Iridium – Bismuth Carbonyl Cluster Complexes: Precursors for New Selective Oxidation Catalysts

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Abstract

Selective oxidations are one of the widely discussed and extensively studied catalytic reactions in recent decades which provides promising pathways for the production of higher value oxyfunctionalized chemicals starting from cheaper and more abundant starting materials like light alkanes (ex: synthesis of acrylic acid from propane). Adams et al. have previously shown the merits of using Bi in ReBi\textsuperscript{1} and FeBi\textsuperscript{2} catalysts known to catalyze ammoxidation reactions. Therefore ideas were raised in Adams group in 2012 to synthesize novel Iridium-Bismuth carbonyl cluster complexes, as an attempt to address the major challenges in selective oxidation, namely the C-H bond activation and selective incorporation of oxygen into these activated C-H bonds, where iridium is known to catalyze C-H activation and bismuth is known to catalyze selective incorporation of oxygen.

The first known IrBi carbonyl cluster complex, Ir\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{3}-Bi) dates back to 1982, which was synthesized by a German group of scientists. Recently we have synthesized a series of new IrBi carbonyl clusters (Ir\textsubscript{3}(CO)\textsubscript{6}(GePh\textsubscript{3})\textsubscript{3}(μ\textsubscript{3}-Bi)(μ\textsubscript{3}-H)\textsubscript{3} , Ir\textsubscript{3}(CO)\textsubscript{6}(GePh\textsubscript{2})\textsubscript{3}(μ\textsubscript{3}-Bi) etc. ) by adding Ge and Sn ligands on to Ir\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{3}-Bi) which are well known to be valuable modifiers for heterogeneous transition metal catalysts\textsuperscript{3}. Few other high nuclear IrBi clusters are synthesized and one of them (Ir\textsubscript{5}(μ\textsubscript{3}-Bi\textsubscript{2})(μ\textsubscript{4}-Bi)(CO)\textsubscript{10} ) and Ir\textsubscript{5}(CO)\textsubscript{6}(μ\textsubscript{3}-Bi) have being tested as catalyst precursors for the conversion of 3-picoline to nicotinonitrile and have shown promising results\textsuperscript{4}. The first IrAuBi cluster, Ir\textsubscript{3}(CO)\textsubscript{6}(Ph)(μ\textsubscript{3}-Bi)[μ-Au(NHC)]\textsuperscript{5} with the shortest Au-Bi bond is synthesized as an attempt to expand IrBi bimetallics into trimetallics. This complex was further reacted with Ph\textsubscript{3}SnH to obtain IrAuBiSn tetrametallics. The DFT studies will further explain the nature of Au-Bi bonding. We have further synthesized a IrRuBi\textsuperscript{6} carbonyl cluster and also a very interesting IrBi metallaheterocycle [Ir\textsubscript{4}(CO)\textsubscript{10}(μ-BiPh\textsubscript{2})(μ-H)]\textsubscript{2}. The synthesis, chemistry, structural characterizations, DFT studies and catalytic studies of IrBi carbonyl cluster complexes will be discussed further highlighting the importance of IrBi carbonyl cluster complexes as viable catalyst precursors for selective oxidation reactions.
References:

5. Adams, R. D. and Elpitiya, G. Submitted
6. Adams, R.D. and Elpitiya, G. Submitted