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Synthesis and structural characterization of copper(I) halide complexes containing bis(azol-1-yl)methane derived bisphosphines

Sajad A. Bhat [a], Joel T. Mague [b], Maravanji S. Balakrishna [a,*]

[a] Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
[b] Department of Chemistry, Tulane University, New Orleans, LA 70118, United States

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ABSTRACT

The copper(I) complexes containing bisphosphines such as bis(2-diphenylphosphinoimidazol-1-yl)methane (**1**), bis(5-diphenylphosphinopyrazol-1-yl)methane (**2**) and bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (**3**) have been synthesized. The reaction of **1** with CuX (X = Cl, I) afforded homoleptic dinuclear complexes $[Cu_2(\mu\text{-}X)_2\{CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2\}_2\text{-}\kappa^2P,P]$ (X = Cl, **4**; I, **6**). However, a mononuclear complex $[CuBr(CH_3CN)\{CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2\}\text{-}\kappa^2P,P]$ (**5**) was isolated in the reaction of **1** with CuBr. The reaction of **2** with CuX (X = Cl, Br, I) also produced dinuclear complexes $[Cu_2(\mu\text{-}X)_2\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_2\text{-}\kappa^2P,P]$ (X = Cl, **7**; Br, **8**; I, **9**). The reaction of **3** with CuCl yielded a novel 1D coordination polymer $[Cu_2(\mu\text{-}Cl)_2\{CH_2(1,2,4\text{-}C_2HN_3PPh_2)_2\}\text{-}\kappa^2P,N]_n$ (**10**), whereas homoleptic dinuclear complexes $[Cu_2(\mu\text{-}X)_2\{CH_2(1,2,4\text{-}C_2HN_3PPh_2)_2\}_2\text{-}\kappa^2P,P]$ (X = Br, **11**; I, **12**) were obtained in the reactions of **3** with CuX (X = Br, I). Bisphosphines **1** and **2** showed bidentate (κ^2P,P) chelating mode of coordination, whereas **3** has adopted bidentate (κ^2P,N) chelating mode of coordination in **10**. The crystal structures of **4**–**7** and **10**–**12** have been established by single crystal X-ray crystallography.

1. Introduction

Copper(I) complexes have attracted considerable attention over the years because of their structural diversities, rich photophysical properties [1–16], and catalytic applications [17–22]. Several mono- to tetranuclear copper(I) complexes of nitrogen heterocycles and phosphines have been reported in the literature; their formation often depends on the nature of the ligands used, metal to ligand ratio and several other factors including the solvents employed and the reaction conditions [23–30]. Many of the di- and tetranuclear copper(I) complexes have been found to be emissive [31–36]. The most commonly employed bisphosphines in copper(I) complexes are bis [2-(diphenylphosphino)phenyl] ether (POP), 1,2-bis(diphenylphosphino)-benzene (dppb), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)-propane (dppp) and 1,l′-bis(dipheny1phosphino)ferrocene (dppf) (Chart 1). Tertiary phosphines containing imidazole, 1,2,3- and 1,2,4-triazoyl moieties represent an intriguing class of hetero-donor ligands (Chart 1), as their reactions with CuX have produced several interesting copper(I) complexes with remarkable photophysical properties [16,37].

Given the numerous reports dealing with the diversity of copper(I) complexes of various mono- and bisphosphines, copper(I) complexes of bisphosphines anchored on five membered nitrogen heterocycles with methylene bridge have not been reported. In this context and as a part of our continued interest on transition metal chemistry of phosphorus based ligands and their applications [38], herein we report the synthesis and structural characterization of various copper(I) complexes of bis(2-diphenylphosphinoimidazol-1-yl)methane (**1**), bis(5-diphenylphosphinopyrazol-1-yl)methane (**2**) and bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (**3**).

2. Results and discussion

2.1. Synthesis of bisphosphines

The bisphosphine ligands, bis(2-diphenylphosphinoimidazol-1-yl)methane (**1**), bis(5-diphenylphosphinopyrazol-1-yl)methane (**2**) and bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (**3**) were synthesized according to the reported literature procedures as shown in Scheme 1 [39,40].

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* Corresponding author. Fax: +91 22 5172 3480/2576 7152.
E-mail addresses: krishna@chem.iitb.ac.in, msb_krishna@iitb.ac.in (M.S. Balakrishna).

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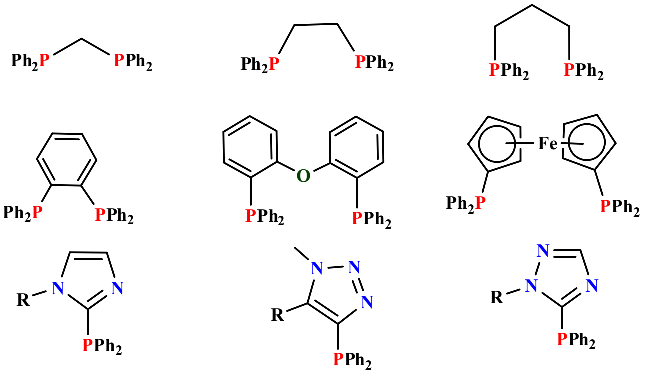
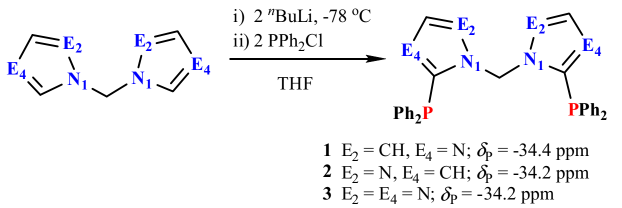
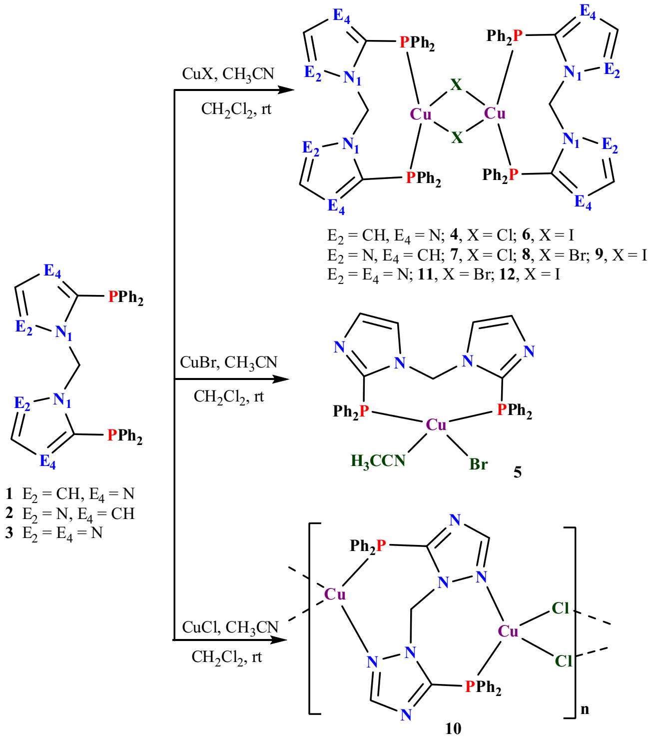


Chart 1. Different phosphine ligands used in copper(I) complexes.



1 E_2 = CH, E_4 = N; δ_P = -34.4 ppm
2 E_2 = N, E_4 = CH; δ_P = -34.2 ppm
3 E_2 = E_4 = N; δ_P = -34.2 ppm

Scheme 1. Synthesis of ligands **1**–**3**.



E_2 = CH, E_4 = N; **4**, X = Cl; **6**, X = I
E_2 = N, E_4 = CH; **7**, X = Cl; **8**, X = Br; **9**, X = I
E_2 = E_4 = N; **11**, X = Br; **12**, X = I

1 E_2 = CH, E_4 = N
2 E_2 = N, E_4 = CH
3 E_2 = E_4 = N

Scheme 2. Copper(I) complexes of bisphosphines **1**–**3**.

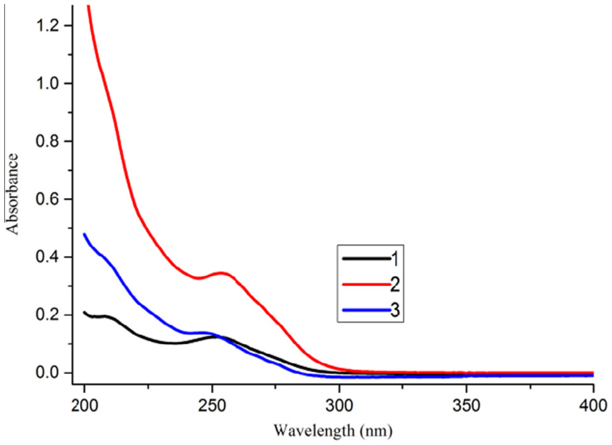


Fig. 1. UV–Vis spectra of ligands **1**–**3**.

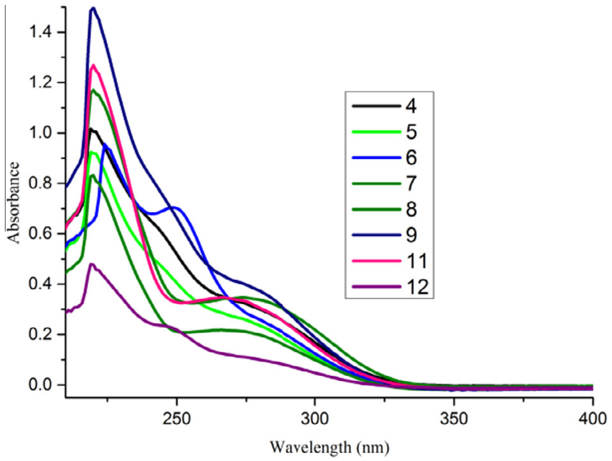


Fig. 2. UV–Vis spectra of complexes **4**–**9**, **11** and **12**.

2.2. Syntheses of copper(I) halide complexes

The reaction of **1** with CuX (X = I, Cl) in 1:1 M ratio afforded dinuclear complexes, $[Cu_2(\mu\text{-}X)_2\{CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2\}_2\text{-}\kappa^2 P,P]$ (X = Cl, **4**; I, **6**) containing Cu_2X_2 rhombic unit with each copper atom coordinated by the ligand in homoleptic chelating ($\kappa^2 P,P$) mode as shown in Scheme 2. The reaction of **1** with CuBr in 1:1 M ratio afforded a mononuclear complex $[CuBr(NCCH_3)\{CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2\}\text{-}\kappa^2 P,P]$ (**5**). Similarly, the reactions of **2** and **3** with CuX (X = I, Br, Cl) in 1:1 M ratio also yielded dinuclear complexes of the type $[Cu_2(\mu\text{-}X)_2\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_2\text{-}\kappa^2 P,P]$ (X = Cl, **7**; Br, **8**; I, **9**) and $[Cu_2(\mu\text{-}X)_2\{CH_2(1,2,4\text{-}C_2HN_3PPh_2)_2\}_2\text{-}\kappa^2 P,P]$ (X = Br, **11**; I, **12**) with rhombic Cu_2X_2 units. In contrast, similar reaction between **3** and CuCl in 1:1 ratio produced a novel 1D coordination polymer $[Cu_2(\mu\text{-}Cl)_2\{CH_2(1,2,4\text{-}C_2HN_3PPh_2)_2\}\text{-}\kappa^2 P,N]_n$ (**10**) with ligand exhibiting heteroleptic chelating ($\kappa^2 P,N$) mode of coordination (Scheme 2). The coordination modes observed in the case of complexes **4**, **6**–**9**, **11** and **12** are routinely adopted by many chelating bisphosphines and N-heteroaromatic ligands [12,26,41]. Surprisingly, the $^{31}P\{^1H\}$ NMR spectra of the complexes **4**–**12** in DMSO-d_6 showed single resonances around −32 ppm and no considerable coordination shifts were observed. In the ^1H NMR spectra of **4**–**12**, the signals corresponding to the CH_2 protons are merged with the aromatic protons. The product formation in case of **2** and **3** was found to be independent of stoichiometry of the reactants as both 1:1 and 1:2 reactions led to the formation of the same product as confirmed from CHN-analysis and mass spectrometry.

2.3. UV–Vis absorption spectroscopy

The absorption spectra of free ligands and their corresponding Cu^I complexes are given in Figs. 1 and 2, respectively. Ligands **1**–**3** contain two types of aromatic groups: a bridging bis(azol-1-yl) methane group and auxiliary phenyl groups on phosphorus atoms.