Synopsis

"Diphosphinoamines" with a P-N-P framework are one of the most versatile ligand systems studied in transition metal chemistry. The most attractive feature is the ease with which a variety of ligands can be synthesized by altering the substituents on nitrogen and phosphorus. This results in attendant changes in the P-N-P bond angle and conformation, giving rise to profound changes in steric and electronic properties. Fairly small differences in these ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes.

A large number of transition metal complexes of these ligands have been reported in the literature. But studies on group 11 metals, especially copper(I) complexes of these ligands are few. The present investigation includes three ligands $(PPh_2)_2N(R)$, R = ^{i}Pr (dppipa), Ph (dppan) and H (dppa). A variety of copper(I) complexes of these diphosphinoamine ligands were synthesized in the presence of different anions including non-coordinating ions like BF_4^- and PF_6^-, weakly coordinating ions like ClO_4^-, NO_3^-, SO_4^{2-} and strongly coordinating ions like halides and pseudohalides. Anion orchestrated structural diversity was observed, with the counter anion dictating the mode of binding of the ligand (chelate or bridge) in these cases.

A non-coordinating anion like perchlorate forced the ligand (dppipa) to adopt a chelating mode of binding. The result was a bis chelate monomer with copper in a distorted tetrahedral environment (Figure 1(a)). Ambidentate thiocyanate ion also forced the ligand to chelate with copper(I) and formed a dimeric complex. In case of halide ions, different clusters were isolated depending upon the metal to ligand ratio employed. A ratio of 2:1 resulted in a tetrameric core with two bridging ligands and four μ_2-chloride bridges. With 1:1 or 1:2 ratio, the complex that crystallized over a period of 4-5 days was found to be a trimer with $[Cu_3L_3Cl_2]^+$ core with ligands in the bridging mode. When the same complex was crystallized overnight, a dimeric complex was obtained with one ligand in a bridging mode and the other in a chelating mode (Figure 1(b)). The trimeric and dimeric complexes were found to be interconvertible. Variable temperature $^{31}P\{^1H\}$-NMR experiments revealed the instability of the chelated structures resulting in a dynamic equilibrium involving non-chelated structures in solution.

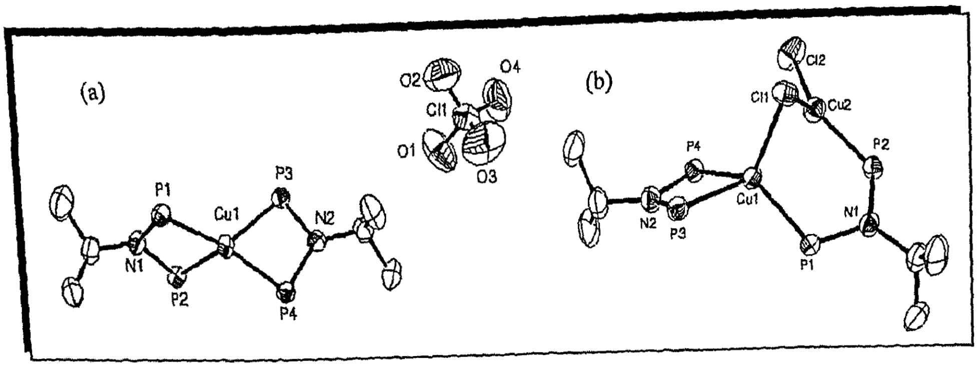
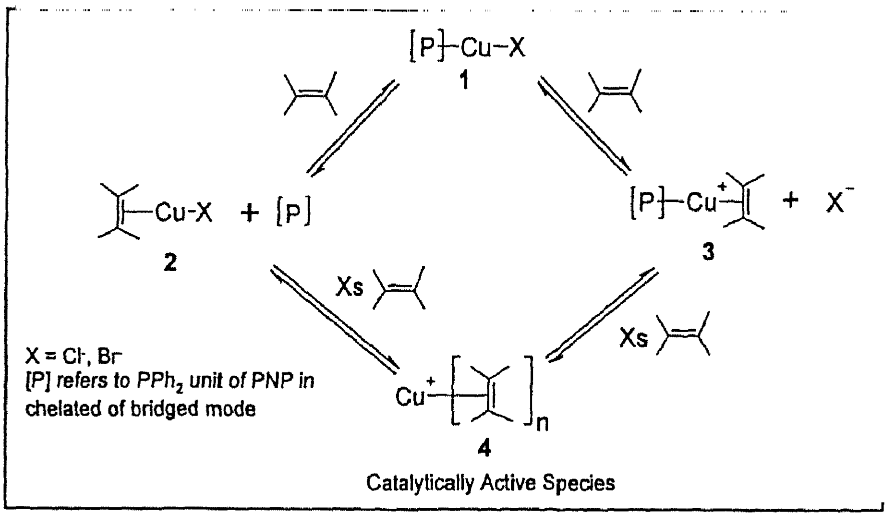


Figure 1. ORTEP Plots of (a) $[Cu(dppipa)_2]ClO_4$ and (b) $[Cu_2(dppipa)_2Cl_2]$ at 50% Thermal Ellipsoid Probability. Phenyl Rings on Phosphorus and Hydrogen atoms Omitted for Clarity.

The dppan ligand gave isostructural complexes in the case of perhchlorate and the halide ions. On the other hand, the thiocyanate ion yielded a monomer with one ligand in a chelating mode and the other in a η^1 mode. The thiocyanate ion was bound to the copper only through its nitrogen end. Subtle differences were found in the solution behavior exhibited by complexes of these two ligand systems. These complexes were found to be more stable in solution as compared to the analogous dppipa complexes.

Two copper(I) complexes of dppa ligand were synthesized in the presence of either ClO_4^- and BF_4^-. Both yielded unsymmetrical dimers with two bridging ligands. One copper was found four coordinated and the other three coordinated. The former has one copper bound to two phosphorus and one nitrogen from acetonitrile and the other has two phosphorus, one water oxygen and one η^1-bound ClO_4^-. On the other hand, the latter complex has one copper with two phosphorus and one nitrogen (CH_3CN) and the other copper, apart from two phosphorus has two acetonitrile nitrogen atoms bound. The former has a Cu-Cu distance of 2.7483(9) Å (within the van der Waal's radii sum of two copper atoms, 2.8 Å). On the other hand, the BF_4^- complex has a longer Cu-Cu distance (2.8217(8) Å). Correlation between short Cu-Cu distances and unsymmetrical structures was established by a Cambridge Structural Database analysis.

Further, these Cu(I) complexes were tested for catalytic cyclopropanation of olefins using ethyl diazoacetate (EDA) as the precursor. The reactions were carried out in a NMR tube with $CDCl_3$ as the solvent at 40°C and the decay of EDA was monitored at regular time intervals. The substituent on the nitrogen was found to have an influence on the rate of cyclopropanation and the reaction rates were found to be dependent on the copper : phosphine ratio. Complexes with different counter anions gave good yields of the cyclopropane. But the most significant result obtained from comparing the three ligand systems was that the yield of the cyclopropane from styrene (~85%) as well as the *trans* to *cis* ratio of the cyclopropane (~75:25) was found to be similar. On the other hand, the reactions carried out with cyclohexene, yielded ~77% cyclopropane with *trans* to *cis* ratio of ~76:24. These results show that it is the olefin that plays a role in the catalytically active species and not the phosphine or the counter anion. The catalytically active species is probably an olefin bound copper catalyst (**4**), as the yield of cyclopropane changes only upon changing the olefin (Scheme 1).



Scheme 1. Proposed Mechanism for the Generation of Catalytically Active Species.

Several attempts were made to synthesize a polymerizable diphosphinoamine ligand system including functionalization of *p*-amino acrylate, glycine O-allyl ester and 2-amino-ethyl vinyl ether. The first successful attempt was to form a diphosphinoamine ligand of the vinyl ether. But the polymerization results were not very promising. Subsequently a *p*-vinyl substituted diphosphinoamine ($(CH_2{=}CH\text{-}C_6H_4\text{-}CH_2N(PPh_2)_2$; vbzpnp) was synthesized and polymerized using n-BuLi to form a soluble polymer. Complexation with copper(I) perchlorate yielded an insoluble networked complex. The solid state $^{31}P\{^1H\}$-MAS NMR of the polymer gave a broad singlet at 85.5 ppm and a band at 1098 cm^{-1} for the perchlorate ion in the IR spectrum. Catalytic cyclopropanation of styrene was attempted with this heterogeneous catalyst. Three cycles were carried out giving almost similar selectivity (*trans* : *cis* cyclopropane-76:24) but a marginally lower yield of the cyclopropane in subsequent cycles due to leaching of metal from the polymer.

Cobalt mediated "Pauson Khand" reactions were also attempted using these diphosphinoamine systems. The stoichiometric reactions was tried with $[Co_2(CO)_4(PA)(dppipa)]$ (**1**) (PA = Phenylacetylene) yielding 66% of the cyclopentenone. The reaction with $[Co_2(CO)_4(PA)(vbzpnp)]$ (**2**) gave 50% yield. The cobalt-loaded polymer was synthesized and characterized by IR spectroscopy. The catalytic reactions (1 atm. CO, THF reflux with 1:10 ratio of cobalt precursor and alkyne, alkene in excess) with **1** and the polymer were not successful due to decomposition of the catalyst under the reaction conditions.

The nuclearity of copper(I) complexes were determined by the anions used. The importance of weak interactions between anions and their role in structure determination was probed. This study is relevant in the light of recent reports regarding anions engaged in π-interactions in electron deficient ring systems. The importance of the heteroatoms and frequency of anion-phenyl contacts in complexes was probed through a critical Cambridge Structural Database (CSD) study. Supramolecular interactions of nitrogen heterocyclics: pyridine, bipyridine, phenanthroline and terpyridine with anions: NO_3^-, ClO_4^-, BF_4^- and PF_6^- were analyzed. A significant number of short contacts (within the sum of van der Waal's radii of the interacting atoms) are shown to exist in heterocyclic ring systems. The results are compared with interactions of anions with a phenyl ring in order to evaluate the effect of a heteroatom. The most electron deficient center is the carbon atom α to the heteroatom and shows the maximum number of short contacts. In general, most contacts are weak C-H···O and C-H···F hydrogen bonds, but there are also some observations of O/F···π interactions, which are virtually absent for simple phenyl groups.