

## Abstract

A new class of pyrrole-based diphosphine ligands, 2,5-bis(diphenylphosphinomethyl)pyrrole (PNP pincer) and 1,9-bis(diphenylphosphinomethyl)diphenyldipyrrolylmethane (PNNP), were readily synthesized by a new method involving two and three steps from pyrrole in excellent yields, respectively. The oxidation reactions of the PNP and PNNP ligands with H<sub>2</sub>O<sub>2</sub> and S<sub>8</sub> afforded the corresponding phosphoryl and thiophosphoryl compounds.

The reaction of the PNP-pincer ligand with [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] in the presence and absence of Et<sub>3</sub>N, gave the mononuclear [PdCl{C<sub>4</sub>H<sub>2</sub>N-2,5-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-κ<sup>3</sup>PNP}] and the binuclear [Pd<sub>2</sub>Cl<sub>4</sub>{μ-C<sub>4</sub>H<sub>3</sub>N-2,5-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-κ<sup>2</sup>PP}]<sub>2</sub> complexes, respectively. The binuclear complex, [Pd<sub>2</sub>{μ-C<sub>4</sub>H<sub>2</sub>N-2,5-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-κ<sup>2</sup>PN,κ<sup>1</sup>P}]<sub>2</sub> was isolated when the PNP ligand was treated with [Pd<sub>2</sub>(dba)<sub>3</sub>]·CHCl<sub>3</sub>. This dimer exhibits two weak interactions between the two palladium and the phosphorus atoms which were analyzed by DFT calculation. The analogous reaction of the PNNP ligand with [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] gave the mononuclear complex, [PdCl<sub>2</sub>{Ph<sub>2</sub>C(C<sub>4</sub>H<sub>2</sub>NH)<sub>2</sub>-1,9-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-P,P}]. In addition, as a preliminary study, complex [PdCl(PNP)] was found to be a very good catalyst for the Suzuki coupling reactions in water. The reaction of the PNP-pincer ligand with Ni(II) precursors such as [Ni(OAc)<sub>2</sub>] or [NiCl<sub>2</sub>(DME)] gave the mononuclear complexes formulated as [NiX{C<sub>4</sub>H<sub>2</sub>N-2,5-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-κ<sup>3</sup>PNP}], [X = OAc, Cl, Br, and I] in very good yields. Further, treatment of this Ni(II) complex (X = Cl or Br) with MeLi afforded the binuclear Ni(I) complex, [Ni<sub>2</sub>{μ-C<sub>4</sub>H<sub>2</sub>N-2,5-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-κ<sup>2</sup>PN,κ<sup>1</sup>P}]<sub>2</sub>. Interestingly, treatment of these Ni(II) complexes with AgBF<sub>4</sub> yielded the binuclear Ag(I) complexes, [Ag<sub>2</sub>(μ-X)(μ-PNP-P,P)]BF<sub>4</sub> via an unusual transmetallation reaction of Ni(II) by Ag(I).

The reaction of the PNP-pincer ligand with an equimolar quantity of CuX (X = Cl, Br, and I) afforded the binuclear copper(I) complexes [Cu(μ-X)(μ-PNP-P,P)]<sub>2</sub> in very good yields (87–90%). Conversely, the analogous reaction between the PNNP ligand and CuX (X = Cl, Br, and I) yielded the mononuclear Cu(I) complexes [CuX(PNNP-P,P)] in very good yields (~88%), in which the diphosphine ligand is chelated to the copper metal. Interestingly, when this reaction was carried out with 1:2 mole ratio of ligand:metal, the cubane-like tetranuclear Cu(I) complex, [Cu<sub>4</sub>I<sub>4</sub>{μ-Ph<sub>2</sub>C(C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>-1,9-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-P,P}]<sub>2</sub> was isolated in 68% yield. In addition, the reaction between the PNNP ligand and CuCl in the presence of one equivalent of 1,10-phenanthroline monohydrate and NaBF<sub>4</sub> afforded a novel ionic binuclear Cu(I) complex, [Cu<sub>2</sub>(μ-

$X)(\mu\text{-PNNP-}P,P)(\text{NN})_2\text{]BF}_4$  where NN = 1,10-phenanthroline in 57% yield. Additionally, the reaction of the PNP-pincer ligand with  $\text{Ag}_2\text{O}$  in dichloromethane afforded  $[\text{Ag}(\mu\text{-Cl})(\mu\text{-PNP-}P,P)]_2$  which is similar to Cu(I) dimer complex.

The reactions of  $[\text{Cp}^*\text{CrCl}_2]_2$  with different mole ratios of the 3,5-dimethylpyrazolate ligand gave the mono- and dinuclear Cr(III) complexes containing bridging and terminally coordinated pyrazolate ligand. The structures of the most of the complexes were determined by X-ray diffraction method and are further supported by spectroscopic methods.