 131.54, 134.90 (Ph + PhOH), 146.96 (C_{PhOH}-N), 164.43 (C_{PhOH}-O), 167.88 (C=N), 174.34 (C=S), 177.28 (C=O).

FAB^+ MS (m/z): 602 (36%, $[M + H]^+$); 527 (28%, $[M - Gly]^+$).

4.3.2.13 [ReO(L^1)(R^1R^2btu)], (20)

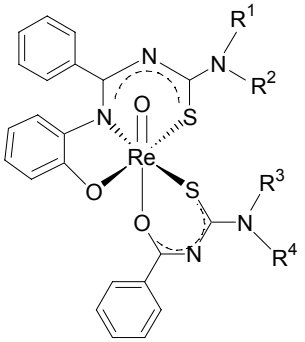
Method 1. Compound **14** (0.1 mmol) was dissolved in CH_2Cl_2 (5 mL) and HR^1R^2btu (0.1 mmol) and three drops of NEt_3 were added. The red colored solution was warmed at 35 ^oC for 2 h and the solvent was removed in *vacuo*. The resulting residue was either washed with cold MeOH or recrystallized from CH_2Cl_2/MeOH to give a red crystalline product. Yield: 70 - 90%.

Method 2. H_2L^1 (0.1 mmol) in 3 mL CH_2Cl_2 and three drops of Et_3N were added to a solution of $[ReOCl_2(R^1R^2btu)(PPh_3)]$ (**1**) (0.1 mmol) in 5 mL CH_2Cl_2. The mixture was heated on reflux for 3 h, whereupon the colour changed from green-yellow to deep red. The solvent was removed under reduced pressure and the residue was treated as described for method 1. Yield: 30 - 53%.

Method 3. A mixture of H_2L^1 (0.1 mmol) and HR^1R^2btu (0.1 mmol) in 3 mL MeOH was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL CH_2Cl_2. After stirring at room temperature for 15 min, three drops of NEt_3 were added and the mixture was kept at 35 °C for 2h. This resulted in the formation of a dark red solution. The solvent was removed under vacuum and the resulting residue was treated as described for method 1. Yield: 72 - 85 %.

Method 4. A mixture of H_2L^1 (0.1 mmol) and HR^1R^2btu (0.1 mmol) in 3 mL CH_2Cl_2 was added to a suspension of $[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) in 3 mL CH_2Cl_2. After stirring at room temperature for 15 min, the sparingly soluble rhenium complex dissolved and a clear solution was formed, the colour of which slowly turned to red. The addition of three drops of NEt_3 resulted in an immediate change of the colour and a deep red solution was obtained within a few seconds. The solvent was removed under vacuum and the resulting residue was treated as described for method 1. Yield: 67 - 81%

Data for 20a ($R^1 = R^2 = Et$, $R^3 = R^4 = Ph$)



Elemental analysis:

Calcd. for $C_{38}H_{34}N_5O_3S_2Re$: C, 53.13; H, 3.99; N, 8.15; S, 7.47.

Found: C, 53.02; H, 4.07; N, 8.01; S, 7.67.

IR (ν in cm^{-1}): 3051 (w), 2978 (w), 2923 (w), 1539 (vs), 1473 (vs), 1414 (vs), 1357 (s), 1250 (vs), 1172 (w), 1141 (w), 1026 (w), 980 (s), 748 (m), 698 (m).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.22 (t, 6H, CH_3), 3.80 (m, 2H, CH_2), 3.97 (m, 1H, CH_2), 4.05 (m, 1H, CH_2), 6.25 (t, J = 7.6 Hz, 1H, PhOH), 6.38 (d, J = 6.5 Hz, 1H, PhOH), 6.72 (t, J = 7.7 Hz, 1H, PhOH), 6.91 (t, J = 7.8 Hz, 2H, Ph), 7.01 (d, J = 6.8 Hz, 1H, PhOH), 7.1-7.7 (m, 18H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.44 (CH_3), 13.51 (CH_3), 47.17 (CH_2), 47.20 (CH_2), 117 -135 (Ph + PhOH) 145.30 (C_{ar}-N), 163.67 (C_{ar}-O), 171.46 (C=N, $\{L^{1a}\}^{2-}$), 173.02 (C=S, $\{L^{2a}\}^-$), 179.24 (C=S, $\{L^{1a}\}^{2-}$), 187.97 (C=O, $\{L^{2a}\}^-$).

FAB^+ MS (m/z): 882 (6%, $[M + Na]^+$); 860 (36%, $[M + H]^+$); 665 (39%, $[M - (Ph_2NC{\equiv}N)]^+$), 543 (8%, $[M - \{L^2\}^- + H]^+$).

Data for 20b ($R^1 = R^2$ = Et, NR^3R^4 = morph)

Elemental analysis:

Calcd. for $C_{30}H_{32}N_5O_4S_2Re$: C, 46.36; H, 4.15; N, 9.01; S, 8.25%.

Found: C, 46.27; H, 4.03; N, 8.85; S, 8.28%.

IR (ν in cm^{-1}): 3055 (w), 2978 (w), 2924 (w), 2854 (w), 1527 (vs), 1488 (vs), 1427 (vs), 1359 (s), 1250 (vs), 1110 (s), 1026 (s), 964 (s), 771 (m), 694 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.23 (t, 3H, CH_3), 1.25 (t, 3H, CH_3), 3.80 (m, 2H, N$\underline{CH_2}CH_3$), 4.00 (m, 5H, NCH_2 (morph) + N$\underline{CH_2}CH_3$), 4.02 (m, 1H, NCH_2 (morph)), 4.20 (m, 1H, OCH_2), 4.37 (m, 1H, OCH_2), 4.42 (m, 1H, OCH_2), 4.62 (m, 1H, OCH_2), 6.25 (t, *J* = 7.6 Hz, 1H, PhOH), 6.38 (d, *J* = 7.9 Hz, 1H, PhOH), 6.69 (t, *J* = 7.6 Hz, 1H, PhOH), 6.91 (d, *J* = 8.0 Hz, 1H, PhOH), 7.01 (t, *J* = 7.8 Hz, 2H, Ph), 7.28 (m, 3H, Ph), 7.30 (t, *J* = 7.3 Hz, 1H, Ph), 7.53 (d, *J* = 8.2 Hz, 2H, Ph) , 7.57 (d, *J* = 7.2 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.43 (CH_3), 13.54 (CH_3), 47.25 (NCH_2), 47.37 (NCH_2), 48.36 (NCH_2), 49.97 (NCH_2), 67.25 (OCH_2), 67.74 (OCH_2), 117.14, 118.40, 120.95, 124.57, 127.52, 128.13, 129.47, 130.73, 130.86, 131.78, 135.58 and 135.64 (Ph), 145.36 (C_{ar}-N), 163.87 (C_{ar}-O), 171.04 (C=N, $\{L^{1a}\}^{2-}$), 172.01 (C=S, $\{L^{2b}\}^-$), 178.17 (C=S, $\{L^{1a}\}^{2-}$), 184.73 (C=O, $\{L^{2b}\}^-$).

FAB^+ MS (m/z): 800, 15%, $[M+Na]^+$; 778, 41%, $[M+H]^+$; 691, 41%, $[M\text{-morph}]^+$; 665, 45%, $[M\text{-(morphC}\equiv\text{N)}]^+$; 543, 8%, $[M\text{-}\{L^{2b}\}^-+H]^+$.

Data for 20c (NR^1R^2 = morph, NR^3R^4 = morph)

Elemental analysis:

Calcd. for $C_{30}H_{30}N_5O_5S_2Re$: C, 45.56; H, 3.80; N, 8.86; S, 8.10%.

Found: C, 45.38; H, 3.90; N, 8.59; S, 8.45%.

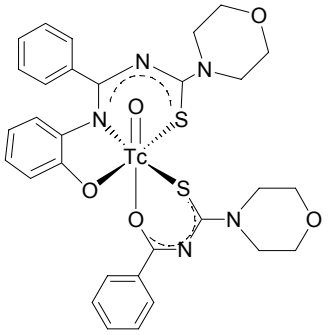
IR (ν in cm^{-1}): 3053 (w), 2970 (w), 2912 (w), 2855 (w), 1519 (vs), 1493 (vs), 1435 (vs), 1380 (s), 1353 (m), 1265 (s), 1250 (s), 1229 (s), 1115 (s), 1026 (s), 976 (s), 798 (m), 694 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.55 (m, 1H, NCH_2), 3.65 (m, 1H, NCH_2), 3.76 (m, 2H, NCH_2), 3.92 (m, 3H, NCH_2), 3.99 (m, 1H, NCH_2), 4.02– 4.20 (m, 5H, OCH_2), 4.27 (m, 1H, OCH_2), 4.50 (m, 1H, OCH_2), 4.70 (m, 1H, OCH_2), 6.26 (t, *J* = 7.6 Hz, 1H, PhOH), 6.41 (d, *J* = 7.9 Hz, 1H, PhOH), 6.71 (t, *J* = 7.6 Hz, 1H, PhOH), 6.92 (d, *J* = 7.9 Hz, 1H, PhOH), 7.05 (t, *J* = 7.8 Hz, 2H, Ph), 7.22 (m, 3H, Ph), 7.31 (t, *J* = 7.3 Hz, 1H, Ph), 7.55 (m, 4H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 48.67 (NCH_2), 49.17 (NCH_2), 49.83 (NCH_2), 50.18 (NCH_2), 66.53 (OCH_2), 66.61 (OCH_2), 67.33 (OCH_2), 67.58 (OCH_2), 117.31, 118.60, 121.22, 125.03, 127.62, 128.19, 129.59, 130.88, 131.34, 131.96 and 135.54 (Ph), 145.91 (C_{ar}-N), 164.86 (C_{ar}-O), 171.40 (C=N, $\{L^{1b}\}^{2-}$), 172.16 (C=N,$\{L^{2b}\}^-$), 178.37 (C=S, $\{L^{1b}\}^{2-}$), 184.69 (C=O, $\{L^{2b}\}^-$).

4.3.2.14 [TcO(L^{1b})(morphbtu)], (21b)

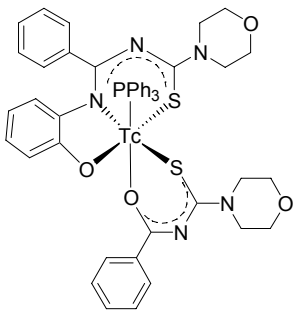
The technetium complex **21b** was prepared by the procedures described above for rhenium complexes **20** as method 1 (from **15b** and Hmorphbtu) and method 3 from $(NBu_4)[TcOCl_4]$ and a mixture of H_2L^{1b} and Hmorphbtu. In both procedures, a green solution was obtained. The solvent was removed under vacuum and the residue was washed with cold MeOH to obtain a green solid. Single crystals were obtained by slow evaporation of an acetone/CH_2Cl_2 solution.Yield: 86% (60 mg).



Elemental analysis:
Calcd. for $C_{30}H_{30}N_5O_5S_2Tc$: Tc, 14.1%. Found: Tc, 14.0%.
IR (KBr, cm^{-1}): 3063 (w), 2962 (w), 2916 (w), 2854 (w), 1504 (vs), 1475 (m), 1435 (s), 1350 (s), 1265 (s), 1218 (s), 1111 (s), 1026 (s), 957 (s), 798 (m), 694 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.35 (m, 2H, NCH_2), 3.72 (m, 2H, NCH_2), 3.85 (m, 2H, NCH_2), 3.98 (*m*, 3H, NCH_2 + OCH_2), 4.1 - 4.3 (m, 4H, OCH_2), 4.35 (m, 1H, OCH_2), 4.53 (m, 1H, OCH_2), 4.75 (m, 1H, OCH_2), 6.36 (m, 2H, PhOH), 6.81 (t, J = 7.5 Hz, 1H, PhOH), 6.97 (d, J = 6.7 Hz, 1H, PhOH), 7.09 (t, J = 7.1 Hz, 2H, Ph), 7.23 (m, 3H, Ph), 7.41 (t, J = 7.5 Hz, 1H, Ph), 7.64 (br, t, J = 7.5 Hz, 4H, Ph).

4.3.2.15 [Tc(PPh_3)(L^{1b})(morphbtu)], (22b)

Compound **21b** (70 mg, 0.1 mmol) was dissolved in 10 mL CH_2Cl_2 and PPh_3 (131 mg, 0.5 mmol) was added. The mixture was stirred at room temperature for three hours whereupon the color changed from yellow green to red. The volume of the solvent was reduced to 2 mL, and then 3 mL of MeOH was added. Red crystals of the product were obtained by slow evaporation of the reaction mixture. Yield: 89% (85 mg).

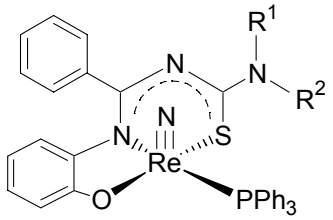


Elemental analysis:
Calcd. for $C_{48}H_{45}N_5O_4PS_2Tc$: Tc, 10.4%. Found: Tc, 10.6%.
IR (KBr, cm^{-1}): 3051 (w), 2962 (w), 2843 (w), 1497 (vs), 1466 (vs), 1420 (vs), 1350 (s), 1265 (s), 1207 (s), 1119 (s), 1022 (s), 721 (w), 694 (m).

4.3.2.16 [ReN(L^1)(PPh_3)], (23)

Solid [$ReNCl_2(PPh_3)_2$] (80 mg, 0.1 mmol) was added to a stirred solution of H_2L^1 (0.1 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 15 min and then 3 drops of Et_3N were added. This resulted in a complete dissolution of [$ReNCl_2(PPh_3)_2$] and the formation of a red solution. The solvent was removed under vacuum, and the residue was crystallized and isolated from a CH_2Cl_2/MeOH solution as red blocks.

Data for 23a (R^1= R^2 = Et)



Calcd. for $C_{36}H_{34}N_4OPSRe$: C, 54.88; H, 4.35; N, 7.11; S, 4.07%.

Found: C, 54.78; H, 4.30; N, 7.07; S, 4.15%.

IR (KBr, cm^{-1}): 3059 (w), 2978 (w), 2932 (w), 1512 (vs), 1492 (vs), 1477 (vs), 1439 (s), 1393 (m), 1354 (m), 1254 (vs), 1096 (m), 1065 (m), 1026 (w), 744 (m), 686 (s), 528 (s), 505 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.08 (t, *J* = 7.0 Hz, 3H, CH_3), 1.26 (t, *J* = 7.1 Hz, 3H, CH_3), 3.68 (m, 1H, CH_2), 3.80 (q, *J* = 7.1 Hz, 2H, CH_2), 4.17 (m, 1H, CH_2), 6.27 (t, *J* = 7.6 Hz, 1H, PhOH), 6.47 (d, *J* = 7.8 Hz, 1H, PhOH), 6.62 (t, *J* = 7.0 Hz, 1H, PhOH), 6.83 (d, *J* = 7.8 Hz, 1H, PhOH), 7.26 (t, *J* = 7.3 Hz, 2H, Ph), 7.35 (m, 10H, Ph + PPh_3), 7.79 (m, 8H, Ph + PPh_3).

^{31}P NMR (400 MHz, $CDCl_3$, ppm): 29.64 (s).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 12.82, 13.19 (CH_3), 46.33, 47.70 (CH_2), 117.0-135.8 ($C_{aromatic}$), 141.33 (C_{PhOH}-N), 162.06 (C_{PhOH}-O), 166.75 (C=N), 171.63 (C=S).

ESI^+ MS (m/z): 811, 100%, $[M + Na]^+$; 789, 40%, $[M + H]^+$.

Data for 23b (NR^1R^2 = morph)

Calcd. for $C_{36}H_{32}N_4O_2PSRe$: C, 53.92; H, 4.02; N, 6.99; S, 4.00%.

Found: C, 53.87; H, 4.15; N, 7.10; S, 4.09%.

IR (KBr, cm^{-1}): 3051 (w), 2970 (w), 2905 (w), 2858 (w), 1507 (vs), 1477 (vs), 1435 (s), 1388 (s), 1357 (w), 1257 (s), 1219 (m), 1096 (m), 1068 (m), 1026 (m), 745 (m), 690 (s), 528 (s), 505 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.59 (s, br, 1H, NCH_2), 3.70 (s, br, 2H, NCH_2), 3.81 (s, br, 1H, NCH_2), 3.96 (s, br, 1H, OCH_2), 4.16 (s, br, 2H, OCH_2), 4.32 (s, br, 1H, OCH_2), 6.27 (t, *J* = 7.6 Hz, 1H, PhOH), 6.49 (d, *J* = 7.8 Hz, 1H, PhOH), 6.64 (t, *J* = 7.6 Hz, 1H, PhOH), 6.84 (d, *J* = 7.9 Hz, 1H, PhOH), 7.27 (t, *J* = 7.3 Hz, 2H, Ph), 7.37 (m, 10H, Ph + PPh_3), 7.77 (m, 8H, Ph +PPh_3).

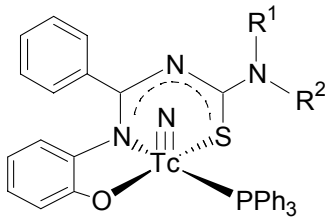
^{31}P NMR (400 MHz, $CDCl_3$, ppm): 28.83 (s).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 48.80, 49.72 (NCH_2), 66.66, 66.90 (OCH_2), 117.2-135.7 (Ph), 140.90 (C_{PhOH}-N), 162.99 (C_{PhOH}-O), 167.06 (C=N), 171.31 (C=S).
ESI^+ MS (m/z): 825, 100%, $[M + Na]^+$; 803, 40%, $[M + H]^+$.

4.3.2.17 [TcN(L^1)(PPh_3)], (24)

The technetium complexes **24** were prepared following the procedure described for their analogous rhenium complexes **23** except that the precusor $[TcNCl_2(PPh_3)_2]$ was used.

Data for 24a (R^1= R^2 = Et)



Calcd. for $C_{36}H_{34}N_4OPSTc$: Tc, 14.1%. Found: Tc, 14.1%.
IR (KBr, cm^{-1}): 3051 (w), 2970 (w), 2924 (w), 1504 (vs), 1477 (vs), 1434 (s), 1396 (m), 1350 (m), 1307 (m), 1258 (vs), 1095 (m), 1057 (m), 1026 (w), 798 (m), 741 (m), 690 (s), 528 (s), 497 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.09 (t, *J* = 7.1 Hz, 3H, CH_3), 1.26 (t, *J* = 7.1 Hz, 3H, CH_3), 3.67 (m, 1H, CH_2), 3.75 (m, 2H, CH_2), 4.00 (m, 1H, CH_2), 6.23 (t, *J* = 7.5 Hz, 1H, PhOH), 6.37 (d, *J* = 7.7 Hz, 1H, PhOH), 6.63 (t, *J* = 7.1 Hz, 1H, PhOH), 6.79 (d, *J* = 7.8 Hz, 1H, PhOH), 7.26 (t, *J* = 7.4 Hz, 2H, Ph), 7.30 (m, 10H, Ph + PPh_3), 7.73 (m, 8H, Ph + PPh_3).
^{31}P NMR (400 MHz, $CDCl_3$, ppm): 45.36 (s).

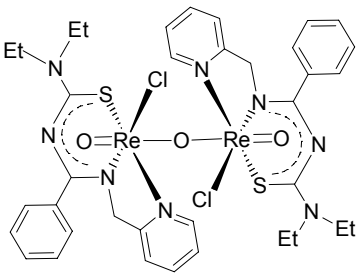
Data for 24b (NR^1R^2 = morph)

Calcd. for $C_{36}H_{32}N_4O_2PSTc$: Tc, 13.8%. Found: Tc, 13.9%.
IR (KBr, cm^{-1}): 3051 (w), 2970 (w), 2909 (w), 2843 (w), 1498 (vs), 1477 (vs), 1431 (s), 1400 (s), 1357 (w), 1312 (m), 1265 (s), 1215 (m), 1095 (m), 1060 (m), 1026 (m), 844 (m), 748 (s), 691 (s), 524 (s), 505 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.61 (s, br, 1H, NCH_2), 3.70 (m, 2H, NCH_2), 3.76 (s, br, 1H, NCH_2), 3.98 (s, br, 1H, OCH_2), 4.05 (m, br, 2H, OCH_2), 4.20 (s, br, 1H, OCH_2), 6.22 (t, *J* = 7.5 Hz, 1H, PhOH), 6.38 (d, *J* = 7.8 Hz, 1H, PhOH), 6.65 (t, *J* = 7.6 Hz, 1H, PhOH), 6.79 (d, *J* = 7.8 Hz, 1H, PhOH), 7.22 (t, *J* = 7.4 Hz, 2H, Ph), 7.34 (m, 10H, Ph + PPh_3), 7.71 (m, 8H, Ph +PPh_3).
^{31}P NMR (400 MHz, $CDCl_3$, ppm): 44.59 (s).

4.3.2.18 [{ReOCl(L^2)}$_2$O], (25)

Method 1. HL^2 (36 mg, 0.11 mmol) in 3 mL of acetone and three drops of NEt_3 were added to a stirred suspension of [$ReOCl_3(PPh_3)_2$] (83 mg, 0.1 mmol) in 3 mL of CH_2Cl_2. The mixture was heated under reflux for 30 min, whereupon the precursor complex completely dissolved and the color of the reaction mixture changed from yellow-green to violet. The solvent was removed under reduced pressure, and the resulting residue was washed with methanol and recrystallized by slow evaporation of a CH_2Cl_2/acetone solution to yield violet block-like crystals of **25**. Yield: 91% (52 mg).

Method 2. HL^2 (36 mg, 0.11 mmol) was dissolved in 3 mL of acetone and three drops of NEt_3 were added. This solution was added dropwise to a solution of (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) in 2 mL of acetone. The mixture was stirred at ambient temperature for 2 h and the solvent was removed. The residue was carefully washed with MeOH. Recrystallization from CH_2Cl_2/acetone yielded violet crystals. Yield 40% (23 mg).



Elemental analysis:

Calcd. for $C_{36}H_{42}Cl_2N_8O_3S_2Re_2$: C, 37.85; H, 3.68; N, 9.81; S, 5.61%.

Found: C, 37.52; H, 3.44; N, 10.02; S, 5.35%.

IR (KBr, cm^{-1}): 3050 (w), 2983 (w), 2950 (w), 1488 (s), 1420 (s), 1374 (s), 1250 (s), 949 (w), 855 (m), 770 (m), 683 (s), 571 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.99 (t, J = 7.0 Hz, 3H, CH_3), 1.06 (t, J = 7.0 Hz, 3H, CH_3), 3.19 (m, 1H, CH_2), 3.39 (m, 1H, CH_2), 3.95 (m, 1H, CH_2), 4.03 (m, 1H, CH_2), 5.03 (d, J = 19.2 Hz, 1H, pyCH_2), 5.99 (d, J = 19.2 Hz, 1H, pyCH_2), 7.39 - 7.48 (m, 6H, Ph), 7.37 (t, J = 7.4 Hz, 1H, Ph), 8.79 (d, J = 5.6 Hz, 2H, py).

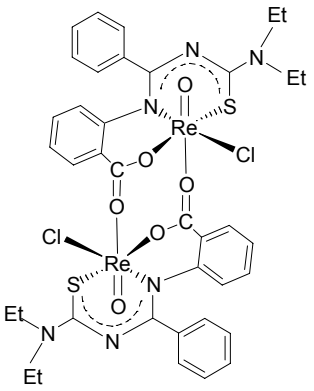
^{13}C NMR (400 MHz, $CDCl_3$, ppm): 48.06 48.70 (NCH_2), 65.99, 66.51 (OCH_2), 117.29, 120.50, 124.60, 127.00, 127.63, 128.40, 128.49, 128.92, 131.04 and 134.24 (Ph + Py), 149.45 (C=N), 187.57 (C=S).

FAB$^+$ MS (m/z): 544, 32% [$ReO_2(L^2)$]$^+$; 528, 30% [$ReO(L^2)$]$^+$.

4.3.2.19 [ReOCl(L^3)]$_2$, (26)

(NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) was added to a solution of H_2L^3 (36 mg, 0.1 mmol) in 5 mL of MeOH. The mixture was stirred at room temperature for 15 min and reduced in

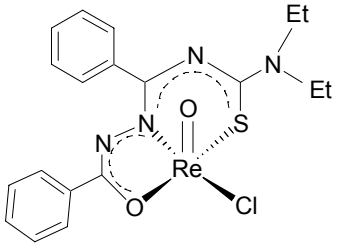
volume to about 2 mL. X-ray quality green crystals of **26** deposited from this solution within several days. Yield: 87% (49 mg).



Elemental analysis:
Calcd. for $C_{38}H_{38}Cl_2N_6O_6S_2Re_2$: C, 38.60; H, 3.22; N, 7.11; S, 5.42%.
Found: C, 38.75; H, 2.98; N, 6.52; S, 5.27%.
IR (KBr, cm^{-1}): 3062 (w), 2977 (w), 1542 (s), 1527 (s), 1442 (s), 1350 (s), 1218 (m), 1141 (m), 1072 (w), 1002 (s), 918 (w), 756 (m), 732 (m), 679(m).
^{1}H NMR ((400 MHz, DMSO-d_6, ppm): 1.31-1.38 (m, 6H, CH_3), 3.80-4.20 (m, 4H, CH_2), 6.51 (d, J = 8.1 Hz, 1H, PhCOO), 6.95 (t, J = 8.0 Hz, 1H, PhCOO), 7.16 (t, J = 7.5 Hz, 1H, PhCOO), 7.34 (m, 3H, Ph), 7.63 (d, J = 8.1 Hz, 1H, Ph), 8.18 (d, J = 8.2 Hz, 2H, Ph).

4.3.2.20 [ReOCl(L^4)], (27)

H_2L^4 (0.1 mmol) dissolved in 2 mL MeOH was added dropwise to a stirred solution of (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) in 1 mL MeOH. The color of the solution immediately turned deep red and the reaction mixture was stirred for 6h at room temperature. The formed red powder was filtered off, washed with cold methanol. X-ray quality single crystals of **27** were obtained by slow evaporation of a dichloromethane/methanol solution. Yield: 61% (36 mg).



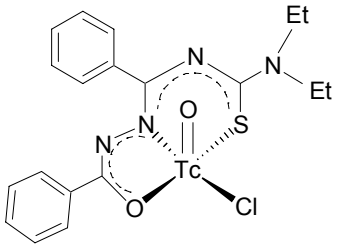
Elemental analysis:
Calcd. for $C_{19}H_{20}ClN_4O_2SRe$: C, 38.67; H, 3.42; N, 9.49; S, 5.43.
Found: C, 38.17; H, 3.50; N, 9.41; S, 5.22.
IR (KBr, cm^{-1}): 3055 (w), 2989 (w), 2932 (w), 1508 (vs), 1438 (m), 1389 (m), 1326 (m), 1292 (m), 1145 (w), 1072 (w), 1026 (w), 991 (s), 775 (m), 709 (m), 691 (s).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.33 (t, J = 7.1 Hz, 3H, CH_3), 1.39 (t, J = 7.1 Hz, 3H, CH_3), 3.90 (m, 2H, CH_2), 4.12 (m, 2H, CH_2), 7.32 (t, J = 7.2 Hz, 2H, Ph), 7.38 (t, J = 7.0 Hz, 1H, Ph), 7.43 (t, J = 7.5 Hz, 2H, Ph), 7.51 (t, J = 7.4 Hz, 1H, Ph), 7.85 (d, J = 7.9 Hz, 2H, Ph), 8.05 (d, J = 8.3 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 12.91, 13.20 (CH_3), 47.41, 47.83 (NCH_2), 127.70, 127.78, 128.45, 128.65, 130.94, 131.76, 132.10 and 134.98 (Ph), 166.69 (C=N), 172.70 (C=S), 173.73 (C=O).

4.3.2.21 [TcOCl(L^4)] (28).

The red microcrystalline **28** was prepared from (NBu_4)[$TcOCl_4$] and H_2L^4 by a similar procedure described for **27** except the reaction mixture was stirred at room temperature for 2 h. Yield: 50% (26 mg).

Elemental analysis:
Calcd. for $C_{19}H_{20}ClN_4O_2STc$: Tc, 20.8%. Found: Tc, 20.6%
IR (KBr, cm^{-1}): 3055 (w), 2985 (w), 2932 (w), 2870 (w), 1504 (vs), 1434 (m), 1389 (s), 1354 (m), 1327 (m), 1292 (m), 1174 (w), 1095 (w), 1064 (w), 1026 (w), 976 (s), 775 (m), 698 (s).

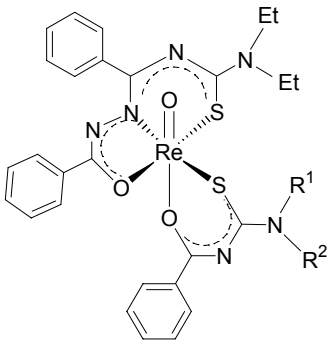


^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.30 (t, *J* = 7.1 Hz, 3H, CH_3), 1.37 (t, *J* = 7.1 Hz, 3H, CH_3), 3.90-4.00 (m, 4H, CH_2), 7.32 (t, *J* = 7.4 Hz, 2H, Ph), 7.36 (t, *J* = 6.9 Hz, 1H, Ph), 7.42 (t, *J* = 7.7 Hz, 2H, Ph), 7.50 (t, *J* = 7.3 Hz, 1H, Ph), 7.84 (d, *J* = 7.9 Hz, 2H, Ph), 8.01 (d, *J* = 8.1 Hz, 2H, Ph).

4.3.2.22 [ReO(L^4)(R^1R^2btu)] (29)

Method 1. A mixture of the tridentate benzamidine ligand H_2L^4 (35 mg, 0.1 mmol) and HR^1R^2btu (0.1 mmol) in 3 mL MeOH was added to a solution of (NBu_4)[$ReOCl_4$] (0.1 mmol) in 3 mL CH_2Cl_2. After stirring at room temperature for 10 min., three drops of NEt_3 were added and the mixture was heated under reflux for 2 hours. This resulted in the formation of a dark red solution. The solvent was removed under vacuum to dryness. The resulting residue was either washed with cold MeOH or recrystallized from CH_2Cl_2/MeOH to give a red crystalline product.
Method 2. Compound **27** (59 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (10 mL), HR^1R^2btu (0.1 mmol) and three drops of NEt_3 were added. The red solution was stirred under reflux for 2 h, the solvent was removed *in vacuo* and the residue was treated as described in method 1.

Data for 29a ($R^1 = R^2 = Ph$)



Yield: 63% for method 1, 71% for method 2.

Elemental analysis:

Calcd. for $C_{39}H_{35}N_6O_3S_2Re$: C, 52.86.; H, 3.98; N, 9.48; S, 7.24.

Found: C, 52.00; H, 3.25; N, 9.37; S, 6.93.

IR (KBr, cm^{-1}): 3055 (w), 2978 (w), 2924 (w), 1512 (vs), 1450 (s), 1427 (vs), 1404 (vs), 1334 (m), 1257 (m), 972 (s), 694 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.23 (t, 3H, CH_3), 1.25 (t, 3H, CH_3), 3.74 (m, 2H, CH_2), 3.91 (m, 1H, CH_2), 4.00 (m, 1H, CH_2), 6.99 (t, *J* = 7.9 Hz, 2H, Ph), 7.2-7.4 (m, 19H, Ph), 7.79 (d, *J* = 8.4 Hz, 2H, Ph), 7.99 (d, *J* = 8.4 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.35 (CH_3), 13.38 (CH_3), 46.58 (CH_2), 47.49 (CH_2), 127 - 136 (Ph), 163.20 (C=N, L^4), 173.10 (C=S, btu), 174.05 (C=S, L^4), 176,18 (C=O, L^4), 186.95 (C=O, btu).

FAB$^+$ MS (m/z): 909, 11%, $[M + Na]^+$; 887, 40%, $[M + H]^+$; 814, 6%, $[M - NEt_2]^+$; 692, 65%, $[M - Ph_2NC{\equiv}N]^+$.

Data for 29b (NR^1R^2 = morph)

Yield: 40% for method 1, 59% for method 2.

Elemental analysis:

Calcd. for $C_{31}H_{33}N_6O_4S_2Re$: C, 46.31; H, 4.14; N, 10.55; S, 7.98

Found: C, 46.12; H, 4.05; N, 10.47; S, 7.79.

IR (KBr, cm^{-1}): 3062 (w), 2978 (w), 2926 (w), 1520 (vs),1488 (vs), 1420 (vs), 1350 (s), 1311 (s), 1234 (m), 1110 (m), 1065 (m), 1026 (m), 972 (s), 771 (m), 694 (s).

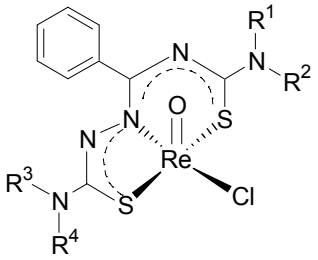
^1H NMR (400 MHz, $CDCl_3$, ppm): 1.23 (t, 3H, CH_3), 1.25 (t, 3H, CH_3), 3.74 (m, 2H, NCH_2 Mor), 3.89 (m, 2H, Mor-NCH_2), 3.95 - 4.05 (m, 4H, Et-CH_2), 4.29 (m, 1H, Mor-OCH_2), 4.34 (m, 1H, Mor-OCH_2), 4.46 (m, 1H, Mor-OCH_2), 4.58 (m, 1H, Mor-OCH_2), 7.09 (t, *J* = 7.7 Hz, 1H, Ph), 7.21-7.27 (m, 4H, Ph), 7.34 - 7.41 (m, 3H, Ph), 7.68 (d, *J* = 7.1 Hz, 2H, Ph), 7.81 (d, *J* = 8.3 Hz, 2H, Ph), 7.90 (d, *J* = 8.3 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.37 (CH_3), 13,40 (CH_3), 46.59 (NCH_2), 47.57 (NCH_2), 48.32 (NCH_2), 49.81 (NCH_2), 67.12 (OCH_2), 67.34 (OCH_2), 127.37, 127.72, 127.96, 128.48, 129.56, 129.80, 130.42, 130.67, 131.44, 132.01, 135.42 and 136.47 (Ph), 163.25 (C=N, L^4), 171.99 (C=S, btu), 173.93 (C=S, L^4), 176,19 (C=O, L^4), 184.85 (C=O, btu).

FAB$^+$ MS (m/z): 827, 9%, $[M+Na]^+$; 805, 38%, $[M+H]^+$; 692, 37%, $[M\text{-}MorC{\equiv}N]^+$; 572, 35%, $[ReO_2(L^2)]^+$.

4.3.2.23 [ReOCl(L^5)], (30)

H_2L^5 (0.1 mmol) dissolved in 3 mL MeOH was added dropwise to a stirred solution of $(NBu_4)[ReOCl_4]$ (50 mg, 0.1 mmol) in 2 mL MeOH. The color of the solution immediately turned deep red and a red precipitate deposited within a few minutes. The red powder was filtered off, washed with cold methanol and recrystallized from CH_2Cl_2/MeOH.



Data for 30a ($R^1 = R^2 = Et$, $R^3 = R^4 = Me$): Yield: 84% (48 mg).

Elemental analysis:

Calcd. for $C_{15}H_{21}ClN_5OS_2Re$: C, 31.43; H, 3.69; N, 12.22; S, 11.19%.

Found: C, 31.35; H, 3.64; N, 12.19; S, 11.05%.

IR (KBr, cm^{-1}): 2964 (w), 2924 (w), 1519 (vs), 1450 (m), 1360 (m), 1261 (w), 1070 (w), 984 (s), 775 (w), 698 (w).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.36, 1.39 (t, J = 7.2 Hz, 3H, CH_3), 3.16 (s, 6H, NCH_3), 3.99 (m, 4H, CH_2), 7.38 (t, J = 7.7 Hz, 2H, Ph), 7.43 (t, J = 7.2 Hz, 1H, Ph), 7.68 (d, J = 7.5 Hz, 2H, o-Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.12, 13.21 (CH_3), 41.88 (NCH_3), 47.12, 47.52 (NCH_2), 127.66, 130.63, 131.30, 136.43 (Ph), 166.94 (C=N), 168.90 (C=S), 169.73 (C=S).

Data for 30b ($R^1 = R^2 = Et$, $R^3R^4 = -(CH_2)_4-$): Yield: 80% (48 mg).

Elemental analysis:

Calcd. for $C_{17}H_{23}ClN_5OReS_2$: C, 34.08; H, 3.87; N, 11.69; S, 10.70%.

Found: C, 33.95; H, 3.59; N, 11.39; S, 11.01%.

IR (KBr, cm^{-1}): 2970 (w), 2931 (w), 1520 (vs), 1481 (m), 1458 (m), 1377 (m), 1361 (m), 1312 (w), 1037 (w), 980 (s), 770 (w).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.20 (m, 6H, CH_3), 1.86 (s, 4H, CH_2), 3.41 (s, 4H, pyrolidine NCH_2), 3.5-3.9 (m, 4H, NCH_2), 7.30-7.37 (m, 3H, Ph), 7.67 (d, J = 7.0 Hz, 2H, o-Ph).

ESI^+ MS (m/z): 596, 5%, $[M - Cl + MeOH]^+$; 618, 100%, $[M - HCl + MeOH + Na]^+$.

Data for 30c ($R^1 = R^2 = Et$, $R^3R^4 = -(CH_2)_5-$): Yield: 76% (46 mg).

Elemental analysis:

Calcd. for $C_{18}H_{25}ClN_5OReS_2$: C, 35.26; H, 4.11; N, 11.42; S, 10.46 %.

Found: C, 35.33; H, 3.98; N, 11.26; S, 11.01%.

IR (KBr, cm^{-1}): 2931 (w), 1519 (vs), 1438 (m), 1359 (m), 1245 (w), 1226 (8), 1030 (w), 979 (s), 770 (w).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.34 (t, J = 6.0 Hz, 3H, CH_3), 1.39 (t, J = 6.0 Hz, 3H, CH_3), 1.58 (m, 6H, CH_2), 3.66 (s, 4H, piperidine NCH_2), 3.8-4.1 (m, 4H, NCH_2), 7.35 (t, J = 7.3 Hz, 2H, Ph), 7.42 (t, J = 7.3 Hz, 1H, Ph), 7.63 (d, J = 7.7 Hz, 2H, *o*-Ph).

ESI^+ MS (m/z): 610, 20%, $[M - Cl^- + MeOH]^+$; 632, 100%, $[M - HCl + MeOH + Na]^+$; 648, 15%, $[M - HCl + MeOH + K]^+$.

Data for 30d ($R^1 = R^2$ = Et, R^3R^4 = -$(CH_2)_6$-): Yield: 71% (45 mg).

Elemental analysis:

Calcd. for $C_{19}H_{27}ClN_5OReS_2$: C, 36.38; H, 4.34; N, 11.17; S, 10.22 %.

Found: C, 36.43; H, 4.34; N, 11.15; S, 10.14%.

IR (KBr, cm^{-1}): 2927 (m), 2850 (m), 1527 (vs), 1442 (m),, 1440 (w), 1357 (m), 1296 (w), 1172 (w), 983 (s), 771 (w), 698 (w), 682 (w).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.37 (t, J = 7.2 Hz, 3H, CH_3), 1.42 (t, J = 7.1 Hz, 3H, CH_3), 1.54 (m, 4H, CH_2), 1.67 (s, 4H, CH_2), 3.69 (m, 4H, azepine NCH_2), 4.00 (m, 4H, NCH_2), 7.3-7.4 (m, 3H, Ph), 7.65 (d, J = 8.0 Hz, 2H, *o*-Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 13.16, 13.21 (CH_3), 26.87 (CH_2), 28.34 (CH_2), 47.10, 47.47 (NCH_2), 52.77 (NCH_2), 127.63, 130.51, 131.10, 136.38 (Ph), 166.66 (C=N), 168.81 (C=S), 168.79 (C=S).

ESI^+ MS (m/z): 624, 25%, $[M - Cl^- + MeOH]^+$; 646, 100%, $[M - HCl + MeOH + Na]^+$; 662, 15%, $[M - HCl + MeOH + K]^+$.

Data for 30e ($R^1 = R^2$ = Et, R^3 = Me, R^4 = Ph): Yield: 62% (39 mg).

Elemental analysis:

Calcd. for $C_{20}H_{23}ClN_5OReS_2$: C, 37.82; H, 3.65; N, 11.03; S, 10.09 %.

Found: C, 37.88; H, 3.81; N, 11.26; S, 10.30%.

IR (KBr, cm^{-1}): 2981 (w), 2931 (w), 1530 (vs), 1438 (m), 1354 (s), 1301 (w), 1072 (w), 984 (s), 771 (w), 694 (m).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.35 (m, 6H, CH_3), 3.40 (s, 3H, NCH_3), 3.9-4.0 (m, 4H, NCH_2), 7.21 (m, 3H, Ph), 7.28 (t, J = 7.5 Hz, 2H, Ph), 7.40 (m, 3H, Ph), 7.69 (d, J = 8.1 Hz, 2H, Ph).

ESI^+ MS (m/z): 654, 90%, $[M - HCl + MeOH + Na]^+$; 670, 100%, $[M - HCl + MeOH + K]^+$.

Data for 30f (NR^1R^2 = Morph, R^3R^4 = -$(CH_2)_6$-): Yield: 78% (50 mg).

Elemental analysis:

Calcd. for $C_{19}H_{25}ClN_5O_2ReS_2$: C, 35.59; H, 3.93; N, 10.92; S, 10,00%.

Found: C, 35.45; H, 3.84; N, 10.77; S, 10.03%.

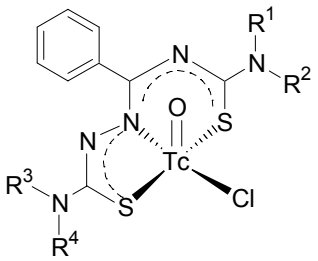
IR (KBr, cm^{-1}): 2964 (w), 2845 (w), 1524 (vs), 1453 (m), 1362 (m), 1270 (w), 1076 (w), 981 (s), 770 (w), 696 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.55 (s, 4H, CH_2), 1.69 (s, 4H, CH_2), 3.4-4.2 (m, 12H, NCH_2), 7.3-7.4 (m, 3H, Ph), 7.69 (d, *J* = 8.1 Hz, 2H, *o*-Ph).

4.3.2.24 [TcOCl(L^5)], (31)

The compounds **31** were prepared from $(NBu_4)[TcOCl_4]$ and H_2L^5 by a similar procedure as described for their rhenium analogous **30**.

Data for 31a (R^1 = R^2 = Et, R^3 = R^4 = Me): Yield: 82% (39 mg).



Elemental analysis:

Calcd. for $C_{15}H_{21}ClN_5OS_2Tc$: Tc, 20.4%. Found: Tc, 20.6%.

IR (KBr, cm^{-1}): 2981 (w), 2942 (w), 1519 (vs), 1451 (m), 1363 (m), 1266 (w), 1072 (w), 957 (s), 771 (w), 697 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.27 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.2 Hz, 3H, CH_3), 3.01 (s, 6H, NCH_3), 3.83 (m, 2H, CH_2), 3.89 (m, 1H, CH_2), 3.96 (m, 1H, CH_2), 7.31-7.39 (m, 3H, Ph), 7.65 (d, *J* = 8.0 Hz, 2H, *o*-Ph).

Data for 31d (R^1 = R^2 = Et, R^3R^4 = -$(CH_2)_6$-): Yield: 85% (45 mg).

Elemental analysis:

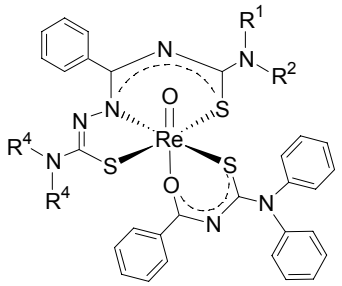
Calcd. for $C_{19}H_{27}ClN_5OS_2Tc$: Tc, 18.3%. Found: Tc, 18.4%.

IR (KBr, cm^{-1}): 2923 (w), 2850 (w), 1519 (s), 1458 (m), 1434 (m), 1357 (s), 1261 (m), 1172 (w), 1072 (w), 961 (s), 767 (w), 679 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.26 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 1.47 (s, 4H, CH_2), 1.59 (s, 4H, CH_2), 3.51 (s, 4H, NCH_2), 3.80 (m, 2H, CH_2), 3.89 (m, 1H, CH_2), 3.97 (m, 1H, CH_2), 7.31 - 7.36 (m, 3H, Ph), 7.61 (d, *J* = 7.0 Hz, 2H, *o*-Ph).

4.3.2.25 [ReO(L^5)(R^1R^2btu)], (32)

HR^1R^2btu (0.1 mmol) was dissolved in MeOH (3 mL) and then added to a stirred solution of compound **30** (0.1 mmol) in CH_2Cl_2 (3 mL). After 5 minutes, 3 drops of NEt_3 were added. The resulting red solution was stirred for 2 h at room temperature, the solvent was removed in *vacuo* and the residue was washed with cold MeOH to get a red powder of **32**. Single crystals were obtained by slow evaporation of a CH_2Cl_2/MeOH solution.



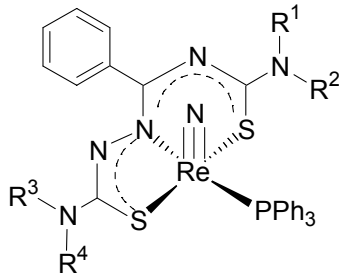
Data for [ReO(Ph_2btu)(L^{5a})] (32a): Yield: 69% (69 mg).
Elemental analysis:
Calcd. for $C_{35}H_{36}N_7O_2ReS_3$: C, 48.37; H, 4.18; N, 11.28; S, 11.07%.
Found: C, 48.37; H, 2.67; N, 11.11; S, 11.21%.
IR (KBr, cm^{-1}): 2974 (w), 2927 (w), 2869 (w), 1531 (vs), 1427 (s), 1353 (s), 1257 (w), 1141 (w), 1072 (w), 968 (s), 752 (w), 698 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.16-1.24 (m, 6H, CH_3), 3.03 (s, 6H, NCH_3), 3.58-3.69 (m, 2H, CH_2), 3.91-4.04 (m, 2H, CH_2) , 7.00 (t, J = 7.8 Hz, 2H, Ph), 7.18-7.52 (m, 16H, Ph), 7.70 (d, J = 7.8 Hz, 2H, Ph).
ESI^+ MS (*m/z*): 870, 50%, $[M + H]^+$; 892, 100%, $[M + Na]^+$; 908, 40%, $[M + K]^+$.

Data for [ReO(Ph_2btu)(L^{5c})] (32c): Yield: 78 % (72 mg).
Elemental analysis:
Calcd. for $C_{39}H_{43}N_7O_2ReS_3$: C, 50.68; H, 4.69; N, 10.61; S, 10.41%.
Found: C, 49.12; H, 3.93; N, 10.36; S, 10.74%.
IR (KBr, cm^{-1}): 2931 (w), 1512 (vs), 1427 (s), 1358 (m), 1249 (m), 1071 (w), 968 (s), 773 (w), 698 (w).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.16-1.23 (m, 6H, CH_3), 1.45 (s, br, 6H, CH_2, piperidine), 3.41-3.49 (m, 4H, NCH_2, piperidine), 3.60-3.70 (m, 2H, NCH_2), 3.90-4.00 (m, 2H, NCH_2), 7.00 (t, J = 7.8 Hz, Ph), 7.18-7.55 (m, 16H, Ph), 7.67 (dd, J = 7.6 Hz, ^4J = 2.0 Hz, 2H, Ph).
ESI^+ MS (*m/z*): 910, 45%, $[M + H]^+$; 932, 100%, $[M + Na]^+$; 948, 70%, $[M + K]^+$.

4.3.2.25 [ReN(L^5)(PPh_3)], (33)

A mixture of H_2L^5 (0.1 mmol), $[ReNCl_2(PPh_3)_2]$ (80 mg, 0.1 mmol) and three drops of Et_3N in CH_2Cl_2 (10 mL) was stirred at room temperature for 2 h, whereupon a clear red solution

was obtained. The solvent was removed to dryness and the residue was washed with MeOH and then dried under vacuum. The products were collected as red, analytically pure powders.



Data for 33a ($R^1 = R^2 = Et$, $R^3 = R^4 = Me$): Yield: 69% (55 mg).

Elemental analysis:

Calcd. for $C_{33}H_{36}N_6PReS_2$: C, 49.67; H, 4.55; N, 10.53; S, 8.04%.

Found: C, 49.63; H, 4.50; N, 10.39; S, 8.01%.

IR (KBr, cm^{-1}): 3055 (w), 2923 (m), 2854 (w), 1508 (vs), 1431 (s), 1354 (s), 1099 (m), 1060 (m), 914 (m), 744 (m), 705 (m), 690 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.05 (t, J = 7.0 Hz, 3H, CH_3), 1.15 (t, J = 7.1 Hz, 3H, CH_3), 2.95 (s, 6H, NCH_3), 3.68 (m, 4H, NCH_2), 7.2 - 7.7 (m, 20 H, Ph).

$^{31}P\{H\}$ NMR (400 MHz, $CDCl_3$, ppm): 33.47.

ESI^+ MS (m/z): 799, 100%, $[M + H]^+$.

Data for 33d ($R^1 = R^2 = Et$, $R^3R^4 = -(CH_2)_6-$): Yield: 68% (58 mg).

Elemental analysis:

Calcd. for $C_{37}H_{42}N_6PReS_2$: C, 52.15; H, 4.97; N, 9.86; S, 7.53%.

Found: C, 51.99; H, 4.84; N, 9.70; S, 7.62%.

IR (KBr, cm^{-1}): 3055 (w), 2927 (m), 2860 (w), 1496 (vs), 1423 (s), 1353 (s), 1253 (m), 1095 (m), 1064 (m), 995 (m), 744 (m), 694 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.06 (t, J = 7.0 Hz, 3H, CH_3), 1.17 (t, J = 7.0 Hz, 3H, CH_3), 1.41 (s, 4H, CH_2), 1.47 (s, 4H, CH_2), 3.51 (t, 4H, azepine NCH_2) 3.66 (m, 4H, NCH_2), 7.2-7.8 (m, 20 H, Ph).

$^{31}P\{H\}$ NMR (400 MHz, $CDCl_3$, ppm): 33.69.

ESI^+ MS (m/z): 853, 100%, $[M + H]^+$; 875, 900%, $[M + Na]^+$.

Data for 33f (NR^1R^2 = Morph, $R^3R^4 = -(CH_2)_6-$): Yield: 64% (56 mg).

Elemental analysis:

Calcd. for $C_{37}H_{40}N_6OPReS_2$: C, 51.31; H, 4.66; N, 9.70; S, 7.40%.

Found: C, 51.23; H, 4.71; N, 9.64; S, 7.34%.

IR (KBr, cm^{-1}): 3055 (w), 2912 (m), 2854 (w), 1481 (vs), 1434 (s), 1350 (m), 1064 (m), 1026 (m), 744 (m), 690 (s).

^1H NMR (400 MHz, $CDCl_3$, ppm): 1.46 (s, 4H, CH_2), 1.60 (s, 4H, CH_2), 3.4-3.9 (m, 12H, NCH_2), 7.2-7.9 (m, 20 H, Ph).

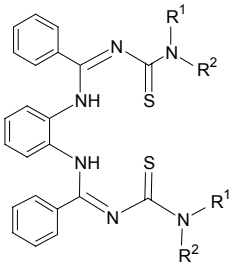
$^{31}P\{H\}$ NMR (400 MHz, $CDCl_3$, ppm): 33.12.

4.3.3 Tetradentate Benzamidine Ligands and their Complexes

4.3.3.1 Bisbenzamidines, H_2L^6

Solid R^1R^2bzm-Cl (5 mmol) was added to a stirred solution of o-phenylenediamine (252 mg, 0.25 mmol) and triethylamine (1.01 g, 10 mmol) in 10 mL of dry THF. After a few minutes, a colourless precipitate of $NEt_3 \cdot HCl$ began to deposit. The mixture was stirred for 4 hours and then cooled to 0 °C. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off, and the solvent was removed under vacuum. The resulting residue was recrystallized from diethyl ether to obtain a pale yellow solid of H_2L^6.

Data for H_2L^{6a} ($R^1 = R^2 = Et$): Yield: 30% (815 mg)



Elemental analysis:

Calcd. for $C_{30}H_{36}N_6S_2$: C, 66.14; H, 6.66; N, 15.43; S, 11.77%.

Found: C, 66.01; H, 6.45; N, 15.29; S, 11.89%.

IR (KBr, cm^{-1}): 3055 (w), 2927 (m), 2860 (w), 1496 (vs), 1423 (s), 1353 (s), 1253 (m), 1095 (m), 1064 (m), 995 (m), 744 (m), 694 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.32 (m, 12H, CH_3), 3.67 (m, 8H, CH_2), 4.12 (m, 6H, CH_2), 6.34 (d, br, 2H, C_6H_4), 6.56 (d, br 2H, C_6H_4), 7.23 (t, J = 7.1 Hz, 4H, Ph), 7.48 (t, J = 7.2 Hz, 2H, Ph), 7.50 (d, J = 7.4 Hz, 4H, Ph).

Data for H_2L^{6b} (NR^1R^2 = morph): Yield: 55% (1.570 g)

Elemental analysis:

Calcd. for $C_{30}H_{32}N_6O_2S_2$: C, 62.91; H, 5.63; N, 14.67; S, 11.20%.

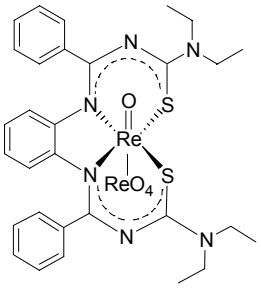
Found: C, 63.10; H, 5.35; N, 14.16; S, 11.08%

IR (KBr, cm^{-1}): 3055 (w), 2927 (m), 2860 (w), 1496 (vs), 1423 (s), 1353 (s), 1253 (m), 1095 (m), 1064 (m), 995 (m), 744 (m), 694 (s).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.66 (t, br, J = 4.9 Hz, 4H, NCH_2), 3.70 (t, br, J = 4.9 Hz, 4H, NCH_2), 4.02 (t, br, J = 4.8 Hz, 4H, OCH_2), 4.10 (t, br, J = 4.8 Hz, 4H, OCH_2), 6.90 (m, 4H, C_6H_4), 7.16 - 7.22 (m, 8H, Ph + C_6H_4), 7.31(t, J = 7.8 Hz, 2H, Ph).

4.3.3.2 [ReO(L^{6a})(ReO_4)], (34)

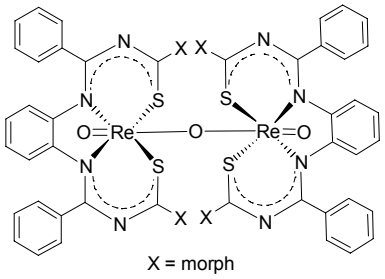
H_2L^{6a} (54 mg, 0.1 mmol) and three drops of NEt_3 were added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in MeOH (3 mL). This solution was heated under reflux for 30 min and the solvent was removed to dryness under vacumm. The residue was dissolved in actone. The resulting clear red solution was slowly evaporated at room temperature to give red crystals of **34**. Yield 15 % (15mg).



Elemental analysis:
Calcd. for $C_{30}H_{34}N_6O_5S_2Re_2$: C, 36.21; H, 3.44; N, 8.44; S, 6.44%.
Found: C, 36.51; H, 3.22; N, 8.59; S, 6.63%.
IR (KBr, cm^{-1}): 3055 (w), 2970 (w), 2936 (w), 1543 (vs), 1477 (s), 1443 (m), 1346 (s), 1280 (m), 1242 (m), 1141 (m), 1076 (m), 983 (m), 921 (s), 875 (s), 767 (m), 698 (m).
^{1}H NMR (400 MHz, acetone-d_6, ppm): 1.43 (t, J = 7.2 Hz, 6H, CH_3), 1.49 (t, J = 7.1 Hz, 6H, CH_3), 4.05 (m, 4H, CH_2), 4.37 (m, 2H, CH_2), 4.45 (m, 2H, CH_2), 6.53 (m, 2H, C_6H_4), 6.60 (m, 2H, C_6H_4), 7.52 (t, J = 7.2 Hz, 4H, Ph), 7.58 (t, J = 7.2 Hz, 2H, Ph), 7.53 (d, J = 7.1 Hz, 4H, Ph).
FAB^+ MS (m/z): 745, 35%, $[ReO(L^{6a})]^+$.
FAB^- MS (m/z): 251, 20%, $[ReO_4]^-$.

4.3.3.3 [{ReO(L^{6b})}$_2$O], (35)

Solid of H_2L^{6b} (57 mg, 0.1 mmol) was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in MeOH (3 mL). The reaction mixture was heated under reflux for 5 min. and 3 drops of Et_3N were added. The heating was continued for 30 min. and the solvent was removed under vacumm. The resulting residue was recrystallized from a CH_2Cl_2/MeOH mixture to give red crystals of **35**. Yield 69 % (54mg).



Elemental analysis:
Calcd. for $C_{60}H_{60}N_{12}O_7S_4Re_2$: C, 46.14; H, 3.87;
N, 10.76; S, 8.21%.
Found: C, 46.12; H, 3.95; N, 10.51; S, 8.06%.
IR (KBr, cm^{-1}): 3055 (w), 2962 (w), 2916 (w), 2854 (w),

1527 (vs), 1477 (vs), 1420 (vs), 1438 (m); 1361 (s), 1265 (m), 1226 (m), 1172 (w), 1114 (m), 1026 (m), 941 (w), 767 (m), 744 (w), 694 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.5-3.7 (m, br 4H, CH_2), 3.8-4.0 (m, br, 5H, CH_2), 4.42 (m, br, 3H, CH_2), 4.64 (d, br, 2H, CH_2), 4.80 (d, br, 2H, CH_2), 5.95 (d, J = 8.3 Hz, 1H, C_6H_4), 6.22 (d, J = 7.8 Hz, 1H, C_6H_4), 6.37 (t, J = 7.7 Hz, 1H, C_6H_4), 6.47 (t, J = 7.7 Hz, 1H, C_6H_4), 7.11 (m, 4H, Ph), 7.29 (m, 4H, Ph), 7.53 (d, J = 7.1 Hz, 2H, Ph).

^{13}C NMR (400 MHz, $CDCl_3$, ppm): 49.02 (NCH_2), 49.46 (NCH_2), 65.08 (OCH_2), 66.55 (OCH_2), 122.12, 125.60, 127.91, 129.45, 129.83, 130.33, 130.63, 137.12 (Ph), 148.08 (C_{ar}-N), 162.55 (C=N), 174.38 (C=S).

FAB$^+$ MS (m/z): 790, 8%, $[ReO_2(L^{6b})]^+$; 774, 90%, $[ReO(L^{6b})]^+$.

4.3.3.4 [ReN(L^{6b})], (36)

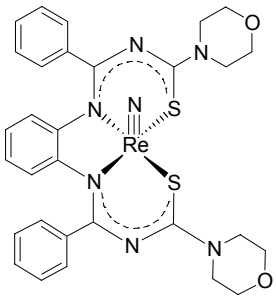
Solid H_2L^{6b} (57 mg, 0.1 mmol) was added to a stirred suspension of $[ReNCl_2(PPh_3)_2]$ (80 mg, 0.1 mmol) in CH_2Cl_2 (3 mL). After 10 min, 3 drops of Et_3N were added. The stirring was continued for 30 min at room temperature and then the solvent was removed. The resulting residue was recrystallized from a CH_2Cl_2/MeOH mixture to give red crystals of **36**. Yield 71 % (54mg).

Elemental analysis:

Calcd. for $C_{30}H_{30}N_7O_2S_2Re$: C, 46.74; H, 3.92; N, 12.72; S, 8.32%.

Found: C, 46.62; H, 4.01; N, 11.53; S, 8.17%.

IR (KBr, cm^{-1}): 3050 (w), 2962 (w), 2912 (w), 2851 (w), 1510 (vs), 1481 (vs), 1469 (m), 1261 (m), 1218 (m), 1111 (m), 1068 (m), 1022 (m), 875 (w), 806 (m), 744 (m).

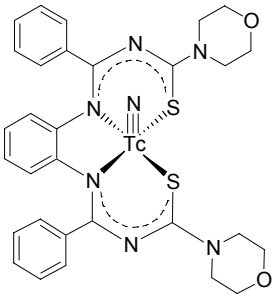


^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.78 (s, br, 4H, NCH_2), 3.82 (s, br, 4H, NCH_2), 4.30 (m, 6H, OCH_2), 4.39 (m, 2H, OCH_2), 6.48 (dd, 2H, C_6H_4), 6.67 (dd, 2H, C_6H_4), 7.30 (m, 6H, Ph), 7.56 (d, br, J = 6.6 Hz, 4H, Ph).

ESI$^+$ MS (m/z): 794, 30%, $[M + Na]^+$; 772, 100%, $[M + H]^+$.

4.3.3.5 [TcN(L^{6b})], (37)

Compound **37** was prepared from $[TcNCl_2(PPh_3)_2]$ and H_2L^{6b} by a similar procedure as described for their rhenium analogue **36**. Yield 75% (51 mg).



Elemental analysis:

Calcd. for $C_{30}H_{30}N_7O_2S_2Tc$: Tc, 14.5%. Found: Tc, 14.6%.

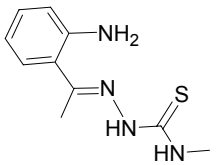
IR (KBr, cm^{-1}): 3050 (w), 2955 (w), 2912 (w), 2858 (w), 1504 (vs), 1477 (vs), 1431 (m), 1381 (m), 1265 (m), 1222 (m), 1114 (m), 1064 (m), 1026 (m), 879 (w), 802 (m), 745 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.78 (m, 8H, NCH_2), 4.21 (m, 6H, OCH_2), 4.36 (m, 2H, OCH_2), 6.45 (d, J = 6.0 Hz, 2H, C_6H_4), 6.67 (d, J^1= 6.1 Hz, 2H, C_6H_4), 7.29 (m, 6H, Ph), 7.47 (d, br, J = 7.2 Hz, 4H, Ph).

4.3.3.6 Benzamidines Derived from 2-Aminoacetophenone-N-(4-methylthiosemicarbazone) H_2L^7

2-Aminoacetophenone-N-(4-methylthiosemicarbazone), (2AAP4M)

The compound 2AAP4M was synthesized from 2-aminoacetophenone and 4-methylthiosemicarbazone following a literature procedure [95].



Elemental analysis:

Calcd. for $C_{10}H_{14}N_4S$: C, 54.03; H, 6.35; N, 25.20; S, 14.42%.

Found: C, 54.20; H, 5.82; N, 24.39; S, 15.65%;

IR (KBr, cm^{-1}): 3237 (w), 2955 (w), 2900 (w), 1605 (vs), 1589 (vs), 1537 (m), 1480 (m), 1267 (s), 1110 (m), 1099 (m), 991 (m), 827 (m), 774 (s), 683 (s).

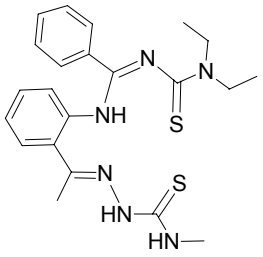
^{1}H NMR (400 MHz, DMSO-d_6, ppm): 2.30 (s, 6H, CH_3), 3.00 (s, 6H, NCH_3), 6.91 (t, J = 7.0 Hz, 1H, C_6H_4), 7.01 (d, J = 7.9 Hz, 1H, C_6H_4), 7.21 (t, J = 7.3 Hz, 1H, C_6H_4), 7.44 (d, J = 6.8 Hz, 1H, C_6H_4), 8.21 (s, br, 1H, NH), 10.20 (s, 1H, NH).

Benzamidines Derived from 2AAP4M, (H_2L^7)

Solid Et_2bzm-Cl (1.018 g, 4 mmol) was added to a mixture of **2AAP4M** (889 mg, 4 mmol) and triethylamine (1,01 g, 10 mmol) in 10 mL of absolute ethanol. The mixture was stirred at 50 ^{o}C for 1h. After being cooled down, H_2L^7 deposited as a yellow crystalline solid, which was filtered off, washed with cold MeOH and dried under vacuo. Yield: 45% (616 mg).

Elemental analysis:

Calcd. for $C_{22}H_{28}N_6S_2$: C, 59.97; H, 6.40; N, 19.07; S, 14.55%.



Found: C, 59.45; H, 6.02; N, 19.86; S, 15.02%;

IR (KBr, cm^{-1}): 3194 (m), 3051 (w), 2974 (m), 2928 (m), 2827 (w), 1717 (s), 1686 (s), 1608 (m), 1574 (s), 1539 (s), 1419 (s), 1335 (m), 1269 (s), 1246 (s), 1180 (m), 1134 (s), 1084 (m), 1026 (m), 898 (m), 759 (m), 694 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.17 (t, J = 7.1 Hz, 6H, CH_3), 1.22 (t, J = 7.1 Hz, 6H, CH_3), 1.86 (s, 3H, CH_3), 3.08 (s, 3H, NCH_3), 3.75 (q, J = 7.1 Hz, 2H, NCH_2), 3.88 (q, J = 7.1 Hz, 2H, NCH_2), 7.07 (t, J = 7.1 Hz, 2H, Ph), 7.13–7.19 (m, 4H, Ph + C_6H_4), 7.26 (m, 3H, Ph + C_6H_4), 7.64 (s, 1H, NH), 8.41 (s, 1H, NH), 12.63 (s, 1H, NH).

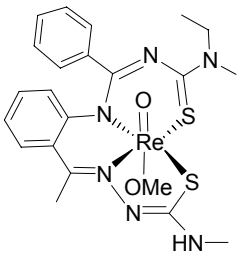
^{13}C NMR (400 MHz, $CDCl_3$, ppm): 11.99 ($CH_2\underline{C}H_3$), 13,53 ($CH_2\underline{C}H_3$), 15.55 (N=C$\underline{C}$H$_3$), 31.40 (NCH_3), 44.92 (NCH_2), 45.63 (NCH_2), 125.45, 126.21, 128.08, 129.03, 129.11, 129.44, 130.49, 132.31, 135.28, 136.67 (Car), 145.52 (Me$\underline{C}$=N), 159.77 (C=N), 178.36 (C=S), 184,95 (C=S).

4.3.3.7 [ReO(L^7)(OMe)], (38)

H_2L^7 (44 mg, 0.1 mmol) was dissolved in 2 mL of CH_2Cl_2 and added to a stirred solution of (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) in MeOH (1 mL). After adding 3 drops of Et_3N, the reaction mixture was warmed to 40 ^{o}C for 30 min. The resulting clear red solution was slowly evaportated to give red crystals of **38**. Yield 60% (40 mg).

Elemental analysis:

Calcd. for $C_{23}H_{29}N_6O_2S_2Re$: C, 41.12; H, 4.35; N, 12.51; S, 9.55%.



Found: C, 40.71; H, 4.09; N, 12.56; S, 9.21%.

IR (KBr, cm^{-1}): 3387 (m), 3070 (w), 2970 (m), 2924 (m), 2800 (w), 1558 (s), 1512 (s), 1425 (m), 1359 (m), 1288 (m), 1250 (m), 1227 (m), 1172 (w), 1110 (m), 942 (s), 810 (w), 771 (w).

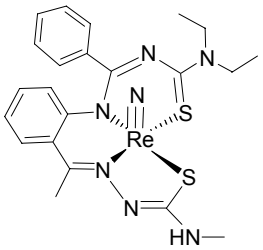
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.36 (t, J = 7.1 Hz, 6H, CH_3), 1.41 (t, J = 7.2 Hz, 6H, CH_3), 2.92 (s, 3H, N=C−$\underline{C}$H$_3$), 3.04 (s, 3H, OCH_3), 3.14 (d, J = 5.0, 3H, NCH_3), 3.74 (m, 2H, NCH_2), 4.33 (m, 1H, NCH_2), 4.53 (m, 1H, NCH_2), 5.26 (s, br, NH), 6.56 (d, J = 7.9 Hz, 1H, C_6H_4), 6.82 (t, J = 7.9 Hz, 1H, C_6H_4), 6.91 (t, J = 8.0 Hz, 1H, C_6H_4), 7.15 (m, 3H, Ph), 7.52 (d, J = 7.8, 2H, Ph), 7.66 (d, J = 7.8, 1H, C_6H_4).

FAB$^+$ MS (m/z): 641, 85%, $[M - OMe + H]^+$.

4.3.3.8 [ReN(L^7)], (39)

A mixture of H_2L^7 (44mg, 0.1 mmol), [$ReNCl_2(PPh_3)_2$] (80 mg, 0.1 mmol) and three drops of Et_3N in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h. The solvent was removed to dryness and the residue was washed with MeOH and then dried under vacuum. The product was recrystalized from a CH_2Cl_2/MeOH mixture. Yield 75% (48 mg).

Elemental analysis:

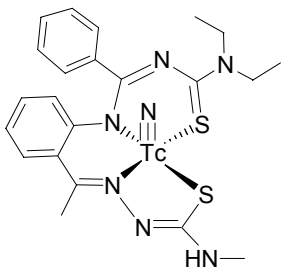


Calcd. for $C_{22}H_{26}N_7S_2Re$: C, 41.36; H, 4.10; N, 15.35; S, 10.04%.
Found: C, 41.11; H, 4.19; N, 14.95; S, 10.13%;
IR (KBr, cm^{-1}): 3417 (m), 3050 (w), 2970 (m), 2924 (m), 1527 (vs), 1440 (m), 1342 (s), 1257 (m), 1219 (m), 1149 (w), 1072 (m), 1033 (w), 810 (w), 764 (m), 671 (w).
^1H NMR (400 MHz, $CDCl_3$, ppm): 1.32 (t, *J* = 7.2 Hz, 6H, CH_3), 1.36 (t, *J* = 7.2 Hz, 6H, CH_3), 3.11 (d, *J* = 5.0, 3H, NCH_3), 3.13 (s, 3H, N=C-$\underline{C}H_3$), 3.58 (m, 1H, NCH_2), 3.68 (m, 1H, NCH_2), 4.32 (m, 1H, NCH_2), 4.40 (m, 1H, NCH_2), 5.28 (s, br, NH), 6.78 (d, *J* = 8.0 Hz, 1H, C_6H_4), 6.93 (t, *J* = 7.6 Hz, 1H, C_6H_4), 7.00 (t, *J* = 7.7 Hz, 1H, C_6H_4), 7.10 (m, 3H, Ph), 7.27 (d, *J* = 7.2 Hz, 2H, Ph), 7.75 (d, *J* = 7.9 Hz, 1H, C_6H_4).
FAB^+ MS (m/z): 639, 90%, $[M + H]^+$; 567, 12%, $[M - NEt_2 + H]^+$.

4.3.3.9 [TcN(L^7)], (40) and [TcN(PPh_3)(Et_2tu)(L^{7b})], (41)

Solid [$TcNCl_2(PPh_3)_2$] (70 mg, 0.1 mmol) was added to a stirred solution of H_2L^7 (44mg, 0.1 mmol) in CH_2Cl_2 (5 mL). After adding 3 drops of Et_3N, the mixture was stirred at room temperature for additional 15 minutes. This resulted in a complete dissolution of [$TcNCl_2(PPh_3)_2$] and the formation of a red solution. The solvent was removed under vacuum, and the residue was recrystalized from a CH_2Cl_2/MeOH mixture to obtain large orange crystals of **40** and yellow needles of **41** which were separated mechanically.

Data for [TcN(L^7)] (40): Yield 40% (21 mg)

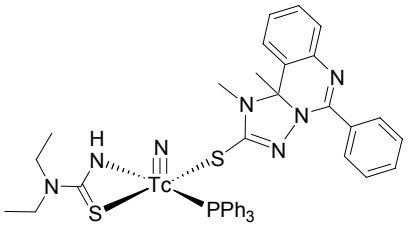


Elemental analysis:
Calcd. for $C_{22}H_{26}N_7S_2Tc$: Tc, 17.9%. Found: Tc, 18.1%;
IR (KBr, cm^{-1}): 3418 (m), 3051 (w), 2970 (m), 2924 (m), 1547 (s), 1528 (vs), 1477 (m), 1431 (m), 1357m), 1338 (m), 1261 (m), 1226 (m),

1145 (w), 1091 (w), 1064 (m), 1037 (w), 810 (w), 756 (m), 675 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.34 (m, 6H, CH_3), 2.97 (s, 3H, N=C-$\underline{C}H_3$), 3.05 (d, J = 4.8, 3H, NCH_3), 3.54 (m, 1H, NCH_2), 3.66 (m, 1H, NCH_2), 4.19 (m, 1H, NCH_2), 4.26 (m, 1H, NCH_2), 5.15 (s, br, NH), 6.67 (d, J = 7.9 Hz, 1H, C_6H_4), 6.89 (t, J = 7.4 Hz, 1H, C_6H_4), 6.95 (t, J = 7.6 Hz, 1H, C_6H_4), 7.10(m, 3H, Ph), 7.28 (d, J = 7.1 Hz, 2H, Ph), 7.66 (d, J = 7.9 Hz, 1H, C_6H_4).

Data for [TcN(PPh$_3$){Et$_2$N(S)NH}(L^{7b})] (41):



Yield 14% (12 mg)

Calcd. for $C_{40}H_{41}N_7PS_2Tc$: Tc, 12.2%. Found: Tc, 12.4%.

IR (KBr, cm^{-1}): 3363 (m), 3044 (w), 2978 (m), 2931 (m), 1558 (vs), 1473 (m), 1434 (m), 1307 (s), 1269 (s), 1238 (s), 1184 (m), 1149 (w), 1095 (m), 1068 (m), 860 (w), 740 (s), 694 (s), 528 (m), 497 (m).

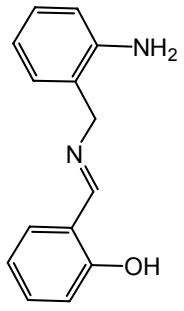
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.49 (t, J = 7.1 Hz , 3H, CH_3), 0.88 (t, J = 7.1 Hz, 3H, CH_3), 1.41 (s, 3H, N=C−$\underline{C}H_3$), 2.25 (m, 1H, NCH_2), 2.39 (m, 1H, NCH_2), 3.12 (m, 2H, NCH_2), 3.66 (s, 3H, NCH_3), 5.76 (s, br, 1H, NH), 7.32 (m, 17H, Ph), 7.60 (m, 6H, Ph), 8.05 (d, J = 7.7 Hz, 1H, Ph).

^{31}P NMR (400 MHz, $CDCl_3$, ppm): 48.86 (s).

4.3.3.10 Benzamidines Derived from o-Aminobenzylsalicylideneimine, H$_2$L^8

o-Aminobenzylsalicylideneimine (V)

The synthesis of compound **V** followed the procedure given in reference [98].



Elemental analysis:

Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38%.

Found: C, 74.19; H, 6.07; N, 12.47%.

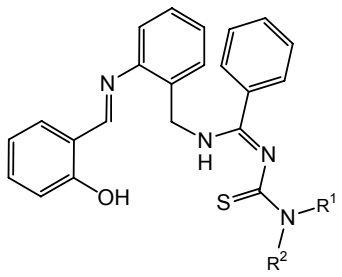
IR (KBr, cm^{-1}): 3390 (m), 3259 (m), 2954 (w), 2889 (w), 1604 (vs), 1485 (s), 1458 (vs), 1350 (m), 1299 (m), 1261 (s), 1072 (m), 1045 (m), 840 (w), 752 (vs).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 4.75 (s, 2H, PhC$\underline{H}_2$), 6.7-7.4 (m, 8H, Ph), 8.40 (s, 1H, CH=N).

H_2L^8

Solid R^1R^2bzm−Cl (4 mmol) was added to a mixture of compound **V** (904 mg, 4 mmol) and triethylamine (1.01 g, 10 mmol) in 10 mL of dry acetone. The mixture was stirred at room temperature for 4h. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off and the filtrate was evaporated under reduced pressure. The resulting residue was treated with diethylether (10 mL) and the mixture was stored at -20 °C. The yellow solid of H_2L^8, which deposited from this solution, was filtered off, washed with diethylether and dried under vacuum. Single crystals of H_2L^8 were obtained by slow evaporation of a $MeOH/CH_2Cl_2$ solution.

Data for H_2L^{8a} ($R^1 = R^2 = Et$)



Elemental analysis:

Calcd. for $C_{26}H_{28}N_4OS$: C, 70.24; H, 6.35; N, 12.60; S, 7.21%.

Found: C, 71.01; H, 6.12; N, 12.69; S, 7.38%.

IR (KBr, cm^{-1}): 3367 (m), 3055 (w), 2966 (w), 2927 (w), 2866 (w), 1612 (vs), 1570 (m), 1519 (s), 1485 (s), 1419 (m), 1373 (m), 1307 (m), 1253 (s), 1137 (m), 1091 (m), 898 (w), 756 (s), 684 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.04 (t, J = 7.1 Hz, 3H, CH_3), 1.13 (t, J = 7.0 Hz, 3H, CH_3), 3.57 (s, br, 2H, $N\underline{CH_2}CH_3$), 3.80 (q, J = 7.1 Hz, 2H, $N\underline{CH_2}CH_3$), 4.60 (s, br, 2H, $PhCH_2N$), 6.87 (t, J = 7.5 Hz, 1H, Ph), 6.92 (d, J = 8.1 Hz, 1H, Ph), 7.02 (d, J = 7.8 Hz, 1H, Ph), 7.22-7.34 (m, 7H, Ph), 7.38 (d, J = 7.9 Hz, 2H, Ph), 7.45 (d, J = 7.6 Hz, 1H, Ph), 8.47 (s, 1H, CH=N).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 0.90 (t, J = 7.0 Hz, 3H, CH_3), 1.02 (t, J = 7.0 Hz, 3H, CH_3), 3.37 (q, J = 7.0 Hz, 2H, $N\underline{CH_2}CH_3$), 3.67 (q, J = 7.0 Hz, 2H, $N\underline{CH_2}CH_3$), 4.60 (d, J = 5.5 Hz, 2H, NCH_2), 6.98 (m, 2H, Ph), 7.30 - 7.43 (m, 10H, Ph), 7.68 (d, J = 6.9 Hz, 1H, Ph), 8.36 (s, br, 1H, NH), 8.89 (s, 1H, CH=N), 12.96 (s, 1H, OH).

Data for H_2L^{8b} (NR^1R^2 = morph)

Elemental analysis:

Calcd. for $C_{26}H_{26}N_4O_2S$: C, 68.10; H, 5.71; N, 12.22; S, 6.99%.

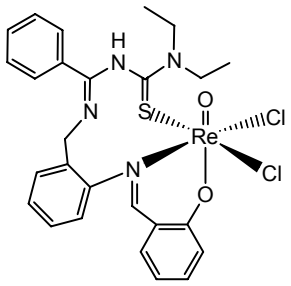
Found: C, 68.35; H, 5.64; N, 12.34; S, 7.12%.

IR (KBr, cm^{-1}): 3452 (m), 3055 (w), 2959 (w), 2889 (w), 2858 (w), 1620 (vs), 1566 (m), 1512 (s), 1485 (m), 1461 (m), 1431 (m), 1365 (w), 1276 (s), 1222 (s), 1111 (s), 1045 (m), 1026 (m), 906 (w), 764 (s), 702 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.49 (s, br, 2H, NCH_2), 3.61 (t, J = 4.7 Hz, 2H, NCH_2), 3.70 (s, br, 2H, OCH_2), 4.06 (t, J = 4.8 Hz, 2H, OCH_2), 4.87 (s, 2H, $PhCH_2N$), 6.88 (t, J = 7.4 Hz, 1H, Ph), 6.92 (d, J = 8.5 Hz, 1H, Ph), 7.0 - 7.4 (m, 11H, Ph), 8.49 (s, 1H, CH=N), 13.00 (s, br, 1H, OH).

4.3.3.11 [$ReOCl_2(HL^{8a})$], (42)

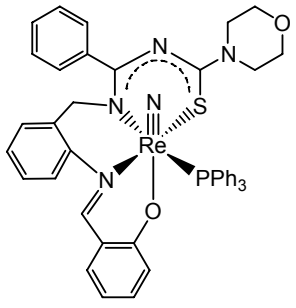
H_2L^{8a} (45 mg, 0.1 mmol) was added to a stirred solution of $(NBu_4)[ReOCl_4]$ (50 mg, 0.1 mmol) in 5 mL MeOH. The color of the solution immediately turned yellow-green and a green precipitate deposited within a few minutes. The green powder was filtered off, washed with cold methanol and dried under vacuum. Yield 60% (44 mg).



Elemental analysis:
Calcd. for $C_{26}H_{27}Cl_2N_4O_2ReS$: C, 43.57; H, 3.80; N, 7.82; S, 4.47%.
Found: C, 43.26; H, 3.65; N, 7.88; S, 4.35%.
IR (KBr, cm^{-1}): 3271 (m), 3058 (w), 2970 (w), 2932 (w), 2870 (w), 1601 (vs), 1550 (vs), 1519 (vs), 1442 (s), 1300 (s), 1203 (m), 1176 (m), 1145 (w), 1099 (m), 1076 (w), 968 (s), 929 (m), 864 (w), 760 (s), 694 (m), 617 (w).

4.3.3.12 [$ReN(PPh_3)(L^{8b})$], (43)

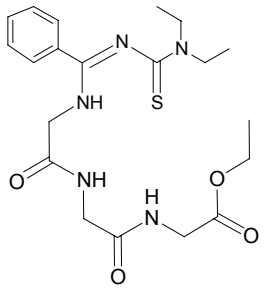
A mixture of H_2L^{8b} (44 mg, 0.1 mmol), $[ReNCl_2(PPh_3)_2]$ (80 mg, 0.1 mmol) and three drops of Et_3N in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h, whereupon a clear red solution was obtained. The solvent was removed to dryness and the residue was recrystalized from a CH_2Cl_2/MeOH mixture. Yield 45% (42 mg).



Elemental analysis:
Calcd. for $C_{45}H_{42}N_5O_2PReS$: C, 57.86; H, 4.53; N, 7.50; S, 3.43%.
Found: C, 57.67; H, 4.65; N, 7.43; S, 3.29%.
IR (KBr, cm^{-1}): 3055(w), 2984 (w), 2923 (w), 2850 (w), 1511 (vs), 1453 (m), 1331 (s), 1212 (m), 1153 (m), 1072 (w), 1026 (w), 880 (w), 775 (m), 694 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.23 (t, J = 7.1 Hz, 3H, CH_3), 1.27 (t, J = 7.0 Hz, 3H, CH_3), 3.71 (s, br, 2H, $N\underline{CH_2}CH_3$), 3.85 (q, J = 7.1 Hz, 2H, $N\underline{CH_2}CH_3$), 4.32 (q, J = 7.1 Hz, 2H, $N\underline{CH_2}CH_3$), 6.91 (t, J = 7.2 Hz, 1H, Ph), 6.96 (d, J = 7.9 Hz, 1H, Ph), 7.2–7.4 (m, 9H, Ph), 7.45(d, J = 7.9 Hz, 2H, Ph), 8.73 (s, 1H, CH=N).
^{31}P NMR (400 MHz, $CDCl_3$, ppm): 23.24 (s).

4.3.3.13 Benzamidine Derived from Triglycine ethylester, (H_3L^9)

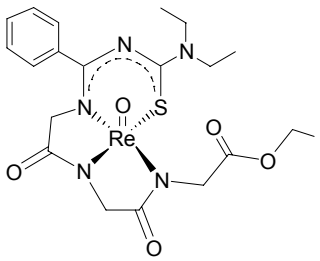
Solid Et_2bzm-Cl (1.27g, 5 mmol) was added to a mixture of triglycine ethylester hydrochloride (1.27 g, 5 mmol) and triethylamine (1,51 g, 15 mmol) in 10 mL of dry THF. The mixture was stirred at room temperature for 4h. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off and the filtrate was washed with water (10mL), dried over $MgSO_4$ and then evaporated under reduced pressure to dryness to obtain H_3L^9. The ligand was used without further purification. Yield 80% (1.74 g).



Elemental analysis:
Calcd. for $C_{20}H_{29}N_5O_4S$: C, 55.15; H, 6.71; N, 16.08; S, 7.36%.
Found: C, 55.00; H, 6.61; N, 16.20; S, 7.29%.
IR (KBr, cm^{-1}): 3294 (s), 3058 (m), 2977 (m), 2931 (w), 2874 (w), 1751 (s), 1670 (s), 1620 (s), 1531 (s), 1488 (s), 1419 (m), 1373 (m), 1242 (m), 1199 (m), 1126 (m), 1076 (m), 1022 (m), 887 (m), 779 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.12 (m, 9H, CH_3), 3.60 (q, J = 7.1 Hz, 2H, N$\underline{CH_2}CH_3$), 3.87 (q, J = 7.1 Hz, 2H, N$\underline{CH_2}CH_3$), 3.97 (d, J = 5.6 Hz, 2H, NH−$\underline{CH_2}$), 4.01 (d, J = 5.6 Hz, 2H, NH−$\underline{CH_2}$), 4.15 (m, 4H, NH−$\underline{CH_2}$ and OCH_2), 6.64 (s, br, 1H, NH), 7.15 (s, br, 1H, NH), 7.38 (t, J = 7.3 Hz, 3H, Ph), 7.45 (t, J = 7.2 Hz, 1H, Ph), 7.49 (d, J = 7.6 Hz, 2H, Ph), 7.67 (s, 1H, NH).

4.3.3.14 [ReO(L^9)], (44)

H_3L^9 (44 mg, 0.1 mmol) and 3 drops of Et_3N were added to a stirred solution of $(NBu_4)[ReOCl_4]$ (50 mg, 0.1 mmol) in 3 mL MeOH. After heating under reflux for 15 min, 0.5 mL H_2O was added. The product deposited from the reaction mixture during standing for several days. Yield 40% (44 mg).



Elemental analysis:
Calcd. for $C_{20}H_{26}N_5O_5ReS$: C, 37.85; H, 4.13; N, 11.03; S, 5.05%.
Found: C, 37.72; H, 4.01; N, 11.17; S, 5.09%.
IR (KBr, cm^{-1}): 3052 (m), 2980 (m), 2941 (w), 2850 (w), 1723 (s), 1702 (s), 1516 (s), 1453 (s), 1419 (m), 1360 (m), 1232 (s), 1180 (w),

1076 (w), 1022 (w), 985(s), 770 (m), 695 (m).

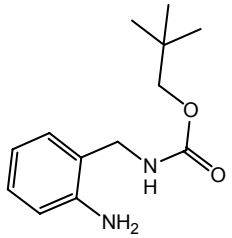
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.21 (m, 9H, CH_3), 3.69 (q, J = 7.1 Hz, 2H, N$\underline{CH_2}CH_3$), 3.95 (q, J = 7.1 Hz, 2H, N$\underline{CH_2}CH_3$), 3.97 (d, J = 5.6 Hz, 2H, NH−$\underline{CH_2}$), 4.02 (s, 2H, NH−$\underline{CH_2}$), 4.07 (q, 2H, J = 7.2 Hz, OCH_2), 4.20 (d, J = 14.0 Hz, 1H, CH_2CO), 4.42 (d, J = 14.0 Hz, 1H, CH_2CO), 4.62 (d, J = 14.1 Hz, 1H, CH_2CO), 4.96 (d, J = 14.1 Hz, 1H, CH_2CO), 7.45 (m, 3H, Ph), 7.69 (d, J = 7.5 Hz, 2H, Ph).

4.3.4 Pentadentate Benzamidine Ligands and their Complexes

4.3.4.1 N – Dialkylaminothiocarbonyl - N' - {2-methylene(phenyliminodiacetic acid)} benzamidine (H_3L^{10})

N-(tert.butoxycarbonyl)-2-aminobenzylamine, (VII)

The compound **VII** was synthesized following the proceduce given in reference [118] except that the purification was carried out by recrystallization of the compound from CH_2Cl_2/n-hexane. Yield 85%.

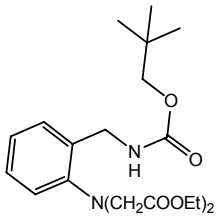


Elemental analysis:
Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.85%.
Found: C, 66.21; H, 8.42; N, 11.60%.
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.43 (s, 9H, CH_3), 4.21 (d, J = 6.2 Hz, 2H, NCH_2), 4.86 (s, br, 1H, NHCO), 6.65 (m, 2H, C_6H_4), 6.92 (d, J = 8.1 Hz, 1H, C_6H_4), 7.00 (d, J = 7.4 Hz, 1H, C_6H_4), 7.08 (t, J = 7.6 Hz, 1H, C_6H_4).

N-(tert.Butoxycarbonyl)-2-(aminodiacetic acid diethyl ester)benzylamine, (VIII)

Compound **VII** (8.891 g, 40 mmol), ethyl bromoacetate (13.8 mL, 125 mmol), (i-Pr)$_2$EtN (27.8 mL, 160 mmol) and finely powdered KI (1.000 g) in toluene (150 mL) was heated under reflux for 48 hours. After being cooled to room temperatue, water (50 mL) was added. The two layers were separated. The aqueous phase was extracted with toluene (50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the diester **VIII** as yellow oil. Yield 95% (14.989 g).

Elemental analysis:



Calcd. for $C_{21}H_{32}N_2O_6$: C, 61.75; H, 7.90; N, 6.86%.

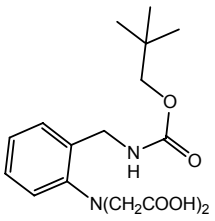
Found: C, 61.57; H, 7.72; N, 6.98%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.13 (t, *J* = 7.1 Hz, 3H, $OCH_2\underline{CH_3}$), 1.36 (s, 9H, CH_3), 3.90 (s, 4H, NCH_2CO), 4.05 (q, *J* = 7.1 Hz, 2H, $O\underline{CH_2}CH_3$), 4.31 (d, *J* = 5.9 Hz, 2H, $\underline{CH_2}NH$) 6.12 (s, br, 1H, NHCO), 7.01 (t, *J* = 7.5 Hz, 1H, C_6H_4), 7.14 (t, *J* = 7.7 Hz, 1H, C_6H_4), 7.22 (d, *J* = 7.7 Hz, 1H, C_6H_4), 7.25 (d, *J* = 8.0 Hz, 1H, C_6H_4).

N-(tert.Butoxycarbonyl)-2-(aminodiacetic acid)benzylamine, (IX)

Compound **VIII** (7.889 g, 20 mmol) and NaOH (2.400 g, 60 mmol) in 50 mL MeOH were stirred at room temperature for 24 h and then the reaction mixture was evaporated to dryness in vacuo. The resulting solid was dissolved in 50 mL cold brine solution, cold HCl (6M) was slowly added (temperature was kept at 5 - 10 ^oC) until the pH of 6 was obtained. The product was extracted with THF (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered, evaporated *in vacuo* to dryness and recrystallized from $CHCl_3$ to give the pure product as a colorless solid. Yield 70% (4.737 g).

Elemental analysis:



Calcd. for $C_{16}H_{22}N_2O_6$: C, 56,80; H, 6,55; N, 8,28%.

Found: C, 56.23; H, 6.52; N, 8.14%

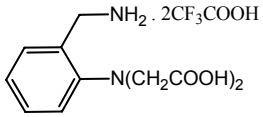
IR (KBr, cm^{-1}): 3394 (s), 3124 (br, s), 1755 (vs), 1705 (vs), 1662 (vs), 1523 (s), 1488 (m), 1454 (m), 1392 (m), 1369 (m), 1303 (m), 1253 (s), 1212 (s), 1184 (s), 1049 (m), 972 (m), 856 (m), 779 (m), 682 (m), 590 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.900 (s, 9H, CH_3), 3.41 (s, 4H, NCH_2CO), 3.80 (s, 2H, $\underline{CH_2}NH$) 6.20 (s, br, 1H, NHCO), 6.52 (t, *J* = 7.4 Hz, 1H, C_6H_4), 6.66 (t, *J* = 7.6 Hz, 1H, C_6H_4), 6.73 (d, *J* = 7.6 Hz, 1H, C_6H_4), 6.80 (d, *J* = 7.9 Hz, 1H, C_6H_4).

2-(Aminodiacetic acid)benzylamonium bis-trifluoroacetate salt, (X)

Compound **IX** (4.737 g) and CF_3COOH (15 mL) were stirred in dry CH_2Cl_2 (15 mL) at room temperature for 2 h. The organic solvents were removed under vacuum to give quantitatively compound as colorless powder.

Elemental analysis:



Calcd. for $C_{25}H_{16}F_6N_2O_8$: C, 38.64; H, 3.46; N, 6.01%.

Found: C, 38.23; H, 3.40; N, 6.19%.

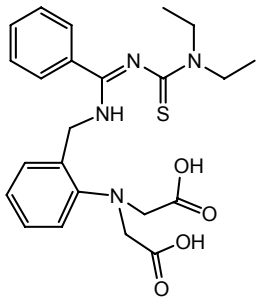
IR (KBr, cm^{-1}): 3144 (br, s), 1782 (vs), 1720 (vs), 1608 (s), 1492 (m), 1458 (m), 1404 (w), 1250 (s), 1218 (s), 1196 (s), 1168 (s), 1068 (w), 968 (w), 786 (w), 721 (w), 698 (w), 605 (w).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 3.92 (s, 4H, NCH_2CO), 4.10 (d, J = 5.1 Hz, 2H, $\underline{CH_2}NH$), 7.16 (t, J = 7.3 Hz, 1H, C_6H_4), 7.35 (m, 2H, C_6H_4), 7.44 (d, 1H, 7.4 Hz, C_6H_4) 8.27 (s, br, 4H, OH).

H_3L^{10}

Et_2bzm-Cl (686 mg, 2.7 mmol), compound **X** (1.409 g, 2.5 mmol) and NEt_3 (2.02 g, 20 mmol) were stirred in 20 mL of dry EtOH for 6 h at room temperature and then at 40 ^{o}C for 1 h. The organic solvent was evaporated under reduced pressure to dryness. The residue was dissolved in 20 mL THF and brine solution (20 mL) was added. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was washed with diethyether and dried in vacuo to give ligand **H_3L^{10}** as a colorless solid. Yield 65% (742 mg).

Elemental analysis:



Calcd. for $C_{23}H_{28}N_4O_4S$: C, 60.51; H, 6.18; N, 12.27; S, 7.02%.

Found: C, 60.30; H, 6.31; N, 12.17; S, 7.15%.

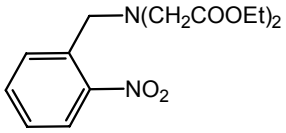
IR (KBr, cm^{-1}): 3250 (br, s), 1720 (br, s), 1596 (br, s), 1573 (s), 1539 (s), 1489 (m), 1454 (s), 1423 (s), 1311 (m), 1257 (s), 1199 (s), 1138 (s), 1076 (m), 968 (w), 883 (w), 779 (m), 698 (m).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.07 (t, J = 7.0 Hz, 3H, CH_3), 1.13 (t, J = 7.0 Hz, 3H, CH_3), 3.52 (q, J = 7.0 Hz, 2H, $N\underline{CH_2}CH_3$), 3.78 (q, J = 7.0 Hz, 2H, $N\underline{CH_2}CH_3$), 3.99 (s, 4H, NCH_2CO), 4.64 (d, J = 5.2 Hz, 2H, $\underline{CH_2}NH$), 7.12 (t, J = 7.3 Hz, 1H, C_6H_4), 7.25 (t, J = 7.2 Hz, 1H, C_6H_4), 7.30 (d, J = 8.0 Hz, 1H, C_6H_4), 7.36 (d, J = 7.6 Hz, 1H, C_6H_4), 7.47 (m, 5H, Ph), 8.35 (s, br, 1H, NHCO), 12.76 (s, br, 1H, COOH).

4.3.4.2 N-Dialkylaminothiocarbonyl-N'-{phenylene-(2-methyliminodiacetic acid)} benzamidine H_3L[11]

2-Nitrobenzyliminodiacetic acid diethylester (XI)

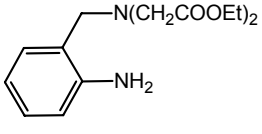
2-Nitrobenzylamine (6.086 g, 40 mmol), ethyl bromoacetate (11 mL, 99 mmol), a mixture of finely powdered K_2CO_3 (16.8 g, 122 mmol), KI (2.0g) and 100 mL of dry MeCN were heated under reflux for 10 h. After being cooled to room temperature, the mixture was filtered and concentrated *in vacuo* to give the product as slightly yellow oil. Yield 96% (12.454 g).



Elemental analysis:
Calcd. for $C_{15}H_{20}N_2O_6$: C, 55.55; H, 6.22; N, 8.64%.
Found: C, 55.36; H, 6.31; N, 8.51%.
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.25 (t, *J* = 7.1 Hz, 6H, $CH_2\underline{CH_3}$), 3.55 (s, 4H, CH_2CO), 4.17 (q, 7.1 Hz, 4H, $\underline{CH_2}CH_3$), 4.26 (s, 2H, $PhCH_2N$), 7.41 (t, *J* = 7.7 Hz, 1H, C_6H_4), 7.59 (t, *J* = 7.5 Hz, 1H, C_6H_4), 7.84 (d, *J* = 7.8 Hz, 1H, C_6H_4), 7.87 (d, *J* = 8.1 Hz, 1H, C_6H_4).

2-Aminobenzyliminodiacetic acid diethylester, (XII)

A mixture of compound **XI** (3.243 g, 10 mmol), Pd/C containing 10% Pd (0.5 g), MeOH (20 mL) and CH_3COOEt (3 mL) was stirred under hydrogen atmosphere at room temperature for 6 h. The reaction mixture was filtered and the organic solvents of the filtrate were completely removed under vacuum. The resulting residue was purified by column chromatography using CH_3COOEt/n-hexane (1:1) as elutant to give **XII** as yellow oil.

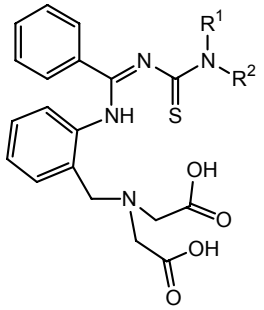


Elemental analysis:
Calcd. for $C_{15}H_{22}N_2O_4$: C, 61.21; H, 7.53; N, 9.52%.
Found: C, 61.01; H, 7.46; N, 9.49%.
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.27 (t, *J* = 7.1 Hz, 6H, $OCH_2\underline{CH_3}$), 3.47 (s, 4H, CH_2CO), 3.85 (s, 2H, $PhCH_2N$), 4.16 (q, 7.1 Hz, 4H, $O\underline{CH_2}CH_3$), 6.62(m, 2H, C_6H_4), 6.94 (d, *J* = 7.0 Hz, 1H, C_6H_4), 7.09 (t, *J* = 7.6 Hz, 1H, C_6H_4).

H_3L^{11}

The ligands H_3L^{11} were synthesized following the procedure described for H_3L^{10}.

Data for H_3L^{11a} (NR^1R^2 = morph)



Elemental analysis:

Calcd. for $C_{23}H_{26}N_4O_5S$: C, 58.71; H, 5.57; N, 11.91; S, 6.81%.

Found: C, 58.43; H, 5.61; N, 12.32; S, 6.64%.

IR (KBr, cm^{-1}): 3201 (br, s), 1720 (br, s), 1616 (s), 1527 (s), 1450 (m), 1427 (s), 1277 (s), 1227 (s), 1110 (s), 1026 (m), 764 (m), 698 (m).

^1H NMR (400 MHz, $CDCl_3$, ppm): 3.44 (s, 4H, CH_2CO), 3.66 (m, 4H, NCH_2), 3.86 (m, 4H, OCH_2), 4.02 (s, 2H, $PhCH_2N$), 6.93 (t, J = 7.0 Hz, 1H, C_6H_4), 7.00 (t, J = 7.6 Hz, 1H, C_6H_4), 7.19 - 7.48 (m, 7H, C_{ar}).

Data for H_3L^{11b} (R^1 = Me, R^2 = Ph)

Elemental analysis:

Calcd. for $C_{26}H_{26}N_4O_4S$: C, 63.66; H, 5.34; N, 11.42; S, 6.54%.

Found: C, 63.47; H, 5.21; N, 11.45; S, 6.33%.

IR (KBr, cm^{-1}): 3304 (br, s), 1721 (br, s), 1616 (s), 1540 (s), 1487 (m), 1451 (s), 1276 (s), 1124 (s), 1099 (s), 1026 (m), 770 (m), 700 (m).

^1H NMR (400 MHz, $CDCl_3$, ppm): 3.46 (s, 4H, CH_2CO), 3.83 (s, 3H, CH_3), 4.00 (s, 2H, $PhCH_2N$), 6.93 (t, J = 7.1 Hz, 1H, C_6H_4), 7.0 - 7.7 (m, 13H, Ph).

4.3.4.3 [ReO(L^{10})], (45)

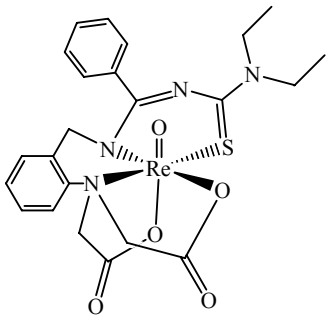
H_3L^{10} (46 mg, 0.1 mmol) and 3 drops of Et_3N were added to a stirred solution of $(NBu_4)[ReOCl_4]$ (50 mg, 0.1 mmol) in 3 mL MeOH. The reaction mixture was heated under reflux for 30 min. After being cooled to room temperature, the formed violet solid was filtered off, washed with cold MeOH and dried under vacuum. Yield 67% (44 mg).

The compound **45** can also be synthesized from other precursors such as $[Re^VNCl_2(PPh_3)_2]$, $[Re^V(NPh)Cl_3(PPh_3)_2]$ or $[Re^{III}Cl_3(MeCN)(PPh_3)_2]$ by refluxing with H_3L^{10} in the presence of a base (Et_3N) under aerobic conditions.

Elemental analysis:

Calcd. for $C_{23}H_{25}N_4O_5ReS$: C, 42.13; H, 3.84; N, 8.54;
S, 4.89%.

Found: C, 42.02; H, 3.61; N, 8.33; S, 4.71%.



IR (KBr, cm^{-1}): 3055 (w), 2963 (m), 2926 (m), 1720 (vs), 1666 (vs), 1512 (s), 1442 (m), 1404 (m), 1350 (m), 1311 (m), 1041 (w), 964 (m), 941 (m), 910 (m), 771 (m), 702 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.30 (t, *J* = 7.2 Hz, 3H, CH_3), 1.33 (t, *J* = 7.1 Hz, 3H, CH_3), 3.77 (m, 1H, N$\underline{CH_2}CH_3$), 3.84 (m, 1H, N$\underline{CH_2}CH_3$), 3.89 (s, 2H, $\underline{CH_2}$N), 4.03 (m, 1H, N$\underline{CH_2}CH_3$), 4.09 (m, 1H, N$\underline{CH_2}CH_3$), 4.53 (d, *J* = 15.5 Hz, 1H, NCH_2CO), 4.83 (d, *J* = 14.0 Hz, 1H, NCH_2CO), 5.06 (d, *J* = 13.8 Hz, 1H, NCH_2CO), 5.68 (d, *J* = 15.6 Hz, 1H, NCH_2CO), 7.00(d, *J* = 7.6 Hz, 1H, C_6H_4), 7.22 (t, *J* = 7.5 Hz, 1H, C_6H_4), 7.33 (m, 2H, C_6H_4), 7.44 (m, 3H, Ph), 7.48 (d, *J* = 7.5 Hz, 2H, Ph).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.26 (t, *J* = 7.2 Hz, 3H, CH_3), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3), 4.00 (m, 4H, N$\underline{CH_2}CH_3$), 4.10 (d, *J* = 18.3 Hz, 1H, $\underline{CH_2}$N), 4.40 (d, *J* = 18.2 Hz, 1H, $\underline{CH_2}$N), 4.78 (d, *J* = 15.2 Hz, 1H, NCH_2CO), 4.82 (d, *J* = 14.1 Hz, 1H, NCH_2CO), 5.37 (d, *J* = 14.5 Hz, 1H, NCH_2CO), 5.63 (d, *J* = 15.6 Hz, 1H, NCH_2CO), 7.13(d, *J* = 7.6 Hz, 1H, C_6H_4), 7.29 (t, *J* = 7.4 Hz, 1H, C_6H_4), 7.43 (m, 2H, C_6H_4), 7.57 (m, 3H, Ph), 7.67 (d, *J* = 8.0 Hz, 2H, Ph).

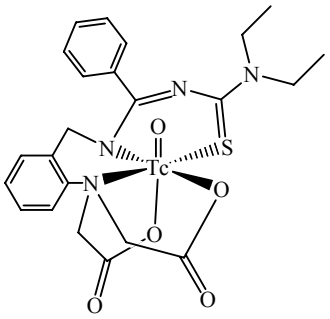
^{13}C NMR (400 MHz, DMSO-d_6, ppm): 12.98, 13.20 ($CH_2\underline{C}H_3$), 46.71, 47.13 (N$\underline{C}H_2CH_3$), 64.00 (N$\underline{C}H_2$), 65.42, 66.71 (N$\underline{C}H_2CO$), 119.38, 127.78, 128.62, 128.84, 129.62, 130.84, 131.53, 132.74, 137.04(Car), 153.83 ($\underline{C_{ar}}$-N), 170.36 (C=N), 173.39, (C=O, 173.72 (C=S), 183.6 (C=O).

4.3.4.4 [TcO(L^{10})], (46)

The technetium complex **46** was prepared from $(NBu_4)[TcOCl_4]$ by the procedure described above as method 2 for its rhenium analogue **45**. Compound **46** was isolated as green solid. Yield 75% (43 mg).

Elemental analysis:

Calcd. for $C_{23}H_{25}N_4O_5TcS$: Tc, 17.4%. Found: Tc, 17.5%

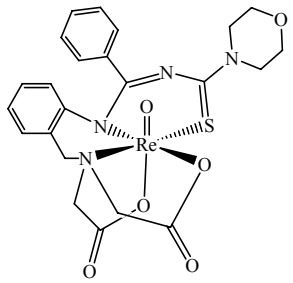


IR (KBr, cm^{-1}): 3066 (w), 2954 (w), 2923 (w), 1701 (vs), 1654 (vs), 1500 (s), 1442 (m), 1407 (m), 1350 (m), 1311 (s), 1288 (m), 1045 (w), 944 (m), 910 (m), 771 (m).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.29 (m, 6H, CH_3), 3.79 (m, 2H, N$\underline{CH_2}CH_3$), 3.84 (s, 2H, $\underline{CH_2}$N), 3.93 (m, 2H, N$\underline{CH_2}CH_3$), 4.43 (d, *J* = 15.3 Hz, 1H, NCH_2CO), 4.79 (d, *J* = 14.1 Hz, 1H, NCH_2CO), 5.01 (d, *J* = 14.1 Hz, 1H, NCH_2CO), 5.11 (d, *J* = 15.3 Hz, 1H, NCH_2CO), 7.04 (d, *J* = 7.5 Hz, 1H, C_6H_4), 7.23 (t, *J* = 7.6 Hz, 1H, C_6H_4), 7.45 (m, 7H, Ph).

4.3.4.5 [ReO(L^{11a})], (47)

H_3L^{11a} (46 mg, 0.1 mmol) and 3 drops of Et_3N were added to a stirred solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL MeOH. The reaction mixture was heated under reflux for 30 min. After being cooled to room temperature, the formed red solid was filtered off, washed with cold MeOH and dried under vacuum. Yield 55% (36 mg).



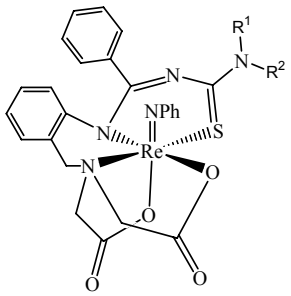
Elemental analysis:
Calcd. for $C_{23}H_{25}N_4O_5ReS$: C, 42.13; H, 3.84; N, 8.54;
S, 4.89%.
Found: C, 42.09; H, 3.72; N, 8.31; S, 4.95%.
IR (KBr, cm^{-1}): 3050 (w), 2962 (w), 2934 (w), 1713 (vs), 1696 (vs), 1535 (s), 1481 (m), 1434 (m), 1296 (m), 1226 (w), 1119 (m) 964 (m), 933 (m), 910 (m), 771 (m), 717 (w).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.47 (d, *J* = 17.2 Hz, 1H, $PhCH_2N$), 3.71 (d, *J* = 17.2 Hz, 1H, $PhCH_2N$), 3.92 (m, 4H, NCH_2), 4.22 (m, 1H, OCH_2), 4.36 (m, 1H, OCH_2), 4.51 (m, 2H, OCH_2), 4.60 (d, *J* = 14.5 Hz, 1H, CH_2CO), 4.71 (d, *J* = 14.4 Hz, 1H, CH_2CO), 5.06 (d, *J* = 12.2 Hz, 1H, CH_2CO), 5.66 (d, *J* = 12.2 Hz, 1H, CH_2CO), 6.68 (d, *J* = 7.9 Hz, 1H, C_6H_4), 6.91 (t, *J* = 7.3 Hz, 1H, C_6H_4), 7.09 (t, *J* = 7.7 Hz, 1H, C_6H_4), 7.18 (m, 3H, Ph + C_6H_4), 7.25 (t, *J* = 7.4 Hz, 1H, Ph), 7.43 (d, *J* = 7.3 Hz, 2H, Ph).

4.3.4.6 [Re(NPh)(L^{11})], (48)

H_3L^{11} (0.1 mmol) and 3 drops of Et_3N were added to a stirred suspension of $[Re(NPh)Cl_3(PPh_3)_2]$ (90 mg, 0.1 mmol) in 5ml of CH_2Cl_2. The reaction mixture was heated on reflux for 1 hour. During this time, the precursor complex completely dissolved and a clear

yellow-green solution was obtained. The solvent was removed under vacuum and the residue was purified by column chromatography using $CHCl_3$/n-hexane as elutant.

Data for 48a (NR^1R^2 = morph): Yield 40% (29 mg)



Elemental analysis:

Calcd. for $C_{29}H_{25}N_5O_5ReS$: C, 46.76; H, 3.79; N, 9.40; S, 4.31%.

Found: C, 46.51; H, 3.60; N, 9.21; S, 4.56%.

IR (KBr, cm^{-1}): 3060 (w), 2990 (w), 2900 (w), 2858 (w), 1701 (vs), 1508 (s), 1481 (s), 1435 (s), 1342 (m), 1299 (m), 1261 (m), 1219 (m), 1110 (m), 1022 (m), 914 (w), 899 (w), 806 (m), 771 (m), 732 (w), 682 (w), 528 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.48 (d, *J* = 17.1 Hz, 1H, $PhCH_2N$), 3.73 (d, *J* = 17.1 Hz, 1H, $PhCH_2N$), 3.89 (m, 4H, NCH_2), 4.23 (d, *J* = 14.6 Hz, 1H, CH_2CO), 4.30 (m, 2H, OCH_2), 4.49 (m, 2H, OCH_2), 4.82 (d, *J* = 14.6 Hz, 1H, CH_2CO), 5.03 (d, *J* = 12.1 Hz, 1H, CH_2CO), 5.27 (d, *J* = 12.1 Hz, 1H, CH_2CO), 6.65 (d, *J* = 8.1 Hz, 1H, C_6H_4), 6.85 (t, *J* = 7.0 Hz, 1H, C_6H_4), 7.00 - 7.22 (m, 9H, C_{ar}), 7.43 - 7.47 (m, 3H, C_{ar}).

^{13}C NMR (400 MHz, DMSO-d_6, ppm): 49.61, 49,83 61.85 ($N\underline{C}H_2$), 66.53, 66.79 ($N\underline{C}H_2CO$), 69.67, 69.99 (OCH_2), 122.16, 124.22, 124.37, 128.24, 128.63, 128.67, 130.11, 130.99, 131.28, 131.45, 132.90, 136.76(Car), 152.62 ($\underline{C}_{ar}$-N), 156.34 ($\underline{C}_{ar}$-N=Re), 166.85 (C=N), 174.39, (C=O, 176.97 (C=S), 181.88 (C=O).

Data for **48b (R^1 = Ph, R^2 = Me):** Yield 45% (34 mg)

Elemental analysis:

Calcd. for $C_{32}H_{28}N_5O_4ReS$: C, 50.25; H, 3.69; N, 9.16; S, 4.19%.

Found: C, 50.02; H, 3.43; N, 9.41; S, 4.30%.

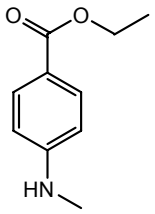
IR (KBr, cm^{-1}): 3051 (w), 2924 (m), 2858 (w), 1697 (vs), 1508 (m), 1474 (s), 1384 (m), 1350 (m), 1327 (m), 1292 (m), 1114 (w), 1091 (w), 1068 (w), 1026 (w), 910 (m), 759 (m), 694 (m), 520 (w).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) two series of signals with ratio 0.55 / 0.45 : 3.49 / 3.41 (d, *J* = 17.1 Hz, 1H, $PhCH_2N$), 3.75 / 3.69 (d, *J* = 17.1 Hz, 1H, $PhCH_2N$), 4.03 / 4.07 (s, 3H, NCH_3), 4.24 / 4.18 (d, *J* = 14.6 Hz, 1H, CH_2CO), 4.84 / 4.76 (d, *J* = 14.6 Hz, 1H, CH_2CO), 5.02 / 5.00 (d, *J* = 11.7 Hz, 1H, CH_2CO), 5.25 (d, *J* = 11.7 Hz, 1H, CH_2CO), 6.4-7.6 (m, 14H, C_{ar}).

4.3.4.7 H_3L^{10}-COOEt

4-(N-Methylamino)benzoic acid ethylester, (XIV)

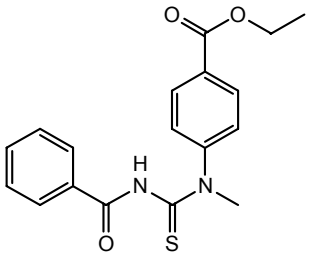
The preparation of the compound **XIV** was adopted from the literature [110].



Elemental analysis:
Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%.
Found: C, 67.16; H, 7.20; N, 7.80%.
IR (KBr, cm^{-1}): 3385 (s), 2975 (w), 2935 (w), 2900 (w), 1685 (s), 1605 (vs), 1535 (s), 1475 (m), 1370 (m), 1310 (w), 1275 (s), 1175 (s), 1105 (m), 770 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.29 (t, J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 2.82 (s, 3H, NCH_3), 4.12 (s, 1H, NH), 4.24 (q, 7.2 Hz, 2H, $\underline{CH_2}CH_3$), 6.48 (d, J = 6.8 Hz, 2H, Ph), 7.82 (d, J = 6.8 Hz, 2H, Ph).

N-(4-Ethoxycarbonylphenyl)-N-(methyl)-N'-benzoylthiourea, (XV)

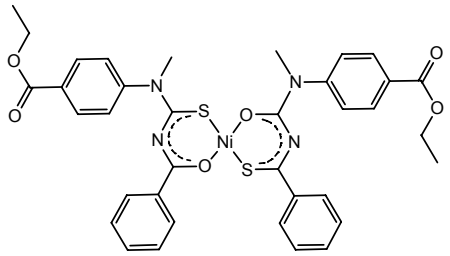
The synthesis of **XV** was performed by the standard procedure [15].



Elemental analysis:
Calcd. for $C_{18}H_{18}N_2O_3S$: C, 63.14; H, 5.30; N, 8.18; S, 9.36%.
Found: C, 62.91; H, 5.14; N, 8.34; S, 9.30%.
IR (KBr, cm^{-1}): 3225 (m), 3190 (w), 3060 (w), 2985 (w), 2940 (w), 2905 (w), 1710 (s), 1690 (s), 1605 (m), 1510 (s), 1450 (w), 1430 (m), 1365 (s), 1315 (m), 1275 (vs), 1180 (m), 1110 (s), 720 (s).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.34 (t, J = 7.1 Hz, 3H, $CH_2\underline{CH_3}$), 3.77 (s, 3H, NCH_3), 4.31 (q, 7.1 Hz, 2H, $\underline{CH_2}CH_3$), 7.38 (d, 4H, Ph), 7.50 (t, J = 7.3 Hz, 1H, Ph), 7.57 (d, J = 7.4 Hz, 2H, Ph), 8.01 (d, J = 8.7 Hz, 2H, Ph), 8.36 (s, 1H, NH).

Bis-[N-(4-ethoxycarbonylphenyl)-N-methyl-N'-benzoylthioureato]nickel(II), (XVI)

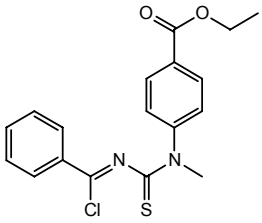
The synthesis of **XVI** was adopted from the general procedure [54].



Elemental analysis:
Calcd. for $C_{36}H_{36}N_4NiO_6S_2$: C, 58.15; H, 4.88;
N, 7.54; S, 8.63%.
Found: C, 58.30; H, 4.80; N, 7.34; S, 8.51%.
IR (KBr, cm^{-1}): 3065 (w), 2975 (w), 2925 (w), 2855 (w), 1720 (s), 1605 (w), 1525 (s), 1420 (s), 1375 (s), 1285 (s), 1110 (m), 1020 (m), 910 (m), 710 (m), 705 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.41 (t, J = 7.0 Hz, 6H, $CH_2\underline{CH_3}$), 3.60 (s, 6H, NCH_3), 4.40 (q, J = 7.0 Hz, 4H, $\underline{CH_2}CH_3$), 7.3-8.1 (m, 18H, Ph).

N-(4-Ethoxycarbonylphenyl)-N-methyl-N'-benzimidoyl chloride, (XVII)

The synthesis of **XVII** was adopted from the general procedure [54].



Elemental analysis:
Calcd. for $C_{18}H_{17}ClN_2O_2S$: C, 59.91; H, 4.75; N, 7.76; S, 8.89%.
Found: C, 59.91; H, 4.75; N, 7.76; S, 8.89%.
IR (KBr, cm^{-1}): 3055 (w), 2981 (w), 2935 (w), 2900 (w), 1716 (s), 1639 (s), 1600 (m), 1505 (m), 1454 (m), 1365 (s), 1273 (s), 1164 (s), 1103 (s), 1014 (m), 910 (m), 775 (m), 690 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.36 (t, J = 7.1 Hz, 3H, $CH_2\underline{CH_3}$), 3.80 (s, 3H, NCH_3), 4.33 (q, J = 7.1 Hz, 2H, $\underline{CH_2}CH_3$), 7.34 (d, J = 8.2 Hz, 4H, Ph), 7.45 (t, J = 7.3 Hz, 1H, Ph), 7.74 (d, J = 7.8 Hz, 2H, Ph), 8.01 (d, J = 8.3 Hz, 2H, Ph).

e. H_3L^{10}-COOEt

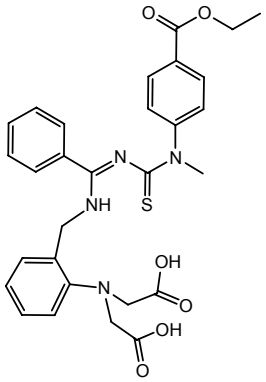
The synthesis of H_3L^{10}-COOEt was adopted from the procedure described for **H_3L^{10}**.

Elemental analysis:
Calcd. for $C_{29}H_{30}N_4O_6S$: C, 61.91; H, 5.37; N, 9.96; S, 5.70%.

Found: C, 61.62; H, 5.24; N, 9.84; S, 5.75%.

IR (KBr, cm^{-1}): 3348 (br, s), 1712 (br, s), 1605 (s), 1542 (s), 1493 (m), 1446 (s), 1276 (s), 1202 (s), 1138 (s), 1099 (s), 1018 (m), 972 (w), 775 (m).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.40 (t, J = 7.1 Hz, 3H, $CH_2\underline{CH_3}$), 3.56 (s, 3H, NCH_3), 3.82 (s, 4H, NCH_2CO), 4.37 (q, J = 7.1 Hz, 2H, $\underline{CH_2}CH_3$), 4.49 (s, 2H, $PhC\underline{H_2}NH$), 6.86 (t, br, 1H, Ph), 6.93 (d, br, 1H, Ph), 7.14 (t, br, 1H, Ph), 7.19 (d, br, 1H, Ph), 7.47 (m, 7H, Ph), 7.91 (d, J = 8.6 Hz, 2H, Ph), 8.67 (s, br, 1H, NH).



4.3.4.8 H_3L^{10}-COOH

Compound H_3L^{10}-COOEt (562 mg, 1 mmol) was added to a solution of NaOH (400 mg, 10 mmol) in MeOH (5 mL). The reaction mixture was stirred at room temperature for 12 h and then the solvent was removed under vacuum. The resulting residue was dissolved in brine solution (5 mL). After being neutralized with 10 mmol of HCl, the mixture was extracted with THF (2 x 5 mL). The organic phase was collected, dried over $MgSO_4$ and the solvent was removed under vacuum to give compound H_3L^{10}-COOH as a slightly yellow powder. Yield 80% (427 mg).

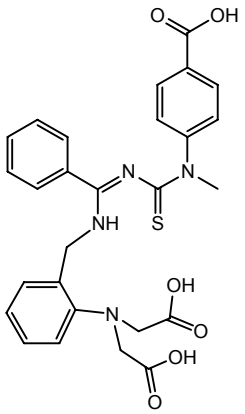
Elemental analysis:

Calcd. for $C_{27}H_{26}N_4O_5S$: C, 60.66; H, 4.90; N, 10.48; S, 6.00%.

Found: C, 60.42; H, 4.84; N, 10.33; S, 6.15%.

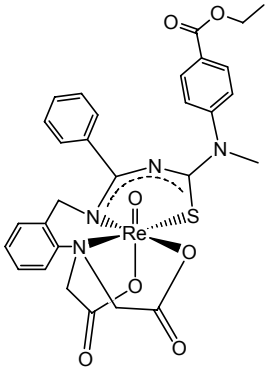
IR (KBr, cm^{-1}): 3062 (br, s), 1717 (s), 1605 (s), 1562 (s), 1423 (s), 1492 (m), 1423 (m), 1381 (m), 1272 (s), 1176 (s), 775 (m), 698 (m).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 3.58 (s, 3H, NCH_3), 3.98 (s, 4H, NCH_2CO), 4.55 (s, 2H, $PhC\underline{H_2}NH$), 6.87 (t, br, 1H, Ph), 6.96 (d, br, 1H, Ph), 7.21 (t, br, 1H, Ph), 7.29 (d, br, 1H, Ph), 7.40 (m, 7H, Ph), 7.94 (d, J = 8.2 Hz, 2H, Ph), 8.70 (s, br, 1H, NH), 12.74 (s, 3H, COOH).



4.3.4.9 [ReOCl(H_3L^{10}-COOEt)], (49)

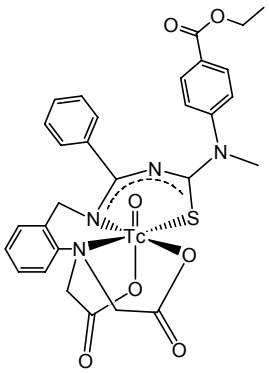
H_3L^{10}-COOEt (56 mg, 0.1 mmol) and three drops of Et_3N were added to a stirred solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL MeOH. The reaction mixture was heated under reflux for 30 min. After being cooled to room temperature, the formed violet solid was filtered off, washed with cold MeOH and dried under vacuum. Yield 63% (48 mg).



Elemental analysis:
Calcd. for $C_{29}H_{27}N_4O_7ReS$: C, 45.72; H, 3.57; N, 7.35; S, 4.21%.
Found: C, 45.60; H, 3.61; N, 7.24; S, 4.07%.
IR (KBr, cm^{-1}): 2985 (w), 2931 (w), 2851 (w), 1716 (vs), 1701 (vs), 1527 (s), 1496 (m), 1388 (m), 1280 (s), 1226 (w), 1114 (w), 1096 (m), 1018 (w), 988 (w), 936 (w), 910 (m), 779 (m), 706 (w).
^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.33 (t, J = 6.9 Hz, 3H, $CH_2\underline{CH_3}$), 3.85 (s, 3H, NCH_3), 4.14 (d, J = 18.1 Hz, 1H, $\underline{CH_2}N$), 4.34 (q, J = 6.9 Hz, 2H, $O\underline{CH_2}CH_3$), 4.44 (d, J = 18.0 Hz, 1H, $\underline{CH_2}N$), 4.78 (d, J = 15.5 Hz, 1H, NCH_2CO), 4.90 (d, J = 15.5 Hz, 1H, NCH_2CO), 5.32 (d, J = 13.5 Hz, 1H, NCH_2CO), 5.69 (d, J = 16.1 Hz, 1H, NCH_2CO), 7.20 (s, br, 1H, Ph), 7.28 (t, J = 7.4 Hz, 1H, Ph), 7.4-7.6 (m, 9H, Ph), 8.11 (d, J = 7.9 Hz, 2H, Ph).

4.3.4.10 [TcOCl(H_3L^{10}-COOEt)], (50)

The technetium complex **50** was prepared from $(NBu_4)[TcOCl_4]$ by the procedure described for its rhenium analogue **49**. The compound **50** was isolated as green solid. Yield 67% (45 mg).

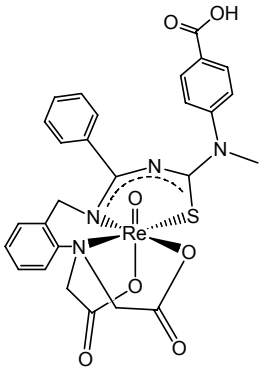


Elemental analysis:
Calcd. for $C_{29}H_{27}N_4O_7TcS$: Tc, 14.6%. Found : Tc, 14.4%.
IR (KBr, cm^{-1}): 2977 (w), 1708 (vs), 1604 (m), 1523 (vs), 1454 (m), 1388 (m), 1276 (s), 1218 (m), 1114 (m), 1018 (w), 956 (m), 910 (m), 779 (m), 705 (m).
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.18 (s, 3H, $OCH_2\underline{CH_3}$), 1.35 (m, 6H, $NCH_2\underline{CH_3}$), 3.68 (m, 5H, $N\underline{CH_2}CH_3$ + $\underline{CH_2}N$), 3.96 (s, 3H, NCH_3), 4.36 (m , 3H, $O\underline{CH_2}CH_3$ + $\underline{CH_2}N$) , 4.49 (d, J = 18.0 Hz, 1H, $\underline{CH_2}N$), 4.74 (d, J = 15.4 Hz, 1H, NCH_2CO), 4.93 (d, J = 15.4 Hz, 1H, NCH_2CO), 5.15 (d, J = 18.0 Hz, 1H, NCH_2CO), 7.1-7.4 (m, 11H, Ph), 8.08 (d, J = 7.6 Hz, 2H, Ph).

4.3.4.11 [ReOCl(H_3L^{10}-COOH)], (51)

H_3L^{10}-COOH (54 mg, 0.1 mmol) and Et_3N (about 0.3 mmol) were added to a stirred solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL MeOH. The reaction mixture was heated

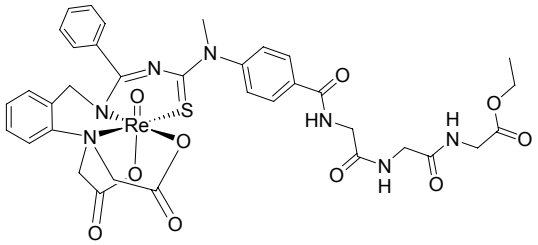
under reflux for 30 min. After standing at room temperature for 24 h, the formed violet solid was filtered off, washed with cold MeOH and dried under vacuum. Yield 52% (38 mg).



Elemental analysis:
Calcd. for $C_{27}H_{25}N_4O_7ReS$: C, 44.07; H, 3.42; N, 7.61; S, 4.36%.
Found: C, 44.20; H, 3.31; N, 7.48; S, 4.31%.
IR (KBr, cm^{-1}): 3066 (m), 1705 (vs), 1535 (s), 1496 (m), 1389 (m), 1354 (m), 1307 (m), 1230 (m), 1172 (w), 1118 (w), 1080 (w), 983 (m), 941 (w), 914 (m), 864 (m), 783 (m), 698 (m).
^{1}H NMR (400 MHz, DMSO-d_6, ppm): 3.85 (s, 3H, NCH_3), 4.09 (d, J = 18.3 Hz, 1H, $\underline{CH_2}N$), 4.44 (d, J = 18.3 Hz, 1H, $\underline{CH_2}N$), 4.78 (d, J = 14.4 Hz, 1H, NCH_2CO), 4.89 (d, J = 15.6 Hz, 1H, NCH_2CO), 5.32 (d, J = 14.4 Hz, 1H, NCH_2CO), 5.69 (d, J = 15.6 Hz, 1H, NCH_2CO), 7.20(d, J = 7.6 Hz, 1H, Ph), 7.28 (t, J = 7.4 Hz, 1H, Ph), 7.4-7.6 (m, 9H, Ph), 8.09 (d, J = 8.4 Hz, 2H, Ph), 13.24 (s, 1H, COOH).

4.3.4.12 [ReO(L^{10}-CON-TriGlyCOOEt)], (52)

Compound **51** (37 mg, 0.05 mmol), N,N'-dicyclohexylcarbodiimide (14 mg, 0.07 mmol) and N-hydrobenzotriazole (9 mg, 0.07 mmol) were disolved in 3 mL dry DMF. The reaction mixture was stirred at room temperature for 30 min. Then, triglycine ethylester (17 mg, 0.07 mmol) was added and the mixture was stirred at room temperature for additional 12 hours. The solvent was removed under vacuum and the residue was suspended in THF (5 mL). The insoluble urea was filtered off and the filtrate was washed with 5 mL of brine solution. After drying the organic phase over $MgSO_4$, the solvent was removed under vacuum. The residue was washed with cold MeOH and the red product was filtered off and dried under vacuum. Yield 95% (45 mg).



Elemental analysis:
Calcd. for $C_{35}H_{36}N_4O_{10}ReS$: C, 45.06;
H, 3.89; N, 10.51; S, 3.44%.
Found: C, 45.19; H, 3.75; N, 10.69; S, 3.41%.
IR (KBr, cm^{-1}): 3325 (m), 3062 (w), 2928 (m), 2850 (w), 1713 (vs), 1655 (vs), 1535 (s), 1497 (m), 1446 (w), 1384 (m), 1307 (m), 1219 (m), 1130 (w), 1084 (w), 980 (m), 941 (w), 910 (m), 864 (w), 787 (m), 605 (m).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.17 (t, J = 7.1 Hz, 3H, $CH_2\underline{CH_3}$), 3.75 (d, J = 5.9 Hz, $NHC\underline{H_2}$), 3.85 (m, 5H, NCH_3 + $NHC\underline{H_2}$), 3.93 (d, J = 5.7 Hz, 2H, $NHC\underline{H_2}$), 4.07 (m, 3H, $NHC\underline{H_2}$ + $NC\underline{H_2}CO$), 4.43 (d, J = 18.4 Hz, 1H, $\underline{CH_2}N$), 4.79 (d, J = 14.5 Hz, 1H, NCH_2CO), 4.89 (d, J = 15.7 Hz, 1H, NCH_2CO), 5.30 (d, J = 14.5 Hz, 1H, NCH_2CO), 5.68 (d, J = 15.7 Hz, 1H, NCH_2CO), 7.20 (d, J = 7.4 Hz, 1H, Ph), 7.28 (t, J = 7.4 Hz, 1H, Ph), 7.4- 7.6 (m, 9H, Ph), 8.03 (d, J = 8.4 Hz, 2H, Ph), 8.24 (t, br, 1H, NH), 8.29 (t, br, 1H, NH), 8.98 (t, br, 1H, NH).
ESI^+ MS (m/z): 956, 100%, $[M + Na]^+$, 972, 90%, $[M + K]^+$.

4.4 Crystal Structure Determination

The intensities for the X-ray determinations were collected on *STOE* IPDS 2T or *Brucker*-Smart-CCD-100-M instruments with Mo/Kα radiation. The space groups were determined using *CHECK-HKL* [119]. Empirical or numerical absorption corrections were carried out by *SADABS* [120] and *X-RED*32 [121] programs, respectively. Structure solution and refinement were performed with *SIR 97* [122], *SHELXS 97* [123] and *SHELXS 86* [123] or *SHELXL 97* [124] programs. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of *SHELXL* 97. Tables containing information about crystal data, refinement, position parameters and ellipsoid drawings are given as Supplementary material on the enclosed CD-ROM.

4.5 Biochemicals and Biological Studies

Cell Culture Conditions. The human MCF-7 breast cancer cell line was obtained from the American Type Culture Collection (ATCC). The cell line was maintained as a monolayer culture in L-glutamine containing Dulbecco`s Modified Eagle`s Medium (DMEM) with 4.5 g/L glucose (PAA Laboratories GmbH, Austria), supplement with 10% fetal calf serum (FCS; Gibco, Germany) using 25 cm^2 culture flasks in a humidified atmosphere (5% CO_2) at 37°C. The cell lines were passaged twice a week after previous treatment with trypsin (0.05%)/ethylenediaminetetraacetic acid (0.02% EDTA; Boehringer, Germany). Jurkat cells were purchased from German Collection of Microorganisms and Cell Culture (Deutsche Sammlung von Mikroorganismen und Zellkulturen, Braunschweig), DSMZ No ACC 282, LOT 7. The cells were maintained in RPMI 1640 (PAA) medium supplemented with 10%

foetal calf serum (PAA), 37°C, 5 % CO_2 and maximum humidity.

In Vitro Chemosensitivity Assay. The *in vitro* testing of the substances for antitumor activity in adherent growing cell lines was carried out on exponentially dividing human cancer cells according to a previously published microtiter assay [125]. Exponential cell growth was ensured during the whole time of incubation. Briefly, 100 µL of a cell suspension was placed in each well of a 96-well microtiter plate at 7200 cells/mL of culture medium and incubated at 37°C in a humidified atmosphere (5% CO_2) for 3 d. By removing the old medium and adding 200 µL of fresh medium containing an adequate volume of a stock solution of metal complex, the desired test concentration was obtained. Cisplatin was dissolved in dimethylformamide (DMF) while dimethylsulfoxide (DMSO) was used for all other compounds. Eight wells were used for each test concentration and for the control, which contained the corresponding amount of DMF and DMSO, respectively. The medium was removed after reaching the appropriate incubation time. Subsequently, the cells were fixed with a solution of 1% (v/v) glutaric dialdehyde in phosphate buffered saline (PBS) and stored under PBS at 4°C. Cell biomass was determined by means of a crystal violet staining technique as described earlier [126]. The effectiveness of the complexes is expressed as corrected T/C_{corr} [%] or τ [%] values according to the following equation:

cytostatic effect: $T/C_{corr}\ [\%] = [(T-C_0)/(C-C_0)] \times 100$

cytocidal effect: $\tau\ [\%] = [(T-C_0)/C_0] \times 100$

Whereby T (test) and C (control) are the optical densities at 590 nm of crystal violet extract of the cells in the wells, i. e. the chromatin-bound crystal violet extracted with ethanol (70%) with C_0 being the density of the cell extract immediately before treatment. For the automatic estimation of the optical density of the crystal violet extract in the wells, a microplate autoreader (Flashscan S 12; Analytik Jena, Germany) was used.