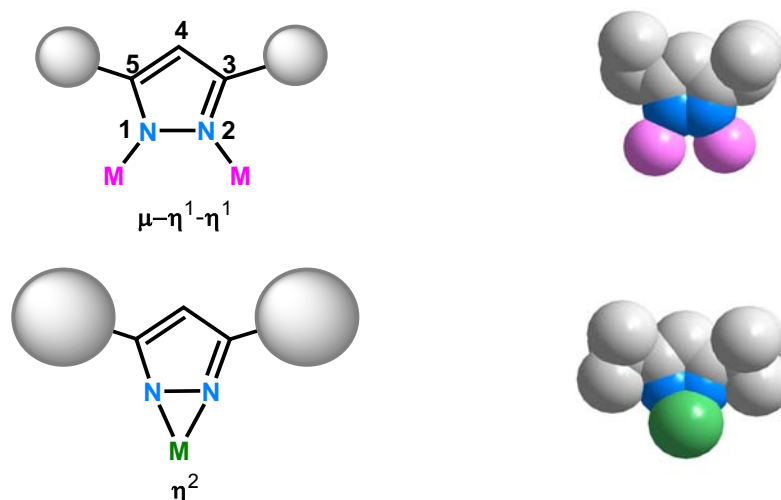


## Coordination chemistry with sterically demanding pyrazolate ligands

Pyrazoles and triazoles represent a class of molecules with ideal ligand properties allowing a wide variety of structures and bonding options. The most common bonding types in these complexes represent  $\eta^1$ , bridging between two metal atoms in a  $\mu\text{-}\eta^1\text{-}\eta^1$  fashion as well as  $\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1$  for triazolato ligands leading mainly to di- and polynuclear compounds. For this reason they were not used for the design of early transition metal complexes. However, sterically demanding groups in 3,5-positions of the heterocycle prevent bridging modes leading to  $\eta^2$  coordination and rendering them a new class of nitrogen-based ligands.



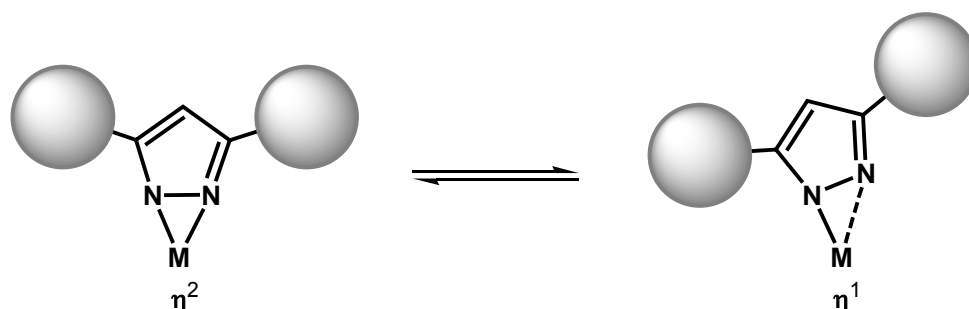
**Figure 1.** Sterically demanding groups in 3,5-positions leads to preferred endobidentate ( $\eta^2$ ) in contrast to the prevalent exobidentate ( $\mu\text{-}\eta^1\text{-}\eta^1$ ) coordination.

Our research interest is to understand the factors governing the unusual  $\eta^2$  bonding type and to investigate their scope in organometallic reactions. In addition, pyrazole belongs to the class of 5-membered heterocycles containing two nitrogen atoms together with imidazole, which is found in the amino acid histidine. We are studying the viability of pyrazolate complexes as models for metalloenzymes.

### Bonding in $\eta^2$ -Pyrazolate Complexes

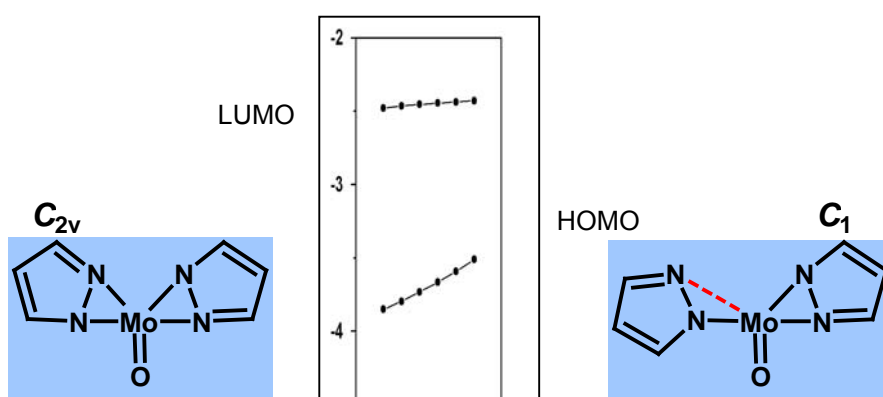
Systematic syntheses of compounds in various oxidation states allowed the study of the influence of *d*-electrons on the bonding. In titanium(III) compounds the ligand

coordinates exclusively  $\eta^2$ , whereas in molybdenum(IV) both  $\eta^2$  and  $\eta^1$  is found. No evidence for  $\mu\text{-}\eta^1\text{-}\eta^1$  coordination has been found in any of the investigated systems.



**Figure 2.** Competition between  $\eta^2$ - and  $\eta^1$ -coordination.

We can conclude that with higher  $d$ -electron count of the metal,  $\eta^1$ - and  $\eta^2$ -coordination compete with each other, but are preferred over bridging modes. DFT calculations on the model compound  $[\text{MoO}(\text{Pz})_2(\text{PMe}_3)_2]$  with the  $d^2$ -metal Mo(IV) indicate a higher stability of  $\eta^2$ -coordinate species. Stepwise change from  $\eta^2$  to  $\eta^1$  shows the HOMO to increase in energy. Orbitals involved in  $\sigma$ - and  $\pi$ -bonding were analysed. However, X-ray crystal structure of the related complex involving the sterically demanding  $t\text{-Bu}_2\text{Pz}$  ligand  $[\text{MoO}(t\text{-Bu}_2\text{Pz})_2(\text{PEt}_3)]$  shows one of the ligands  $\eta^1$ -coordinate, which lets us conclude that steric interactions dominate the bonding.

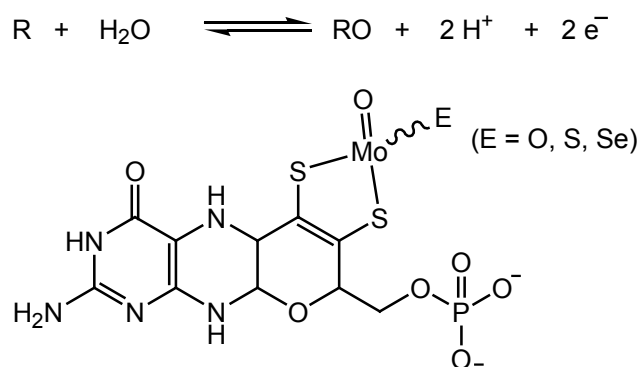


**Figure 3.** Energy increase by change of coordination mode to  $\eta^1$  in one of the ligands.

## Oxygen-transfer reactions with pyrazolate complexes

Molybdenum and tungsten catalysed oxygen-transfer reactions have attracted considerable interest in recent years due to their relevance in biological processes. Molybdenum is found in a class of enzymes that are commonly referred as mononuclear molybdoenzymes or oxotransferases and that catalyse oxygen atom transfer to and from a substrate.

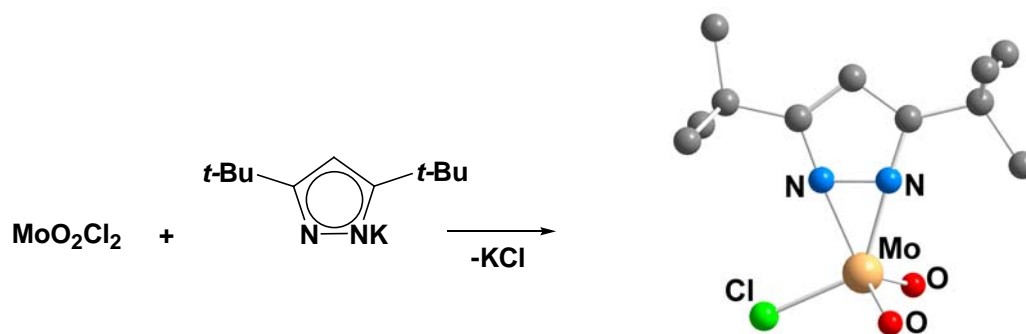
In recent years, crystal structures of several molybdo- and tungstoenzymes were determined. In all cases, the reaction centre contains a mononuclear metal centre coordinated by one or two oxygen as well as one or two molybdopterin ligands, whose dithiolene functionality co-ordinates to the metal atom.



**Scheme 1.** Oxygen-transfer reactions catalysed by oxotransferases, shown is the molybdenum cofactor with one molybdopterin ligand coordinated to molybdenum.

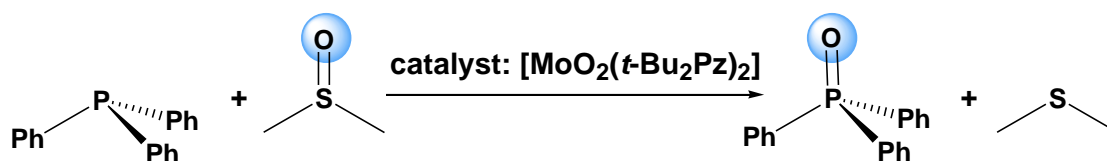
Model chemistry has been focussed on the use of  $\text{MO}_2^{2+}$  cores and on variation of the co-ligands  $\text{LL}'$  ( $[\text{LL}'\text{M}^{\text{VI}}\text{O}_2]$ ,  $\text{M} = \text{Mo}, \text{W}$ ) to influence steric as well as redox properties of the oxygen-transfer reaction.

We use bulky pyrazolate ligands to synthesise  $[\text{MoO}_2\text{X}(t\text{-Bu}_2\text{Pz})]$  ( $\text{X} = \text{Cl}, t\text{-Bu}_2\text{Pz}$ ) complexes as shown in Scheme 2. X-ray analyses of single crystals showed them to be mononuclear with  $\eta^2$ -coordinate  $t\text{-Bu}_2\text{Pz}$  ligands. The geometry at the metal site is interesting as it approaches the situation in natural systems, where in some cases distorted trigonal prismatic geometries at the metal site have been found.



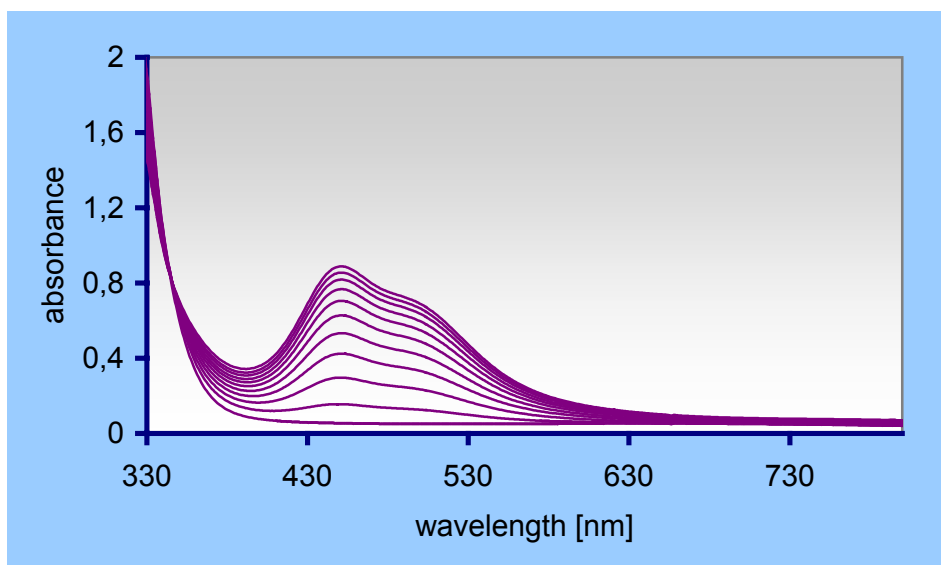
**Scheme 2.** Synthesis of  $\eta^2$ -pyrazolate complexes of a highly oxidised metal centre.

The most interesting feature of these compounds is their ability to catalyse oxygen-transfer from dimethylsulfoxide to triphenylphosphine. This model reaction, commonly used to investigate oxygen-transfer, has biological relevance to molybdenum-containing DMSO reductases, which are able to utilize a variety of dialkyl- and alkylarylsulfoxides as oxo donor.



**Scheme 3.** Oxygen-transfer from DMSO to  $\text{PPh}_3$ .

Detailed mechanistic information was obtained by UV/Vis-spectroscopy allowing the conclusion that a monomeric monooxo compound of the type  $[\text{MoO}(\text{t-Bu}_2\text{Pz})_2]$  is involved in the catalytic cycle. The undesired dimeric molybdenum(V) compound  $[(\text{t-Bu}_2)_2\text{OMo}-\text{O}-\text{MoO}(\text{t-Bu}_2)_2]$  was not observed. Dimerisation is an often occurring reactivity in these type of reactions unless it is prevented by sterically demanding ligands and which is perfectly accomplished by the protein in natural systems.



**Figure 4.** Oxygen-transfer observed by UV/Vis-spectroscopy showing the increase in absorbance due to the formation of brown  $[\text{MoO}(t\text{-Bu}_2\text{Pz})_2(\text{L})_2]$ .

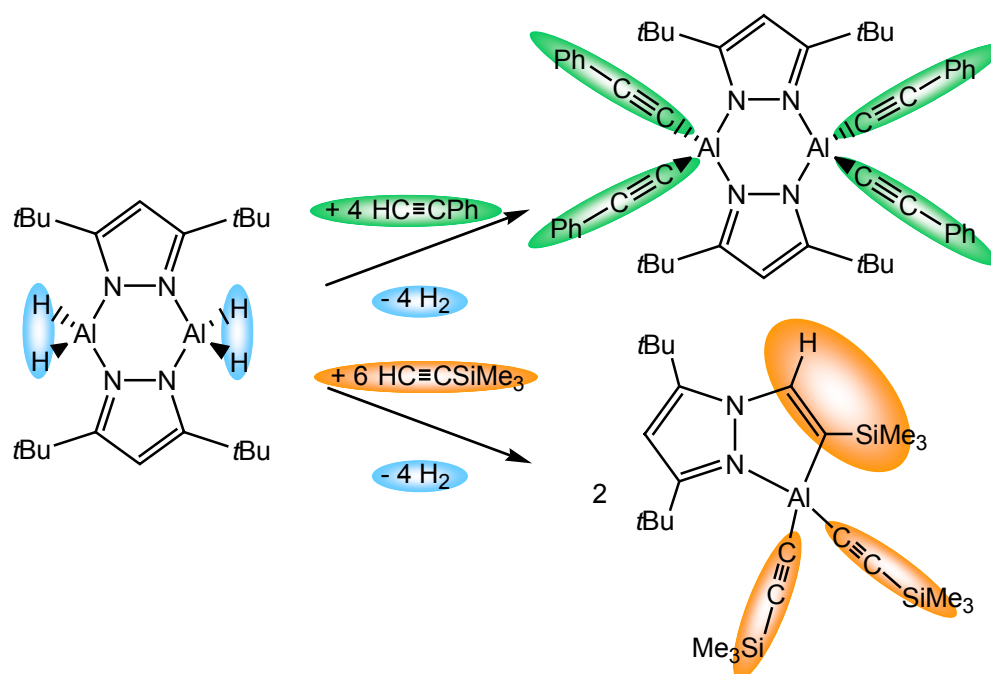
The occurrence of the monomeric intermediate in the pyrazolate systems allows us to use our system as a functional model for oxotransferases and to conclude that sulphur donors are not a prerequisite for oxygen-transfer. However, reactions are in general significantly slower than in sulphur-based systems explaining nature's choice over e. g. histidine-coordinated reaction centres.

We are currently investigating oxygen-transfer reactions employing different substrates as well as other high-valent metal complexes that contain pyrazolate ligands. Furthermore, the success with the nitrogen-based system encouraged us to explore the coordination of other amido ligands to metal oxo centres, which is ongoing research in our group.

### **Coordination chemistry of pyrazolate ligands with main group metal centres**

Hydroaluminations and oligomerisation of olefins and acetylenes by aluminum catalysts are important organic processes. The synthesis of aluminum compounds that are reactive enough towards these substrates but sterically and kinetically hindered allowing the isolation of intermediates is therefore of significant interest. In this regard, sterically demanding pyrazolates represent an ideal class of ligands.

Dimeric aluminium dihydride  $[(\mu\text{-}t\text{Bu}_2\text{Pz})\text{AlH}_2]_2$  that contains two bridging  $t\text{Bu}_2\text{Pz}$  and four terminal hydride ligands proved to be an ideal starting material. The steric demand of the system allowed the isolation of the first aluminium compound that contains terminal acetylide substituents.



**Scheme 4.** Aluminum compounds with terminal acetylide ligands.

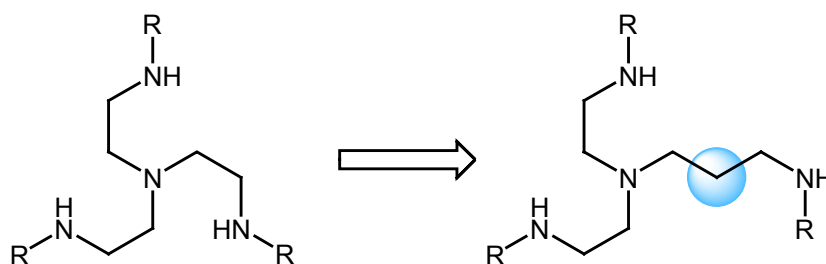
With trimethylsilyl substituted acetylene the reaction proceeds to a monomeric compound under formal addition of the pyrazolate ligand to the  $\text{C}\equiv\text{C}$  triple bond, thereby forming a five-membered metallacycle with the aluminum centre.

## Coordination chemistry with sterically demanding triamidoamine ligands

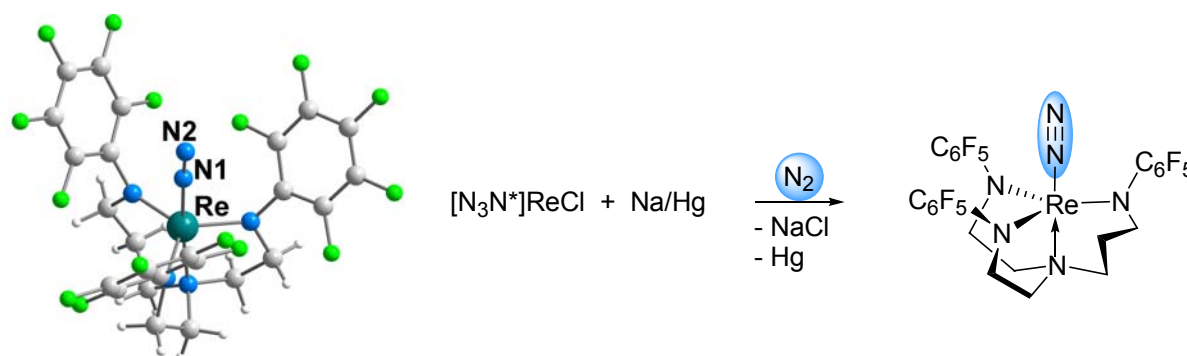
Activation of a small, relatively inert molecules by a metal complex represents an important step in many catalytic processes. Knowledge on factors that govern the activation is therefore of fundamental interest. Complexes employing triamidoamine ligands of the type  $(\text{RNCH}_2\text{CH}_2)_3\text{N}$  ( $\text{R}$  = aryls, silyls) have been extensively used for this purpose and have shown to activate a variety of small molecules. A pivotal feature is the  $C_{3v}$  symmetry imposed by such ligands which leads to three frontier

orbitals that are arranged in such a way that the formation of metal triple bonds is preferred and which represents the driving force for the activation.

We are designing trisamidoamine ligands that break the  $C_{3v}$  symmetry and therefore the degeneracy of the frontier orbitals, in the hope to find unusual activation of small molecules. The first example of this type synthesised is the triamidoamin ligand  $(RNCH_2CH_2)_2NCH_2CH_2CH_2NR$  ( $[N_3N^*]$ ;  $R = C_6F_5$ ) that contains an additional  $CH_2$  unit in one of the amine 'arms' and bulky  $C_6F_5$  groups at nitrogen.

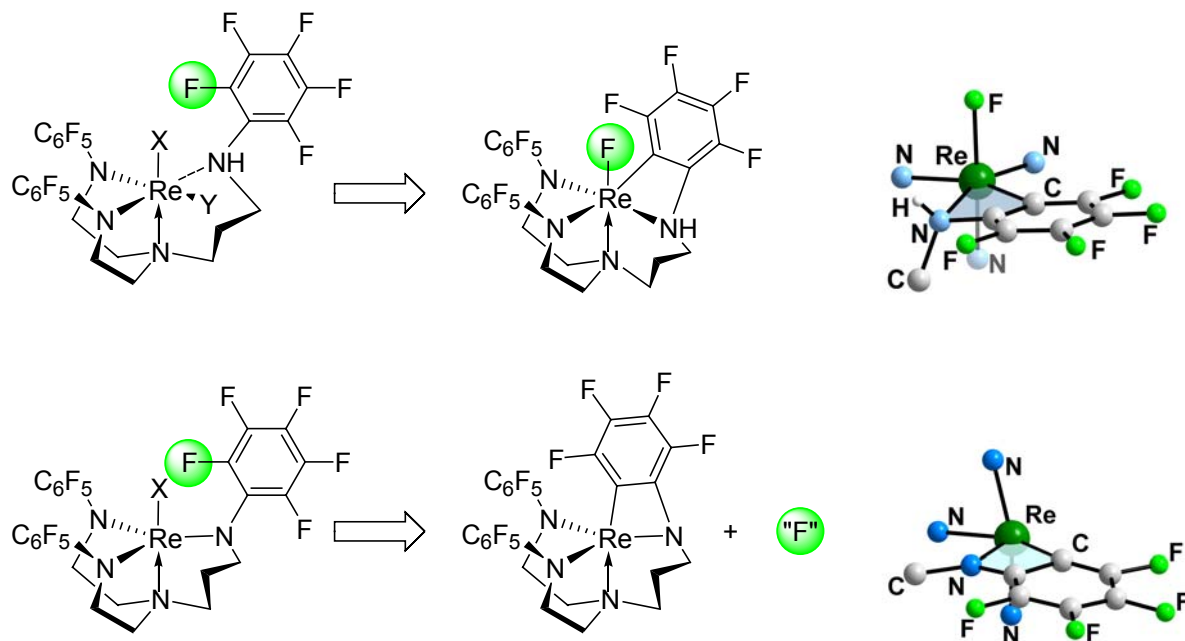


This ligand allowed us to prepare a series of rhenium complexes that can be compared to the  $C_3$  symmetric systems. We found several compounds where the propylene amine substituent remains dangling (e. g.  $[HN_3N^*]ReBr_2$ ) in contrast to the analogous species with the  $C_3$  symmetric ligand ( $[N_3N]ReBr$ ,  $[N_3N] = (C_6F_5NCH_2CH_2)_3N$ ) and in accordance with the stronger chelate effect in the latter. Elimination of  $HX$  and subsequent reduction led to activation of dinitrogen as shown below. Thus, the investigation of the system which a slightly disturbed symmetry allows us to elucidate mechanistic pathways in the activation of small molecules.



**Scheme 5.** Activation of dinitrogen

Major reactivity involves non-innocent behaviour of the ligand. We found that the longer propylene substituent and the thus formed 6-membered metallacycle leads to a pronounced tilting of the  $\text{C}_6\text{F}_5$  group towards the metal and to subsequent C-F bond activation forming metal carbon and metal fluorine bonds.



**Scheme 4.** *Ortho* metallation in the  $\text{C}_6\text{F}_5$ -group of the propylene substituent.

We are investigating this reactivity and the influence of other substituents at nitrogen. Further studies will focus on the development of  $C_2$  symmetric ligand systems that are less prone to *ortho* metallation and will lead to more active compounds towards the activation of small molecules.

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