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Tris(pyrazolyl)phosphines and their Copper(I) Complexes

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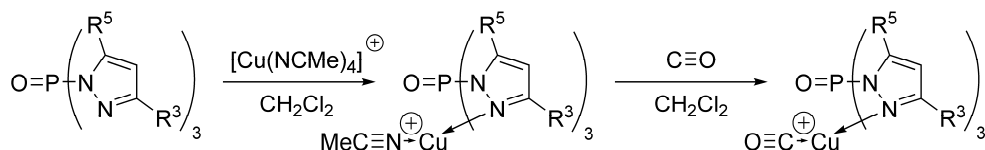
Summary

In coordination chemistry and homogeneous catalysis, different ligands may lead to different chemistry. Therefore, extending the “toolbox” of available ligands and the knowledge about them is useful for the scientific community. In this thesis the chemistry of tris(pyrazolyl)phosphine ligands is extended, alongside the topologically related tris(triazolyl)phosphines. In this work, both ligand types have been complexed exclusively to Cu(I), but the concepts shown here are expected to be readily transferable to other metals.

Chapter 1 gives an overview of the current state of research on tris(azolyl)-phosphines, focusing on their synthesis and coordination chemistry. The imidazolyl based ligands dominate this field and have been applied in enzyme modelling studies for Zn, Fe and Cu containing enzymes, and in a number of other studies, accommodating different metals ranging from Sc to Au. Pyrazolyl based ligands have also been used in coordination chemistry, although to a lesser extent. Their Cu chemistry has been best developed. Recently, these tris(pyrazolyl)phosphines have also been applied as P precursors in a series of publications. 1,2,3-triazolyl based ligands have only emerged in the last decade, but do show some differentiating features that justify further development of this ligand type. Finally, 1,2,4-triazolyl phosphine oxide has been almost exclusively used as a reagent for organic transformations of mostly bioorganic molecules.

Chapter 2 starts with an improved preparation for the tris(pyrazolyl)phosphine oxides that allows isolation of a set of ligands with a diverse steric bulk around the metal binding site of the ligand. Introducing methyl substituents close to the P-N bonds made the resulting ligands less susceptible to hydrolysis.

The coordination chemistry of this set of ligands was explored by reacting each ligand with $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$. Both NMR spectroscopy and X-ray diffraction of selected single crystals indicated the expected $\kappa^3\text{-N}_3$ binding mode of the ligand, with one remaining NCMe ligand completing the distorted tetrahedral surrounding. This monodentate ligand can be exchanged by either triphenylphosphine or CO (Scheme 1). Introduction of the latter gives a measure for the electron density on the metal via the CO stretch frequency. Comparison with Cu-CO complexes of the related tris(pyrazolyl)methanes showed the phosphorus centered ligands to be more electron withdrawing.



Scheme 1. Complexation and ligand exchange reactions as studied experimentally in chapter 2 and computationally in chapter 3.

Computationally, this difference does not stand out. In **chapter 3**, at the BVP86/6-311G(d,p) (SDD for Cu) level of theory, both the parent tris(pyrazolyl)phosphine oxide and tris(pyrazolyl)methane Cu-CO complex are calculated to give the same $\nu(\text{CO})$. Calculations on the related tris(triazolyl) based ligands give marginally higher $\nu(\text{CO})$ values, but the difference is smaller than the deviation from the experimentally determined values for the pyrazolyl based systems. The effect of introducing substituents does show a significant decrease in metal electron density *in silico*.

Complexation energies were calculated to be more exothermic for the triazolyl based systems compared to the tris(pyrazolyl) ligands ($\Delta\Delta G \geq 4.3$) and introduction of substituents also has a similar effect ($\Delta\Delta G \geq 4.1$ kcal/mol). In contrast, the effect of changing the apex is only modest ($\Delta\Delta G \leq 1.3$).

Experimentally, complexation of tris(triazolyl)phosphine oxide to Cu(I) displayed an interesting additional coordination mode. While one nitrogen of each triazolyl ring participates in $\kappa^3\text{-N}_3$ binding, one of the adjacent nitrogen atoms forms a bridge to a second Cu center, leading to a dimeric complex (Figure 1). Considering the relatively small calculated differences between this ligand type and its pyrazolyl analogue, the potential of this ring position seems to be the main differentiator. In the pyrazolyl based systems, it can be substituted to introduce steric bulk around the metal center, whereas it can function as secondary binding site in the triazolyl based ligands.

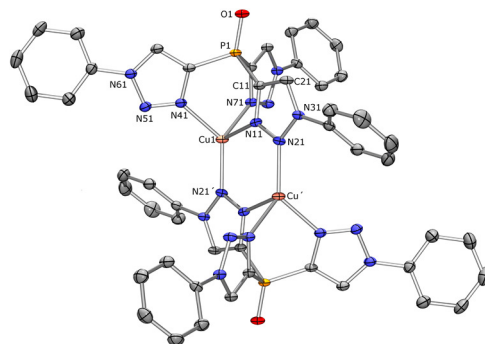
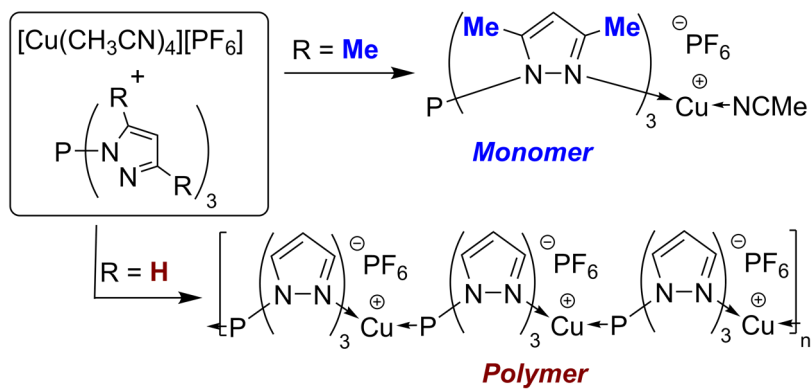


Figure 1. Crystal structure of the dimeric Cu-tris(triazolyl)phosphine oxide complex that was obtained in chapter 3.

Chapter 4 describes the unoxidized tris(pyrazolyl)phosphines that were prepared in modest to excellent yields via a similar protocol as used in chapter 2 for the corresponding phosphine oxides. Based on the NMR spectra of selenides of these phosphines, the P-apex was found to be a rather weak electron donor.

Complexation of the substituted versions of tris(pyrazolyl)phosphine to Cu(I) yields 1 : 1 complexes, regardless of the amount of ligand used. Similar to the phosphine oxide complex, the remaining acetonitrile ligand can be exchanged for triphenylphosphine as demonstrated for the tris(3,5-dimethylpyrazolyl)phosphine Cu(I) complex. A subsequent crystal structure determination showed the expected connectivity to the metal: A κ^3 -N₃ bound tris(pyrazolyl)phosphine, together with a P-bound triphenylphosphine.

The unsubstituted ligand displays a different coordination behavior. When reacted in a 2 : 1 ratio, both ligands coordinate to the metal. One ligand binds in the common κ^3 -N₃ fashion, while the second completes the coordination sphere by acting a phosphine donor. A 1 : 1 stoichiometry leads to a one-dimensional polymer in which Cu ions are linked together by ligands that combine both the N₃ and P coordination modes (Scheme 2). The structure of this complex has been established by ³¹P solid state NMR, X-ray crystallography, and by the isolation of derivatives upon addition of an extra equivalent of tris(pyrazolyl)phosphine or an equivalent of triphenylphosphine.



Scheme 2. The different fates of substituted and unsubstituted tris(pyrazolyl)phosphine when complexed in a 1 : 1 ratio to Cu(I).