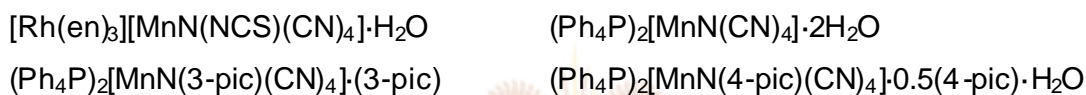
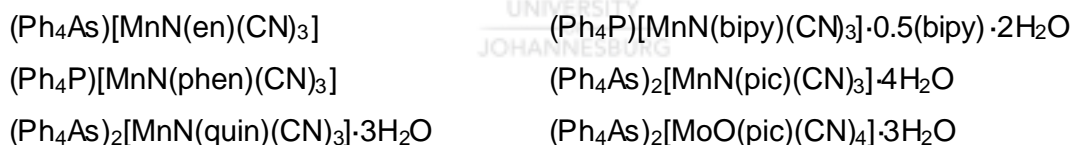

Abstract

The aim of this investigation was to study model complexes containing strong π -ligands as potential nitrogen, oxygen and ligand transfer catalysts. Nitrido containing cyano complexes of group 6 to 8 metals were selected as potential nitrogen transfer catalysts. Solid state and solution studies, investigating different aspects of these systems, were performed. Finally, the knowledge on mechanistic studies were applied to selected examples of 1st generation Grubbs catalyst $[\text{Ru}(\text{=CR})(\text{PX}_3)_2\text{C}_2\text{b}]$ (=CR = carbene) to investigate olefin coordination and oxygen decomposition reactions (both involving strong π -interactions at the metal center thereof).

The crystal structures of the following monodentate substituted nitridotetracyano complexes of manganese(V) are reported:



The crystal structures of the following N,N- and N,O-bidentate substituted nitridotetracyano complexes of manganese(V) are reported:



The monodentate substituted complexes crystallized in the triclinic space group, $P\bar{1}$, except for $[\text{Rh}(\text{en})_3][\text{MnN}(\text{NCS})(\text{CN})_4] \cdot \text{H}_2\text{O}$, which crystallized in the orthorhombic space group, $P2_12_12_1$. Very short Mn=N bond distances [from 1.507(2) Å to 1.540(3) Å] were determined, as well as the significant mode of distortion of the coordination octahedron in these complexes. The large *trans* influence of the nitrido ligand was also evident in the bond distances of the *trans* bonded ligands. The coordination mode of the monodentate ligands was determined, in particular the thiocyanate ligand, which showed that the manganese(V) metal center is a hard acid.

The bidentate substituted complexes crystallized in the triclinic space group, $P\bar{1}$, except for $(\text{Ph}_4\text{As})[\text{MnN}(\text{en})(\text{CN})_3]$ and $(\text{Ph}_4\text{P})[\text{MnN}(\text{phen})(\text{CN})_3]$, which crystallized in

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the monoclinic space group, $P2_1/c$. The short Mn=N bond distances [from 1.523(5) Å to 1.574(3) Å] were also found for the bidentate substituted complexes, as well as the significant distortion of the coordination octahedron. Small bite angles [from 75.3(1)° to 77.5(1)°] and the larger *trans* influence of the *trans* bonded cyano ligands on the bidentate nitrogen atoms in the equatorial plane were detected for the bidentate substituted complexes.

The anation reactions of the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex were too fast to determine on a 3rd generation stopped-flow spectrophotometer. The stability constant of the $[\text{MnN}(\text{CN})_5]^{3-}$ complex (reaction A, Scheme 1) was determined as 115(5) M⁻¹. Monodentate substitution is summarized by reaction A to D in Scheme 1 below.

Only one reaction was observed by means of time resolved UV/visible spectra for the bidentate substitution of the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex. Thus, the substitution reaction of the aqua ligand by the carboxylate moiety of the bidentate ligands (pic⁻, 2,3-dipic²⁻, 2,4-dipic²⁻ and 2,5-dipic²⁻) could not be detected and only the second slower substitution reaction of one of the equatorial cyano ligands was detected. Scheme 1 was constructed to describe the substitution process of the aqua and cyano ligands in $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ with bidentate ligands.

Since only the second slower reaction could be detected, the forward rate constant consists of the equilibrium constant (K_1) and the forward rate constant for the second slower reaction (k_2) (see reactions C and E, Scheme 1). The formation constants for the $[\text{MnN}(\text{N}=\text{O})(\text{CN})_4]^{n-}$ (N=O = picolinate type ligands) complexes were also determined by means of spectrophotometry. The activation parameters for the overall process were also determined using the Eyring equation.

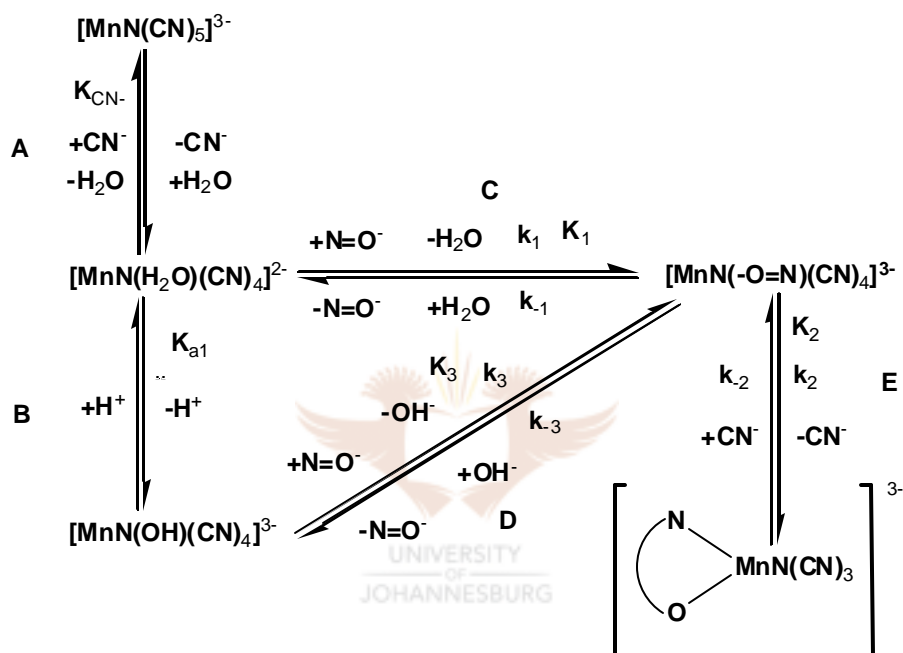
In accordance with Scheme 1, the following rate law, on condition that linear plots are obtained for k_{obs} vs. [LL] data, is given by:

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$$k_{\text{obs}} = \frac{k_2 K_1 [\text{pic}^-]}{1 + K_{a1} / [\text{H}^+]} + k'_{-2} \quad 1$$

Furthermore, at pH values where $K_{a1} \ll [\text{H}^+]$, eq. 1 can be simplified to eq. 2.

$$k_{\text{obs}} = k_2 K_1 [\text{pic}^-] + k'_{-2} \quad 2$$



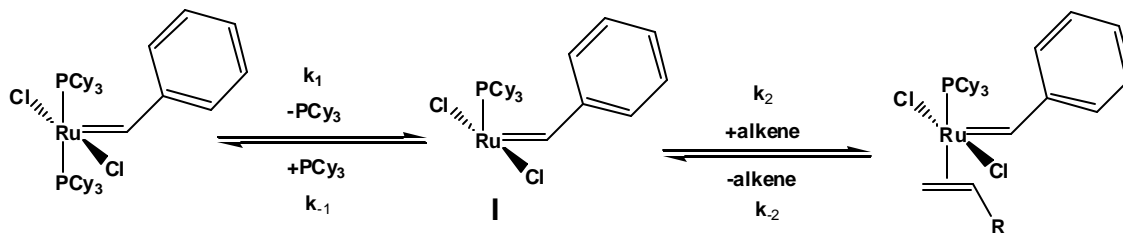
Scheme 1: Schematic presentation of the protonation and monodentate/bidentate substitution behaviour of the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex (N=O = picolate type ligands).

The above-mentioned crystallographic and kinetic results were compared to other known results from studies involving the group 6 b 8 metal complexes containing oxo and nitrido ligands and the mentioned results showed good correlation with the known systems.

The reactivity of 1st generation Grubbs catalyst precursor was investigated towards decomposition of the catalyst precursor (thermal decomposition and with oxygen) and initiation of the catalyst precursor with ethene gas and 1-octene, which entail the

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first two steps of the metathesis catalytic cycle of the 1st generation Grubbs catalyst (see Scheme 2).



Scheme 2: The dissociation of PCy₃ and coordination of alkene during the first two steps of the metathesis catalytic cycle of 1st generation Grubbs catalyst.

In accordance with Scheme 2, the rate law for the initiation of the catalyst precursor is given by:

$$k_{obs} = \frac{k_1 k_2 [alkene]}{(k_{-1} [PCy_3] + k_2 [alkene])} \quad 3$$

Any factors that change the concentration of the four-coordinate intermediate (I) will have a pronounced effect on the subsequent steps of the catalytic cycle. Thus, the rates of thermal decomposition and the reaction of the catalyst precursor with oxygen were determined and it was found that these reaction rates are very slow compared to the initiation rates that were determined with ethene and 1-octene. As expected for a dissociative substitution process, k_2 was independent of [alkene] at high concentrations of alkene. A very good correlation was found between the results from this study and those reported.

The rate law determined for the bidentate substitution of the $[MnN(H_2O)(CN)_4]^{2-}$ complex and the rate law for the initiation reaction of $[Ru(=CHPh)Cl_2(PCy_3)_2]$ with alkenes are very similar (see eq. 1 and 3).