Primary amine pendant arm cross-bridged tetraazamacrocycles and their transition metal complexes

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Cross-bridged tetraazamacrocycles form extremely stable transition metal complexes due to their topological constraint and rigidity. These stable complexes can be used in applications where complex stability is desirable, such as oxidation catalysis or biomedical applications. We have previously described a number of mono-pendant armed cross-bridged tetraazamacrocycles where the pendant arm can function to change the electronic properties of the metal complex with respect to the parent ligand, or provide a site for linking of the ligand to other moieties. Such pendant arms have included carboxylate, amide, pyridine, and phenolic donors. This work details our progress in the synthesis of cross-bridged tetraazamacrocycles having a single primary amine pendant arm. Several related routes involving Phthalimide protection/deprotection have been attempted with mixed results. A route involving the reduction of a primary amide has proven to be more reliable and will be detailed. Multiple transition metal complexes of the resulting ligands have been synthesized and their characterization will also be outlined.

Method #1: Bromoethyl Phthalimide Route

Reference: Hermann, Inorg. Chem. 2017, 56, 13337-13348