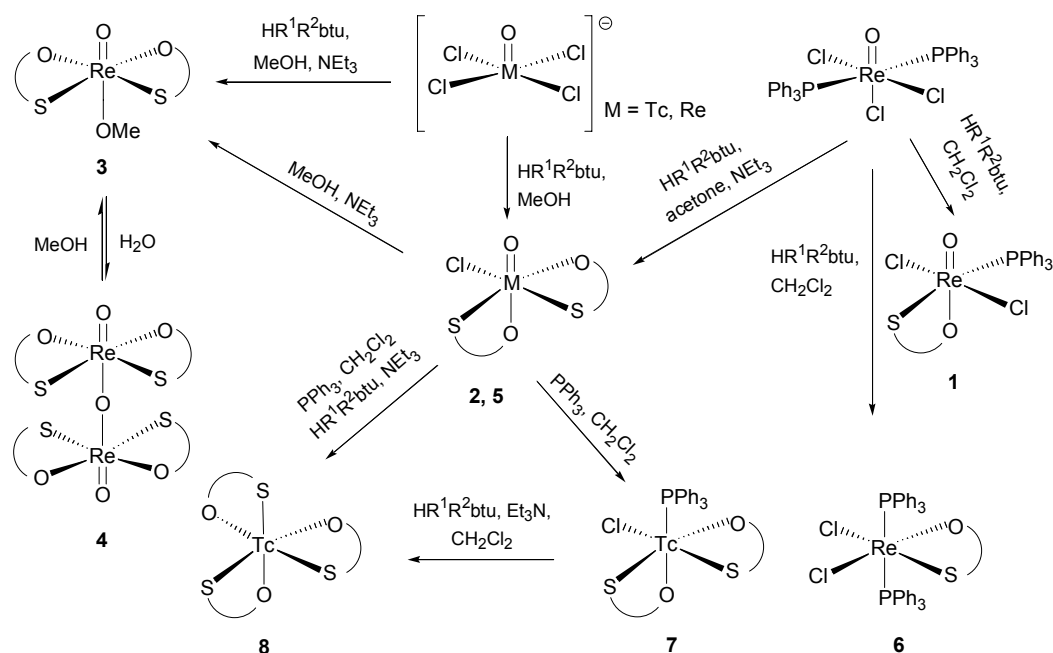


5 Summary

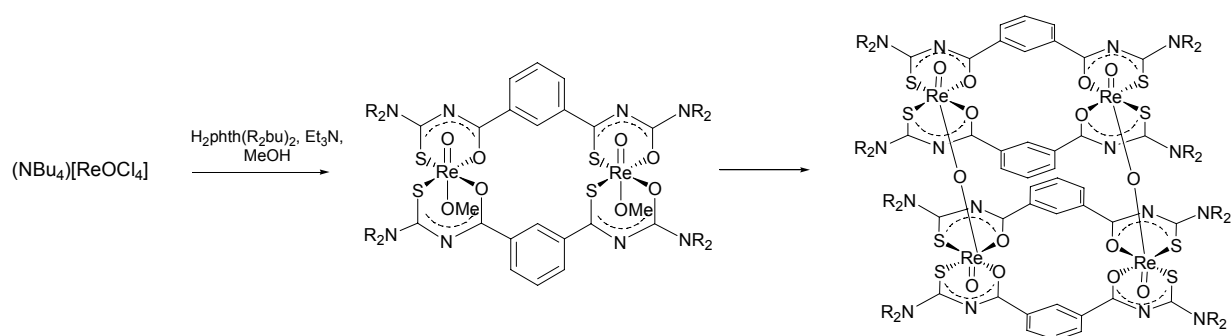
This thesis contains synthesis and structural characterization of novel technetium and rhenium complexes with chelating thiourea ligand systems, which include aroylthioureas and multidentate dialkylamino(thiocarbonyl)benzamidines.

N,N-Dialkylbenzoylthioureas ($\text{HR}^1\text{R}^2\text{btu}$) are versatile ligands and can stabilize rhenium and technetium in different oxidation states and/or with different cores. In all cases, they act as bidentate O,S-monoanionic ligands. Compositions and molecular structures of the products strongly depend on the precursors used and the reaction conditions applied (Scheme 5.1).



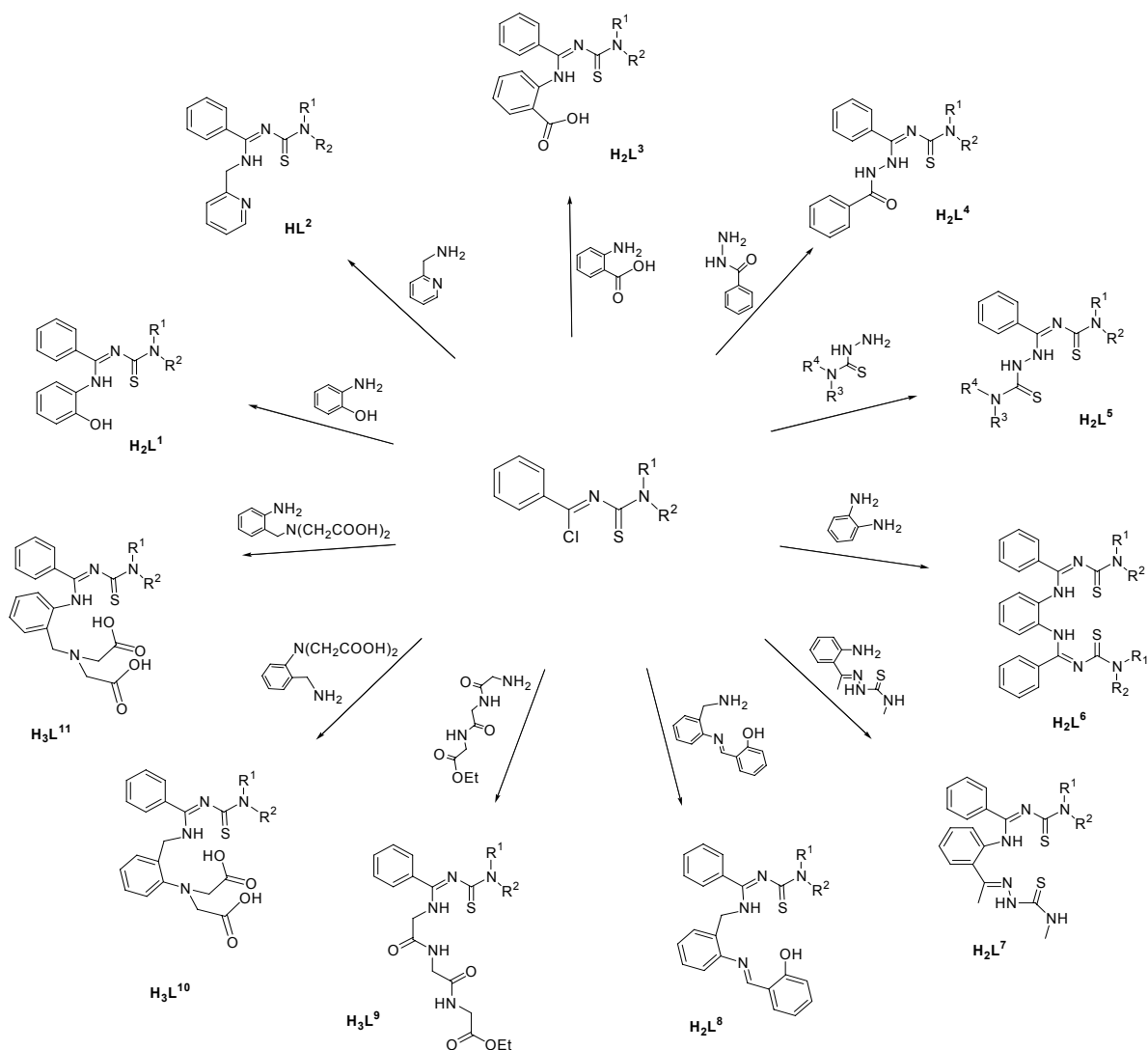
Scheme 5.1 Rhenium and technetium complexes with *N,N*-dialkyl-*N'*-benzoylthioureas and their reactions.

The coordination behaviour of aroyl(bis-thiourea) ligands is similar to that of benzoylthioureas. In methanol and with the addition of a base such as Et_3N , $\text{H}_2\text{phth}(\text{R}_2\text{tu})_2$ react with $(\text{NBu}_4)[\text{ReOCl}_4]$ under formation of the dinuclear complexes **11**, which undergo dimerization via μ -oxo bridges to form the tetranuclear complexes **12** (Scheme 5.2).



Scheme 5.2 Dinuclear and tetranuclear rhenium(V) complexes with bifunctional benzoylthioureas.

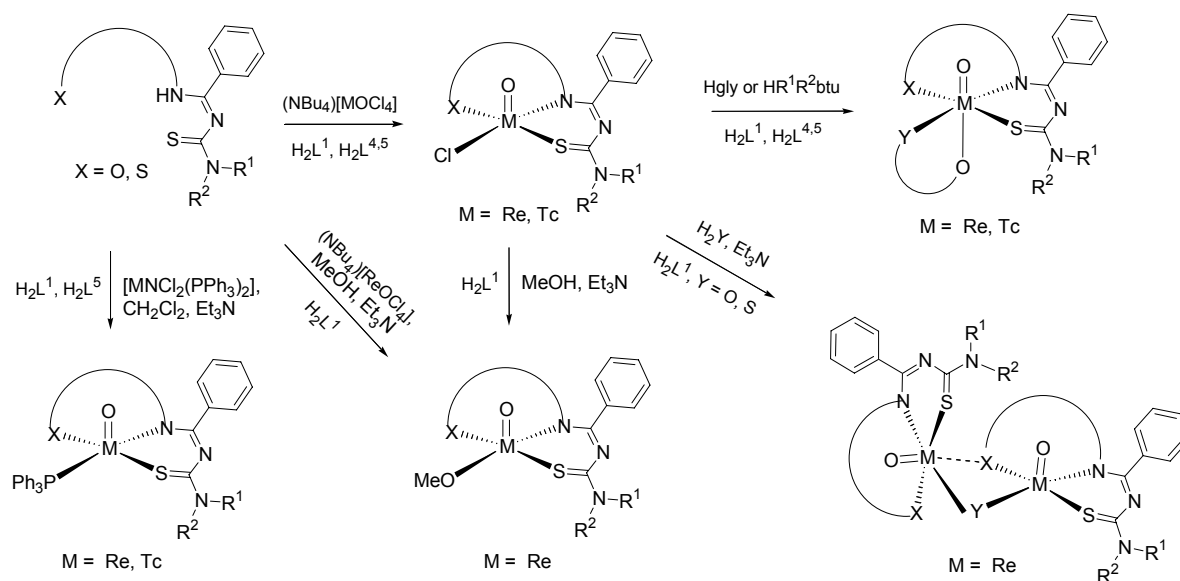
Various novel benzamidines, which can act as tri-, tetra- and pentadentate chelator systems, were successfully synthesized from *N,N*-dialkylamino(thiocarbonyl)benzimidoyl chlorides and functionalized amines (Scheme 5.3).



Scheme 5.3 Tri-, tetra- and pentadentate ligand systems synthesized from *N,N*-dialkylamino-(thiocarbonyl)-benzimidoyl chlorides.

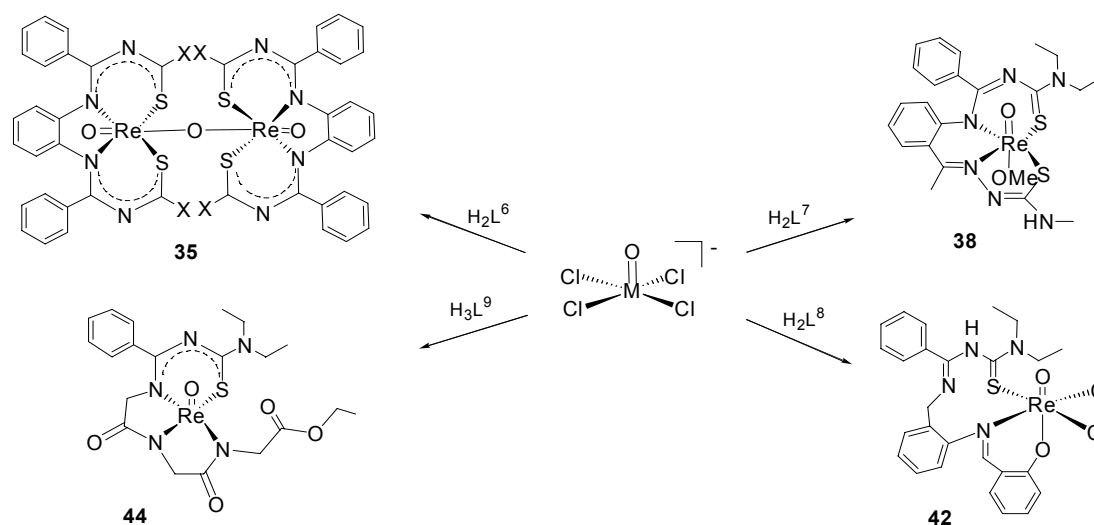
The coordination chemistry of such ligand systems with rhenium and technetium is carefully studied. In most of the isolated complexes, the multidentate benzamidines coordinated to rhenium and technetium via *S,N* donor atoms of the original benzamidines skeleton and additional donor sites which are introduced into the molecule with the amine components.

The tridentate benzamidines prefer meridional coordination to rhenium(V) and technetium(V) oxo and nitrido cores and form stable complexes of the compositions $[MOCl(L)]$ or $[MN(L)(PPh_3)]$ ($M = Re, Tc$). Some ongoing ligand exchange reactions of such complexes, giving access to '3 + 2' mixed ligand complexes, were studied (Scheme 5.4). A high level of cytotoxicity was found for tridentate thiosemicarbazones and the corresponding $[ReOCl(L)]$ complexes. Structure-Activity-Relationship studies of such compound were carried out by variation of substituted groups and/or the metal cores.



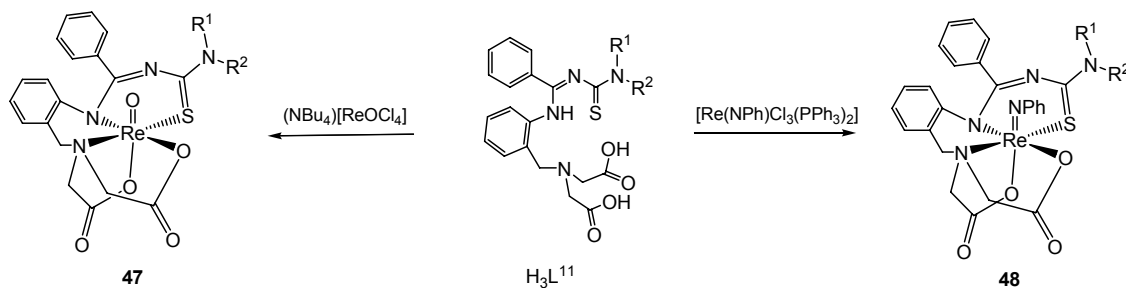
Scheme 5.4 Syntheses and reactions of rhenium and technetium complexes with tridentate benzamidines.

The tetradentate benzamidines are particularly suitable for rhenium(V) and technetium(V) oxo and nitrido cores. The structures of the complexes formed depend on the nature of the individual ligands and the charge compensation situation in the products, which finally leads to the formation of neutral complexes (Scheme 5.5).



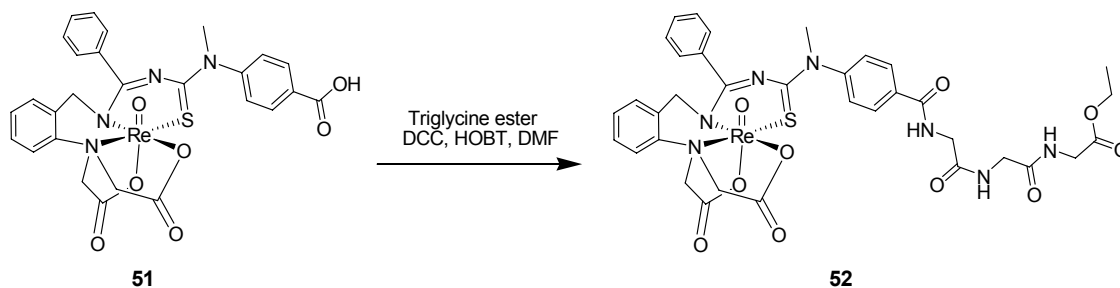
Scheme 5.5 Syntheses and structures of rhenium and technetium complexes with tetradentate benzamidines.

Pentadentate benzamidines were designed as chelator systems, which can fully wrap oxorhenium and oxotechnetium cores and form thermodynamically very stable complexes (Scheme 5.6).



Scheme 5.6 Rhenium complexes with pentadentate benzamidines.

In order to apply the latter, potentially pentadentate ligands to biomolecule labelling, the bifunctional chelator H_3L^{10} -COOH was synthesized. Its oxorhenium(V) complex, $[ReO(L^{10}-COOH)]$ (**51**), was successfully labelled with a small peptide such as triglycine ethyl ester (Scheme 5.7).



Scheme 5.7 Coupling product of $[ReO(L^{10}-COOH)]$ (**51**) with triglycine ethylester.