

## Synthesis and Structural Characterization of Metal Complexes Bearing New N-and P-Donor Ligands with Catalysis and DFT Studies

The aim of this research is to develop a convenient and large scale synthesis of a new type of multidentate N-and P-donor ligands for transition metal complexes and catalysis studies. In 2019, the convenient single step synthetic method for the hexahydropyrimidine-based pincer type procarbene ligand (PCP) and its carbene complexes were reported from our laboratory. This investigation focuses on the synthesis of yet another new hexahydropyrimidine-based pincer procarbene (NCN) ligand containing two pyrazole arms to understand its chemistry relative to the PCP ligand. In addition, the synthesis of new P3 and P4 phosphorus ligands and their metal complexes for catalytic applications are investigated.

A new type of hexahydropyrimidine-based bis(pyrazole) ligand, 1,3-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)hexahydropyrimidine **1** was readily synthesized in one pot method from the reaction of 1,3-diaminopropane, 3,5-dimethylpyrazole and paraformaldehyde. The reaction of **1** with one equivalent of N-bromosuccinimide in DME gave 1,3-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide, **2**; the same reaction in the presence of 4 equivalents of NBS yielded 1,3-bis((4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)methyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide, **4**. Treatment of **2** with  $\text{NH}_4\text{PF}_6$  gave its  $\text{PF}_6^-$  salt, 1,3-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)tetrahydropyrimidin-1-ium hexafluorophosphate, **3**. Conversely, its  $\text{BF}_4^-$  salt, 1,3-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)tetrahydro-pyrimidin-1-ium tetrafluoroborate was obtained directly from the reaction of  $\text{AgBF}_4$  with **1**. Treatment of **3** with palladium(II) precursors gave two monomeric complexes  $[\text{Pd}(\text{OAc})_2\{\text{CH}(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^2\text{-N,N}\}]\text{PF}_6$  and  $[\text{PdCl}_2\{\text{CH}(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^2\text{-N,N}\}]\text{PF}_6$ . Conversely, **1** reacts with Pd(II) source to give the dimeric complex  $[\text{PdCl}_2\{\mu\text{-C}_4\text{H}_8\text{N}_2(\text{CH}_2\text{Me}_2\text{pz})_2-\kappa^2\text{-N,N}\}]_2$ . The dimer complex is fluxional and its low temperature NMR study attributed to the fast interconversion between its conformers. DFT calculations suggested the formation of 6-membered chelate ring and the binuclear complex in terms of 5-and 6-membered ring strain energies.

Another new type of bis(pyrazole) and bis(imidazole) ligands, 1,3-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)imidazolidine and 1,3-bis((1H-imidazol-1-yl)methyl)hexahydropyrimidine were synthesized. The reaction of **1** with Cu(I) salts gave  $[\text{Cu}_2(\mu\text{-I})_2\{\text{CH}_2(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^4\text{-N,N,N,N}\}]$  and  $[\text{Cu}\{\text{CH}_2(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^3\text{-N,N,N}\}]\text{BF}_4$ . Both the complexes are fluxional, as shown by their  $^1\text{H}$  NMR spectra. Hence, their dynamic behaviors were studied by variable temperature NMR method. However, the reaction of ligand **2** and CuI yielded polymeric complex  $[\text{Cu}_2(\mu^2\text{-I})_3\{\text{CH}(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^2\text{-N,N}\}]_n$ . Whereas, the reactions between **3** and Cu(I) halide salts afforded  $[\text{Cu}_3(\mu^3\text{-I})_2(\mu^2\text{-I})_2\{\text{CH}(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^2\text{-N,N}\}]$  and  $[\text{Cu}(\mu\text{-Br})\{\text{CH}(\text{NCH}_2\text{Me}_2\text{pz})_2(\text{CH}_2)_3-\kappa^2\text{-N,N}\}]_2(\text{PF}_6)_2$ . In addition, the reaction between **4** with CuI gave a different complex  $[\text{Cu}_2\text{I}_2(\mu^2\text{-I})_2\{\text{CH}(\text{NCH}_2\text{Me}_2\text{Brpz})_2(\text{CH}_2)_3-\kappa^2\text{-N,N}\}]_2$ . All the complexes were structurally characterized by single crystal X-ray diffraction methods.

New phosphonite-diphosphine  $\text{PhP}(\text{OCH}_2\text{PPh}_2)_2$ , **18**, phosphite-triphosphine  $\text{P}(\text{OCH}_2\text{PPh}_2)_3$ , **19**, and dimethylsilane-diphosphine  $(\text{CH}_3)_2\text{Si}(\text{OCH}_2\text{PPh}_2)_2$  ligands were synthesized from  $\text{Ph}_2\text{PCH}_2\text{OH}$ . The reaction between **18** with  $[\text{NiCl}_2(\text{DME})]$  gave  $[\text{NiCl}_2(\mathbf{18}\text{-}\kappa^3\text{P,P,P})]$ . Conversely, **18** reacts with  $[\text{NiCl}_2(\text{DME})]$  and  $\text{NH}_4\text{PF}_6$  to yield  $[\text{NiCl}(\mathbf{18}\text{-}\kappa^3\text{P,P,P})][\text{PF}_6]$ , **22**. The reactions between **1**,  $[\text{NiCl}_2(\text{DME})]$  and  $\text{KPF}_6$  in the presence of RNC (R = Xylyl, *t*Bu and *i*Pr) yielded the five coordinate monocationic  $[\text{NiCl}(\mathbf{18}\text{-}\kappa^3\text{P,P,P})(\text{RNC})][\text{PF}_6]$  (R = Xylyl) and dicationic  $[\text{Ni}(\mathbf{18}\text{-}\kappa^3\text{P,P,P})(\text{RNC})_2][\text{PF}_6]_2$  (R = *t*Bu and *i*Pr) complexes, respectively. The analogous reaction of **19** with  $[\text{NiCl}_2(\text{DME})]$  and  $\text{KPF}_6$  gave  $[\text{NiCl}(\mathbf{19}\text{-}\kappa^4\text{P,P,P,P})][\text{PF}_6]$ . The reaction of **18** with anhydrous cobalt(II) halides afforded  $[\text{CoCl}_2(\mathbf{18}\text{-}\kappa^3\text{P,P,P})]$  and  $[\text{CoBr}_2(\mathbf{18}\text{-}\kappa^3\text{P,P,P})]$ . The *N*-alkylation reactions were performed between primary aryl amines, benzyl and 4-methoxy benzyl alcohols in the presence of 2.5 mol% of **22** and <0.5 mmol of  $\text{KOBU}^t$  in toluene at 140 °C. Its substrate scope includes sterically encumbered, heterocyclic amines and aliphatic alcohol.