Abstract

Frustrated Lewis pairs (FLPs) are sterically precluded combinations of Lewis acids and Lewis bases that are unable to form a Lewis adduct. The FLPs presented in this thesis are targeted towards the development of novel hydrogenation methods for the reductive coupling of CO_2 to amines. Firstly, we present FLPs based on R_3SnX Lewis acids (R = alkyl and X = Cl^-, OTf^-, NTf_2^- or ClO_4^-) for the reductive coupling of CO_2 and amines in the presence of H_2 gas for the synthesis of N-formamides. R_3SnX Lewis acids with larger R groups (e.g. cyclohexyl) and weakly coordinating X group (e.g. OTf^-, NTf_2^- or ClO_4^-) presented larger activity than Lewis acids with smaller R substituents (e.g. isopropyl) and strongly coordinating X group (Cl^-). Among the tested catalysts, Cy_3SnOTf demonstrated the highest activity (TON > 300), stability in the presence of water and selectivity for CO_2 reduction. In turn, a variety of functionalised amines was selectively N-formylated without the concomitant reduction of unsaturated groups present in the substrate molecule. Secondly, we present the solvent assisted synthesis of azoles from *ortho*-substituted anilines, CO_2 and H_2 gas. Amine based solvents are N-formylated via the R_3SnX FLP catalysed N-formylation reaction with CO_2 and H_2. Subsequent R_3SnX Lewis acid catalysed transfer of the formyl group to the otherwise unreactive *ortho*-substituted aniline substrate and cyclization of N-formylated intermediate yields the desired azole product. Solvent mixtures of polyethyleneimine and N-methylmorpholine (1:1) were the most effective and allowed for a 70-times increase in catalytic activity of the system compared to simple R_3SnX Lewis acid promoted N-formylations in sulfolane. The recorded activities are in line with the best transition metal catalysts for the reaction. Consequently, various functionalised *ortho*-substituted anilines were successfully transformed into the corresponding azoles at low catalyst loadings (<1 mol%). Thirdly, we replaced the tetravalent R_3SnX Lewis acids by hexa-coordinate tin (IV) salen and salophen complexes, which allows for greater variation in steric and electronic properties of the Lewis acids and their FLPs. The complexes can activate H_2 gas at room temperature and act as hydrogenation catalysts at temperatures >150 °C. The novel LA hydrogenated various imine substrates and acted as CO_2 hydrogenation catalysts in the N-formylation reaction. Lastly, the operating temperatures and pressures of the N-formylations were reduced using transfer hydrogenations with γ-terpinene instead of H_2. The reactions are catalysed by metal triflates and proceed at 130°C and 4 bar of CO2 instead of 180°C and >100 bar with H_2 and R_3SnX based FLPs.

Keywords: FLPs, Lewis acids, Lewis bases, catalysis, carbon dioxide, hydrogenation, N-formylamines,