

Diphosphinoamine (PNP) Ligand effects in homogeneous catalysis and radiopharmaceuticals.

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It is without any doubt that throughout Inorganic and Organometallic chemistry, phosphine (mono, bi and tridentate) ligands are the most extensively utilized ligands. This is largely because of the versatility nature of such ligands and the easily coordinating ability through the lone pair on the phosphorus atom. Some of the most widely used phosphine ligands includes triphenylphosphine, 1,1-Bis(diphenylphosphino) methane (dppm), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), 1,2-Bis(diphenylphosphino)ethane (dppe) and 1,3,5-triaza-7-phosphaadamantane (PTA) [1].

More recently, attention has been directed towards diphosphinoamine ligands having the P–N–P backbone in view of the fact that the substituents on both the phosphorus and the nitrogen can be readily altered. Moreover, this provides more opportunities for ligand modification through steric and electronic effects alterations [2]. We have recently reported on the systematic manipulation of these PNP ligands and have translated the steric effect on the nitrogen into a steric parameter coined Effective Tolman-based N-substituent steric parameter (θ_{N-sub}) to better understand the overall catalytic effects of catalysts containing these type ligands. Indeed we found that the steric effect on the nitrogen atom has a profound effect on both the catalyst activity and selectivity [3]. Further studies on the effects of different electronic and steric properties on the Phosphorus atom are still being conducted and the results are at the preliminary stage at the moment.

The overarching aim of this project is to illustrate the critical importance of systematic ligand synthesis not just in organometallic chemistry but in other scientific disciplines such as medicinal chemistry, photochemistry and analytical chemistry (separation). Hence, in this project we've expanded the above application of PNP's on catalyst models to the model radiopharmaceutical fac-[M(CO)₃]⁺ synthons (M=Re(I) and ⁹⁹Tc(I)) and the separation of Niobium and Tantalum. These last parts of the project are still in the preliminary phase.

[1] Appleby, T. et al. (2002). *Coord. Chem. Rev.*, 235, 121-140.

[2] Kuhlmann, . et al. (2007). *J. Cat.*, 245, 279.

[3] Cloete, N. et al. (2013). *Inorg. Chem.*, 52, 2268-2270

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