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Syntheses and Characterization of Phosphorinecopper(I) Halide Complexes

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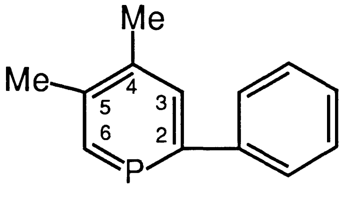
Halogeno(2-phenyl-3,4-dimethylphosphorine)copper(I) complexes were synthesized and characterized by ^{31}P-, ^{13}C-NMR spectroscopy, and X-ray crystallography. It was revealed that the phosphorine coordinates to copper(I) ions as a monodentate ligand and undergoes π-back donation to stabilize Cu-P bonding.

Phosphorines coordinate to transition-metal donating a lone-pair,1) or π-electrons,2) or both simultaneously.3,4) In the case of coordination through the lone-pair, most complexes are organometallic of zero valent metal with phosphorine and additional ligands.5-7) These are very sensitive to air and moisture.8,9) Most complexes synthesized thus far have had CO or diene ligands besides phosphorine on metal centers. Strong π accepting character of the latter two ligands decrease electron density on the central metal so that back bonding. Therefore, we aimed to synthesize complexes of electron rich central metal without CO or diene. Metal complexes with phosphorous donor atom which belongs to aromatic π system should form strong back bonding to phosphorous atom enhancing stability of the ligand against air and/or moisture. This attempt could shed light on the distinct property of metal-phosphorine interaction. We now report syntheses and characterization of copper(I) complexes of 2-phenyl-3,4-dimethylphosphorine (dmppn)10) involving X-ray crystallography.11) These complexes are the first example of the stable complexes with phosphorine as a monodentate ligand.



$Cu^{I}X$(dmppn) (X = Cl (**1**), I (**2**)) were synthesized by mixing $Cu^{I}X$ and dmppn (1:1) in CH_2Cl_2 at room temperature. From the synthetic mixtures above, yellow needle crystals were readily obtained upon addition of hexane. The products were air-stable to allow growing single crystals while the free dmppn is sensitive to the air and/or moisture.

Table 1. ^{31}P- and ^{13}C-NMR data for free ligand and Cu complexes (**1**), (**2**)

sample	$\delta(^{31}P)^{a)}$	$(\Delta\delta)^{c)}$	$\delta(^{13}C)^{b)}$	$(\Delta\delta)^{c)}$		
			C2		C6	
Free dmppn	183.8		168.5		154.8	
Cu(dmppn)Cl (**1**)	149.7	(34.1)	159.3	(9.2)	147.2	(7.6)
Cu(dmppn)I (**2**)	151.0	(32.8)	160.7	(7.8)	149.7	(5.1)

a) Chemical shift in ppm relative to H_3PO_4 (85% aqueous solution). b) Chemical shifts in ppm relative to TMS. c) $\Delta\delta = \delta$(free dmppn) - δ(complex).

Phosphorus 31 resonance for **1** was observed at 149.7 ppm while that for **2** showed at 151.0.[12,13] These observations clearly demonstrate that the phosphorine ring in the copper(I) complexes conserve the aromaticity by comparison with the chemical shifts of metal-bound tertiary phosphines.[14,15] It was noticeable that **1** and **2** showed significant upfield shifts of ^{31}P resonance by 34.1 and 32.8 ppm, respectively, relative to the free dmppn (δ = 183.8 ppm) as shown in Table I indicating that a phosphorine ring undergoes π-back donation from a Cu^I center to stabilize the Cu-P bonding. In addition, in the ^{13}C NMR spectra,[12,13] chemical shifts of adjacent carbon atoms to phosphorus (C2 and C6) also showed upfield shifts in the range of 5-9 ppm as shown in Table I, due to the π-back donation. This is a remarkable feature of dmppn-low valent metal complexes.[1,9]

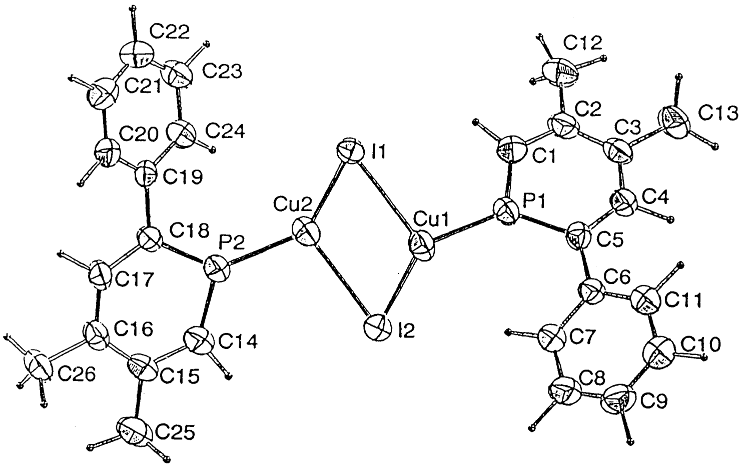


Fig. 1. Structure of fundamental unit, $[Cu(dmppn)I]_2$.

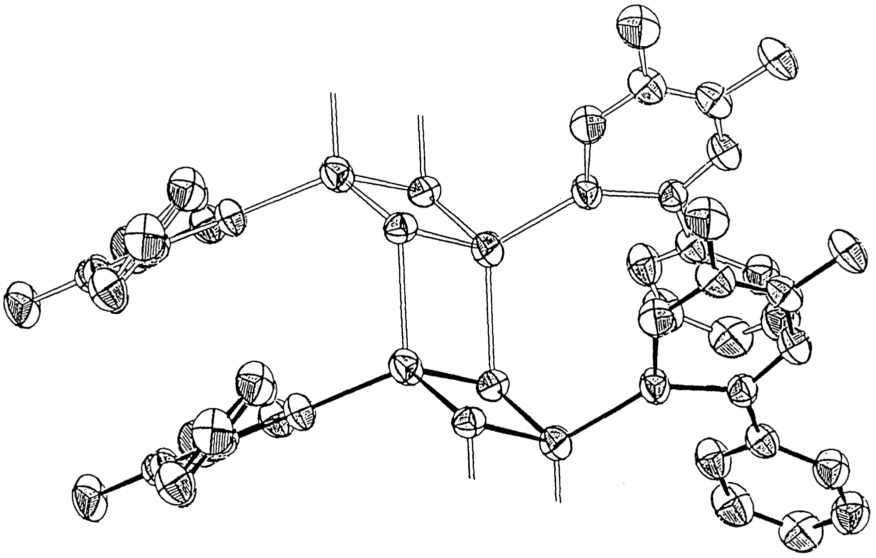


Fig. 2. Infinite stepped straight structure of $[Cu(dmppn)I]_\infty$. Chemical bonds in one binuclear unit are emphasized by colored sticks.

The single crystal of **2** appropriate for X-ray crystallography was obtained as a yellow needle by recrystallization from hexane-CH_2Cl_2 (1:1) mixture. Two units of **2** were placed in the unit cell (Fig. 1). Dmppn was found to be a monodentate ligand and planar structure which suggests the aromaticity of the phosphorine ring is maintained. The fundamental unit is a $[(\mu\text{-I})Cu(dmppn)]_2$ and the iodide binds to another copper center in the corresponding units above and below to form an infinite stepped straight structure as shown in Fig. 2. An analogous structure was reported for [CuCl(py)] complex by White *et al.*[16)]

The copper center of **2** possesses an essentially tetrahedral geometry having one phosphorine and three μ_3-iodides as ligands. As for the copper-phosphorus bond lengths of **2** (2.223(3) Å and 2.224(3) Å), they were found to be shorter than those of $[CuI(PPh_3)]$, $[CuI(PEt_3)]$, and [CuI(dmpp)][17)] in which tertiary phosphines bind to copper(I) ion through only σ-donation of their lone pair. This observation also suggests that the phosphorine coordinates more strongly to the copper center with the aid of π-back donation.

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11) selected crystallographic data and structural parameters for **2** : formula = $C_{26}H_{26}Cu_2I_2P_2$, fw = 781.31, Color of crystal yellow, crystal dimensions 0.1×0.2×0.2 mm^3, crystal system triclinic, space group $P\bar{1}$, temp 293 K, a = 16.082(4) , b = 21.698(4) , c = 4.172(1) Å, α = 101.04(2) , β = 97.38(2) , γ = 68.26(2) deg, V = 1324.7(5) $Å^3$, Z = 2, Dc = 1.959 g cm^{-3}, Do = 1.914 g cm^{-3}, μ(Mo Kα) = 40.496 cm^{-1}, reflections 4535, R = 0.0411, Rw = 0.0481.

12) NMR data for complex **1**: ^{1}H-NMR ($CDCl_3$, TMS) 8.329 (d, J=29 Hz, 1H, 6-H), 7.711 (d, J=11 Hz, 1H, 3-H), 7.20-7.57 (m, 5H, Ph-H), 2.359 (s, 6H, 4- and 5- Me); ^{13}C-NMR ($CDCl_3$, TMS) 137.09 (d, J=13 Hz, 3- phosphorin), 139.09 (d, J=22 Hz, 4- phosphorin), 141.22 (d, J=18 Hz, 5- phosphorin), 149.68 (d, J=12 Hz, 6- phosphorin), 160.71 (d, J=18 Hz, 2- phosphorin); ^{31}P-NMR ($CDCl_3$, 85% H_3PO_4) 151.0 (d, J=17 Hz).

13) NMR data for complex **2**: ^{1}H-NMR ($CDCl_3$, TMS) 8.218 (d, J=28 Hz, 1H, 6-H), 7.794 (d, J=13 Hz, 1H, 3-H), 7.20-7.57 (m, 5H, Ph-H), 2.357 (s, 3H, 4-Me), 2.367 (s, 3H, 5-Me); ^{13}C-NMR ($CDCl_3$, TMS) 137.57 (d, J=13 Hz, 3- phosphorin), 139.15 (d, J=23 Hz, 4- phosphorin), 140.85 (d, J=16 Hz, 5- phosphorin), 147.21 (s, 6- phosphorin), 159.25 (s, 2- phosphorin); ^{31}P-NMR ($CDCl_3$, 85% H_3PO_4) 149.7 (d, J=17 Hz).

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