
9. Evaluation of the Study

9.1 Scientific relevance of the study

The chemical relevance and results of this Ph D study are briefly discussed according to the pre-set goals as given in Chapter 1.

This study was initiated by conducting a thorough literature search, gathering applicable practical and theoretical information, which revealed that a few nitridocyano complexes of manganese(V) have already been reported. The reported procedures were subsequently used to synthesize the $[\text{MnN}(\text{salen})]$ and $[(\text{CH}_3)_4\text{N}]_2\text{Na}[\text{MnN}(\text{CN})_5]\cdot\text{H}_2\text{O}$ complexes as starting compounds for the synthesis of the substituted products that contained the ligands of choice. These model complexes were thoroughly characterized by a variety of techniques, including ^1H NMR, IR, UV/visible spectroscopy and X-ray crystallography.

The ligand systems included in the study were monodentate $[\text{NCS}^-$, 2-methylpyridine (2-pic), 3-methylpyridine (3-pic), 4-methylpyridine (4-pic)] and bidentate nucleophiles [ethylenediamine (en), 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), pyridine-2-carboxylate (pic $^-$), quinaldinate (quin $^-$), pyridine-2,3-dicarboxylate (2,3-dipic $^{2-}$), pyridine-2,4-dicarboxylate (2,4-dipic $^{2-}$), pyridine-2,5-dicarboxylate (2,5-dipic $^{2-}$) and pyridine-2,6-dicarboxylate (2,6-dipic $^{2-}$)]. Several of these ligand systems as well as the nitridocyano complexes of manganese were only investigated to a very limited extent in the past. Most of the complexes were studied structurally, except for the complexes containing the 2-pic and different dipic $^{2-}$ ligands, since the $[\text{MnN}(\text{CN})_4]^{2-}$ complex crystallized instead of $[\text{MnN}(2\text{-pic})(\text{CN})_4]^{2-}$ and although numerous attempts were made, the crystalline substitution products containing the dipic $^{2-}$ ligands could not be obtained. The question of the existence of the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ in solution and in the solid state remains unanswered, since the crystals obtained from aqueous solutions after numerous attempts contained only the $[\text{MnN}(\text{CN})_4]^{2-}$ anion.

The crystal structure determinations of the complexes containing the monodentate ligands [NCS⁻, (3-pic), (4-pic)] and bidentate [(en), (bipy), (phen), (pic⁻), (quin⁻)] ligands gave valuable information in terms of the effect on the geometry of the complexes investigated, as well as the bonding capabilities of the ligands in this system. This is the first study that included all three of the N,N-bidentate ligands (en, bipy, phen) bonded to the same metal center and in complexes with the same fundamental coordination geometry. This study included the first crystal structure determination containing the quinaldinate ligand bonded to a nitridocyano complex of one of the group 6, 7 or 8 elements.

The kinetic investigation of the ligand systems was limited to the ligands with a high solubility in aqueous medium (except en). The kinetic investigation was undertaken to correlate the behaviour of these complexes with the structural properties as well as with previously studied systems. The extremely fast substitution of the aqua ligand by other entering nucleophiles was demonstrated and verified as well as the slow substitution of the equatorial cyano ligand. The substitution reactions of the [MnN(H₂O)(CN)₄]²⁻ complex with 2,6-dipic²⁻ and quin⁻ could not be studied, since no reaction was observed with the 2,6-dipic²⁻ ligand and very small absorbance changes were obtained during the reaction of the complex with quin⁻. It is rather unfortunate that the acid dissociation constants could not be determined more accurately with kinetic and spectrophotometric methods. The signal of the ⁵⁵Mn nuclei in [MnN(CN)₅]³⁻ and [MnN(CN)₄]²⁻ was not observed and the effect of the different ligands on the metal center could not be determined with NMR experiments.

Progress was made in describing the nitridocyano complexes of manganese(V), the first 1st-row element investigated containing the nitrido or oxo axial ligand, as well as some of the ligand systems investigated. Existing knowledge concerning the reactivity of the nitridocyano complexes of group 7 was expanded by the crystallographic and kinetic investigation of the monodentate and bidentate substituted complexes containing the manganese(V) metal center.

The kinetic investigation into the reactions of Grubbs 1st generation catalyst precursor confirmed some of the previously determined kinetic parameters. The reactivity, especially the reaction rates, towards oxygen and the auto-decomposition of this

precursor were also determined. The reactions rates showed that the auto-decomposition reaction and the reaction of the 1st generation Grubbs' catalyst with oxygen are very slow compared to the initiation of the catalyst precursor with ethene and 1-octene. Thus, the decomposition and the reaction with oxygen do not seem to be a problem when the catalyst precursor is used on laboratory scale. However, the decomposition and reaction with oxygen will be a problem if the catalyst precursor is used in industry, where continuous processes are preferred.

In general it is concluded that the study, based on the goals set in Chapter 1, can be considered successful.

9.2 Future research

Although the mechanism for the reaction of $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ with monodentate and bidentate ligands was established as proceeding according to a dissociative pathway, evidence supporting an associative type of mechanism for the stronger bonded *cis* ligands was obtained. A detailed high pressure study of the bidentate substitution reactions would help to clarify and correlate the mechanism of the substitution reactions of the *cis* bonded cyano ligands.

An investigation into the nitridotetracyano complexes of other 1st row metal centers (for example Cr) with regard to the reactivity of these metal centers would also provide additional knowledge on these systems.

A ^{13}C and ^{15}N NMR study of the monodentate substitution reactions of the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex with labelled CN^- and NCS^- would provide more information on the rates of these substitution reactions, as well as the mechanism thereof.

A crystal structure determination of $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ would clarify the question concerning the existence of the anion in solution and with regard to the possible vacant sixth coordination site as determined in the crystal structure of $[\text{MnN}(\text{CN})_4]^{2-}$.

Identification of the auto-decomposition products of 1st generation Grubbs' catalyst as well as the products of the reaction with oxygen would shed more light on the mechanism of decomposition of the catalyst precursor.

A crystal structure determination of initiation product of the reaction of 1st generation Grubbs' catalyst with ethyl vinyl ether would provide more information on the coordination mode of the two alkenes before the formation of the metallacyclobutane and the mechanism of the metathesis reaction. The metathesis reaction is quenched after the catalyst precursor is reacted with ethyl vinyl ether and it should be possible to obtain crystals of the reaction product.

The investigation into the decomposition of the Grubbs' type catalyst precursor should also be extended to the 2nd and 3rd generation catalyst precursors, as well as the reaction of these catalyst precursors with oxygen. Crystal structure determinations of the decomposition products and possible reaction products of the 2nd and 3rd generation catalyst precursors would provide additional knowledge on these systems.

