The manipulation of metal-metal bonding distances by variation of the size of N-substituents on PNP ligand systems

C. van Staden, H.G. Visser, M. Schutte-Smith

University of the Free State, Bloemfontein, South Africa

christovanstaden00@gmail.com

The interaction between metals in homo- and heterometallic complexes are known as metallophilic interactions. The photoluminescent study of metal complexes with metallophilic interactions produces promising results. [1, 2] Bis(diphenylphosphine)amine (PNP) ligand systems were identified as the ligands of choice because they consist of a parameter for the measurement of its steric bulk on the nitrogen atom. The parameter is known as the Tolman based cone angle as introduced by Cloete *et al.* [3] The influence of the steric bulk on the catalytic activity of the ligand was investigated by Cloete *et al.* [3] A wide range of steric substituents are identified and a collection of dimeric metal complexes synthesised. The photoluminescent properties of these complexes were compared as a parameter for the metallophilic interactions present in the complexes. The influence of solvents is investigated and solid state luminescence is used for the luminescence study. The formation of exciplexes are possible with a semi-coordination between the solvent and the complex. [4] The solvent interaction and quenching effects correlate to photoluminescent data from other studies. [5, 6] The structural aspects are compared using single crystal X-ray diffraction analysis and DFT calculations. This makes the comparison between theoretical and experimental data possible. The manipulation of the metal to metal distance is observed and a correlation drawn between the metal to metal distance and the steric bulk of the ligand system. Figure 1 illustrates two metal complexes with metallophilic interactions.

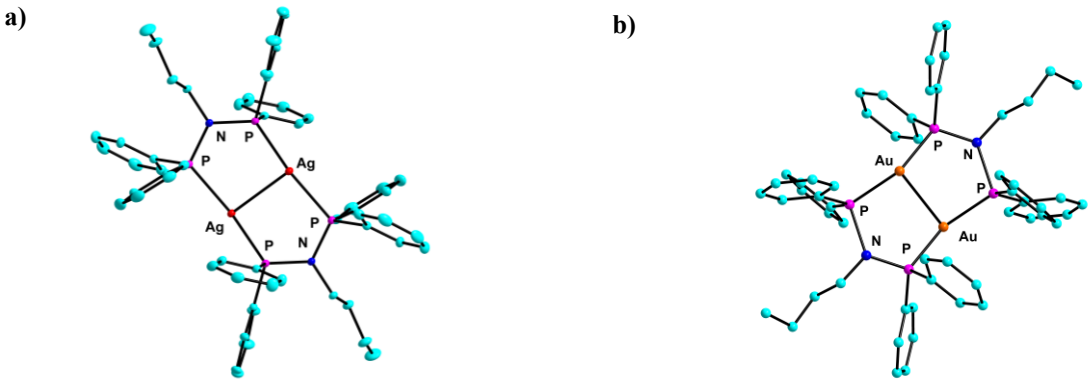

Figure 1: Illustration of the crystal structures of a dimeric **a**) silver and **b**) gold complex with metallophilic interations.

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