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Preface

Ligand development is at the heart of organometallic and coordination chemistry. The proper choice of ligands has allowed great advances in molecular transition metal chemistry, including homogenous catalysis and applications in optoelectronics, medicine and as precursors in material science. This thesis is our contribution to this ever-expanding toolbox for coordination chemistry, focusing on neutral, phosphine centered analogues of the widely used tris(pyrazolyl)borate ligands. These tris(pyrazolyl)- and tris(triazolyl)phosphines have been successfully prepared and applied as ligands for Cu(I). Our findings and results are reported here.

In chapter 1 the occurrence of tris(azolyl)phosphines is reviewed, focusing on their preparation and their use as ligands for transition metal complexes. The majority of reports is on the tris(imidazolyl)phosphines that have been applied in a number of enzyme mimetic studies and have been tested as ligands for several catalytic processes. Tris(pyrazolyl)phosphines and tris(1,2,3-triazolyl)phosphines have also been applied as metal supporting ligands, but to a lesser extent, which is why we focused on these two ligand classes in this thesis. In contrast, tris(1,2,4-triazolyl)phosphine oxide nearly exclusively has been used as reagent to convert functional groups of bioorganic molecules.

In chapter 2, the preparation of a series of tris(pyrazolyl)phosphine oxides is reported, together with their complexation to Cu(I) and subsequent ligand exchange studies. It was found that for these compounds, substituents at the 5-position enhance ligand stability by blocking the facile hydrolysis of the P-N bonds found for non-substituted ligands. The initially introduced acetonitrile ligand that completes the coordination sphere around the Cu center is readily replaced by triphenylphosphine. Although ligand exchange reactions with CO proceed much more sluggishly, the products obtained allow an assessment of the electron density available in the complex. This analysis shows the tris(pyrazolyl)phosphine oxides to decrease the electron density relative to tris(pyrazolyl)methane supported complexes.

In chapter 3, the comparison between selected tripodal N₃ ligands is extended computationally. The parent pyrazolyl and 1,2,3-triazolyl based ligands with either a phosphorus or carbon apex have been considered. The geometry of the unbound ligands and of their Cu(I) complexes has been studied, together with the energetics of both complexation and ligand exchange to arrive at the Cu-CO complexes. Calculating the vibrational frequencies of these species gives insight into the electronic properties that the ligands impose on the complexes.

Finally, in chapter 4, we explore the properties of tris(pyrazolyl)phosphines in Cu(I) coordination chemistry. A series of ligands with 3-substituents with a range of steric requirements has been prepared and complexed to Cu(I). The donor capabilities of the vacant P-apices have been assessed and were used to prepare a one-dimensional coordination polymer.