

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 H₂O₂ and S₈ afforded the corresponding phosphoryl and thiophosphoryl compounds.

The reaction of the PNP-pincer ligand with [PdCl₂(PhCN)₂] in the presence and absence of Et₃N, gave the mononuclear [PdCl{C₄H₂N-2,5-(CH₂PPh₂)₂-κ³PNP}] and the binuclear [Pd₂Cl₄{μ-C₄H₃N-2,5-(CH₂PPh₂)₂-κ²PP}]₂ complexes, respectively. The binuclear complex, [Pd₂{μ-C₄H₂N-2,5-(CH₂PPh₂)₂-κ²PN,κ¹P}]₂ was isolated when the PNP ligand was treated with [Pd₂(dba)₃]·CHCl₃. 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 [PdCl₂(PhCN)₂] gave the mononuclear complex, [PdCl₂{Ph₂C(C₄H₂NH)₂-1,9-(CH₂PPh₂)₂-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)₂] or [NiCl₂(DME)] gave the mononuclear complexes formulated as [NiX{C₄H₂N-2,5-(CH₂PPh₂)₂-κ³PNP}], [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, [Ni₂{μ-C₄H₂N-2,5-(CH₂PPh₂)₂-κ²PN,κ¹P}]₂. Interestingly, treatment of these Ni(II) complexes with AgBF₄ yielded the binuclear Ag(I) complexes, [Ag₂(μ-X)(μ-PNP-P,P)]BF₄ 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)]₂ 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, [Cu₄I₄{μ-Ph₂C(C₄H₃N)₂-1,9-(CH₂PPh₂)₂-P,P}]₂ 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 NaBF₄ afforded a novel ionic binuclear Cu(I) complex, [Cu₂(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 Ag_2O 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.