

Preparation and Catalysis of a Tri-coordinated Copper(I) Complex with Bulky P~N Ligand

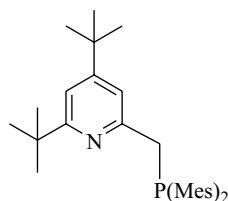
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Coordination of a bulky pyridinyl-phosphine (P~N) ligand toward CuBr was investigated. However, this P~N donor behaves as a monodentate *via* the coordination of phosphine to form a bromide bridged dimeric [(P~N)Cu(μ-Br)₂Cu(P~N)], which was characterized by spectral and crystal structural analysis. It appeared that the "PCu(μ-Br)₂CuP" unit is planar with a short distance between Cu...Cu' [2.7585(9) Å]. The catalytic activity on Sonogashira coupling of phenylacetylene with aryl halides was studied.

Keywords: Bulky phosphine; Copper; Catalysis; Coupling reaction.

INTRODUCTION

Construction of carbon-carbon or carbon-heteroatom bonds involving copper complexes as catalysts is an important research area in organic synthesis.^{1,2} Thus study of coordination of copper ions toward various ligands has received much attention. In this context, there is a considerable interest in the design and synthesis of phosphine-copper complexes owing to their associated catalytic activity in organic transformations.^{1,2} Compared with the extensive information on four-coordinate copper-phosphine complexes, two- or three-coordinate species have been less reported.³⁻²⁴ It is known that both the halides and phosphine ligands influence the coordination sphere of metal centers and the bulky tertiary phosphines generally direct the formation of two- or three-coordinate copper complexes.¹²⁻²⁴ In our recent work, we have synthesized the bulky phosphine-pyridinyl (P~N) ligand and studied its coordination chemistry toward palladium(II) ions.²⁵ Here the preparation of copper(I) complex containing this bulky P~N ligand and its catalytic activity on C-C bond formation will be presented.



P~N (Mes = 2,4,6-Me₃C₆H₂-)

RESULTS AND DISCUSSION

Copper complexes

The desired ligand P~N was prepared according to our previously reported method.²⁵ Ligand substitution reaction of P~N with CuBr in dichloromethane at room temperature readily provided the corresponding copper complex **1** in a quantitative yield. Upon recrystallization, the copper(I) complex yielded colorless crystalline solids. The ³¹P nmr shift of the complex in CDCl₃ appeared at -16 ppm (relative to 85% H₃PO₄), which shifted up-field from the ligand itself. The coordination chemical shift (δ_{complex} - δ_{free ligand}) is 1 ppm, which is quite similar to those of phosphine-copper(I) complexes.³⁻²⁴ The significant difference of ¹H nmr spectra between **1** and P~N comes from the shift of the methylene unit adjacent to the phosphorus. The signal corresponding to those hydrogens showed at 4.21 ppm with phosphorus coupling J_{P-H} = 6.5 Hz, down-field shift from the free ligand (3.99 ppm). Although the shifts of the pyridinyl-carbon in ¹³C nmr changed slightly from the free ligand, it could not be determined whether the pyridinyl-nitrogen donor is coordinated to the metal center. The detailed structure of **1** was confirmed by its X-ray crystal analysis.

Single crystals of **1** were obtained by slow diffusion of ether into a dichloromethane solution at room temperature under nitrogen atmosphere. Fig. 1 displays the ORTEP diagram of the copper complex (drawings with 30% probability ellipsoids). It appears that this copper complex con-

Dedicated to Professor Ching-Erh Lin on the Occasion of his 66th Birthday and his Retirement from National Taiwan University

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tains one centrosymmetric dimer of the form $[(\text{P}\sim\text{N})\text{Cu}(\mu\text{-Br})_2\text{Cu}(\text{P}\sim\text{N})]$. It is quite clear that the pyridinyl-nitrogen does not coordinate to the metal center, i.e. the $\text{P}\sim\text{N}$ behaves as a monodentate. It is known that the bulky monodentate phosphine would coordinate with copper halide in a 2:1 fashion to form a monomeric species $[(\text{R}_3\text{P})_2\text{CuX}]$, where the metal center is bound by two phosphorus donors. However, the nitrogen donor in this $\text{P}\sim\text{N}$ ligand could not coordinate to the metal center, presumably due to the hindrance of the tertiary butyl group next to the nitrogen center.²⁵

Selected bond distances collected of **1** and related complexes **2a-f** are summarized in Table 1 for comparison.^{12a,12e,14,18} The bond distances around the metal center lie in the normal range of the closely related complexes (Table 1). The “ $\text{PCu}(\mu\text{-Br})_2\text{CuP}$ ” unit is essentially planar, resembling those complexes containing $[\text{P}_2\text{Cu}_2\text{X}_2]$ moiety. However, the distance $\text{Cu}\cdots\text{Cu}'$ [2.7585(9) Å] is significantly shorter, while the distance of $\text{Br}\cdots\text{Br}'$ [3.9963(9) Å] is longer than any other related species as indicated in Table 1. This observation is quite similar to that of iodide-bridged species **2f** [$\text{Cu}\cdots\text{Cu}'$ 2.728(3) Å; $\text{I}\cdots\text{I}'$ 4.361(3) Å], indicating a weak interaction between copper centers.^{12e}

This copper complex in a chloroform or dichloromethane solution remains in a dimeric form as evidenced by ^1H and ^{31}P nmr spectroscopy. However, the dimeric form was readily decomposed by the addition of extra phosphine ligands to the solution and led to a mixture of various substituted products, some of which we were not able to characterize.

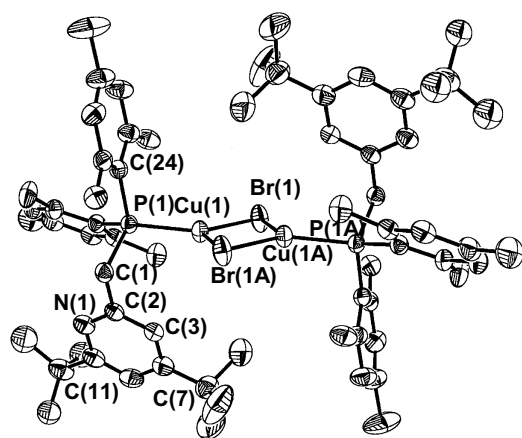
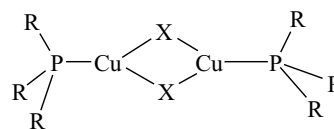


Fig. 1. ORTEP plot of **1**. (Labeling for aromatic rings is omitted for clear view). $\text{P}(1)\text{-C}(1)$ 1.858(3) Å; $\text{Cu}(1)\cdots\text{N}(1)$ 4.692(4) Å; $\text{P}(1)\cdots\text{N}(1)$ 3.494(4) Å; $\text{C}(24)\text{-P}(1)\text{-Cu}(1)$ 103.6(1)°; $\text{C}(15)\text{-P}(1)\text{-Cu}(1)$ 127.1(1)°; $\text{C}(15)\text{-P}(1)\text{-Cu}(1)$ 127.1(1)°.



- 2a** $\text{R}_3 = (o\text{-Tol})_3$, $\text{X} = \text{Br}$
2b $\text{R}_3 = (o\text{-Anis})_3$, $\text{X} = \text{Br}$
2c $\text{R}_3 = \text{Ph}_2(\text{Mes})$, $\text{X} = \text{Br}$
2d $\text{R}_3 = \text{Ph}(\text{Mes})_2$, $\text{X} = \text{Br}$
2e $\text{R}_3 = (\text{Cy})_3$, $\text{X} = \text{Br}$
2f $\text{R}_3 = \text{Ph}(\text{Mes})_2$, $\text{X} = \text{I}$

Catalysis

The catalytic activity of **1** on Sonogashira coupling was investigated. Coupling reaction of aryl or vinyl iodides with terminal alkyne is a useful tool to yield arylalkynes and enynes, and the recent development in this catalysis is to use copper complexes as catalyst instead of the expensive palladium complexes.^{2,26,27} Thus the catalytic activity of copper complex **1** was examined. In a typical experiment for the coupling reaction, aryl halides, phenylacetylene, and potassium carbonate in 1:1.5:1 ratio were added to a freshly distilled toluene solution, followed by the addition of the catalyst. The mixture was heated in an oil bath at 110 °C for 24 h. After the reaction was stopped, the reaction mixture was diluted with dichloromethane and washed with 5 N HCl and water. The organic portion was extracted, concentrated, and characterized by GC and ^1H NMR spectroscopy. All of the results are summarized in Table 2.

In all instances, catalysis proceeded smoothly without using palladium complexes as co-catalysts. It appears that the extra phosphine ligand is required for better conversion. Without an extra phosphine ligand, complex **1** did not catalyze the coupling reaction (entries 1, 13). By comparison of entry 13 to the others, it is quite obvious that the presence of the $\text{P}\sim\text{N}$ ligand readily promotes the catalysis. Complex **1** did catalyze the coupling of phenylacetylene with aryl iodides and activated aryl bromide to provide the corresponding diarylacetylene in reasonable yields except for *o*-iodotoluene; this was presumably due to the steric reason. Typically, the reaction of phenyl iodide with phenylacetylene catalyzed by **1** in the presence of triphenylphosphine provided the diphenylacetylene in 72% yield. As for the phenyl chloride (entry 11) or deactivated aryl bromides (entries 7, 8), the copper complex did not show good activity in the catalysis. It is noticed that the *in situ* generation of copper species for the catalysis is also applied for the coupling reactions (entry 14).



Table 1. Selected bond distances (Å) and angles (deg) of **1** and **2a-f** for comparison

| Complex | 1 (X = Br) | 2a (X = Br) ^a | 2b (X = Br) ^b | 2c (X = Br) ^c | 2d (X = Br) ^c | 2e (X = Br) ^d | 2f (X = I) ^c |
|----------|-------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--------------------------------|
| Cu-X | 2.3506(6) | 2.414(1) | 2.356(1) | 2.397(2) | 2.393(2) | 2.409(1) | 2.554(3) |
| Cu-X' | 2.5032(6) | 2.431(1) | 2.541(1) | 2.441(2) | 2.415(2) | 2.430(1) | 2.589(3) |
| Cu-P | 2.2013(9) | 2.208(1) | 2.194(1) | 2.198(3) | 2.197(3) | 2.191(2) | 2.201(4) |
| X...X' | 3.9963(9) | 3.716(1) | 3.807(1) | 3.748(2) | 3.684(2) | 3.717(1) | 4.361(3) |
| Cu...Cu' | 2.7585(9) | 3.109(1) | 3.085(1) | 3.083(2) | 3.052(3) | 3.098(1) | 2.728(3) |
| Cu-X-Cu' | 69.18(2) | 79.83(4) | 78.01(3) | 79.18(6) | 78.80(7) | 79.62(4) | 63.49(7) |
| X-Cu-X' | 110.82(2) | 100.17(3) | 101.99(3) | 100.8(1) | 100.1(1) | 100.38(5) | 116.0(1) |
| P-Cu-X | 141.46(3) | 130.00(6) | 141.38(5) | 132.2(1) | 130.9(1) | 132.88(6) | 128.3(1) |
| P-Cu-X' | 106.86(3) | 129.64(6) | 116.53(5) | 127.0(1) | 128.7(1) | 126.74(6) | 114.9(1) |

^a Reference 12d. ^b Reference 14b. ^c Reference 12a. ^d Reference 12e.

Table 2. Results of coupling reactions catalyzed by copper complexes^a

| Entry | Catalyst | PPh ₃ ^b | Ar-X | Product | Yield ^c |
|-------|-------------------|-------------------------------|--|--|--------------------|
| 1 | 1 | 0 | C ₆ H ₅ I | C ₆ H ₅ C≡CC ₆ H ₅ | trace |
| 2 | 1 | 0.1 | C ₆ H ₅ I | C ₆ H ₅ C≡CC ₆ H ₅ | 34% |
| 3 | 1 | 0.2 | C ₆ H ₅ I | C ₆ H ₅ C≡CC ₆ H ₅ | 72% |
| 4 | 1 | 0.2 | <i>p</i> -CH ₃ C ₆ H ₄ I | <i>p</i> -CH ₃ C ₆ H ₄ C≡CC ₆ H ₅ | 65% |
| 5 | 1 | 0.2 | <i>o</i> -CH ₃ C ₆ H ₄ I | <i>o</i> -CH ₃ C ₆ H ₄ C≡CC ₆ H ₅ | 22% |
| 6 | 1 | 0.2 | C ₆ H ₅ Br | C ₆ H ₅ C≡CC ₆ H ₅ | 63% |
| 7 | 1 | 0.2 | <i>p</i> -MeOC ₆ H ₄ Br | <i>p</i> -MeOC ₆ H ₄ C≡CC ₆ H ₅ | 19% ^d |
| 8 | 1 | 0.2 | <i>p</i> -MeC ₆ H ₄ Br | <i>p</i> -MeC ₆ H ₄ C≡CC ₆ H ₅ | 22% ^d |
| 9 | 1 | 0.2 | <i>p</i> -CH ₃ COC ₆ H ₄ Br | <i>p</i> -CH ₃ COC ₆ H ₄ C≡CC ₆ H ₅ | 65% ^d |
| 10 | 1 | 0.2 | C ₆ H ₅ Cl | C ₆ H ₅ C≡CC ₆ H ₅ | 20% |
| 11 | CuCl | 0.2 | C ₆ H ₅ I | C ₆ H ₅ C≡CC ₆ H ₅ | 47% |
| 12 | CuCl + P~N | 0 | C ₆ H ₅ I | C ₆ H ₅ C≡CC ₆ H ₅ | trace |
| 13 | CuCl + P~N | 0.1 | C ₆ H ₅ I | C ₆ H ₅ C≡CC ₆ H ₅ | 71% ^e |

^a Phenylacetylene (0.137 mL, 1.25 mmol), aryl halide (1 mmol), K₂CO₃ (0.18 g, 1 mmol) and catalyst (0.1 mmol) in toluene (10 mL) was heated to reflux for 24 h under nitrogen atmosphere. ^b mmol of triphenylphosphine. ^c GC yield. ^d nmr yield. ^e Isolated yield.

SUMMARY

Complexation of the bulky **P~N** ligand with copper bromide readily formed a bromide bridged dimeric complex **1**. The bulky environment around the nitrogen donor prevents its coordination toward metal center, i.e. the **P~N** ligand acts as a monodentate. This copper complex shows the catalytic activity on the coupling of acetylene with aryl halides, which provides a method leading the Sonogashira coupling products without using palladium complexes.

EXPERIMENTAL

General Information

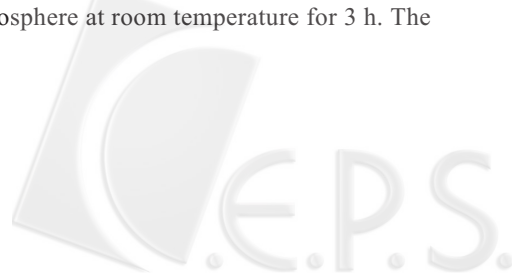
All reaction, manipulation, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran

was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was dried with CaH₂ and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated. Ligand **P~N** was prepared according to a published procedure.²⁵

Nuclear magnetic resonance spectra were recorded in CDCl₃ on either a Bruker AM-300 or AVANCE-400 spectrometer. Chemical shifts are given in parts per million relative to Me₄S for ¹H and relative 85% H₃PO₄ for ³¹P NMR. Infrared spectra were measured on a Perkin-Elmer 983G spectrometer (Series-II) as KBr pellets, unless otherwise noted.

Complex 1

A mixture of CuBr (60 mg, 0.42 mmol) and **P~N** ligand (200 mg, 0.42 mmol) in dichloromethane (10 mL) was stirred under nitrogen atmosphere at room temperature for 3 h. The



reaction solution was evaporated to a volume of about 2 mL. Upon addition of ether, the desired complex was precipitated as white solids (0.25 g, 97%). Recrystallization from dichloromethane/ether gave complex **1** as colorless single crystals. ^1H NMR (CDCl_3 , 400 MHz): δ 7.07 (s, 2H, py- H_5), 6.74 (s, 2H, py- H_3), 6.71 (d, $J = 3.0$ Hz, 8H, Ar- H), 4.21 (d, $J_{\text{P-H}} = 6.5$ Hz, 4H, CH_2), 2.21 (s, 24H, Ar- CH_3), 2.18 (s, 12H, Ar- CH_3), 1.25 (s, 18H, CH_3), 1.09 (s, 18H, $t\text{-Bu}$); ^{31}P NMR (CDCl_3 , 161.9 MHz): δ -16; ^{13}C NMR (CDCl_3 , 100 MHz): δ 169.0, 160.5, 153.6, 141.4 (d, $J = 9.7$ Hz), 139.5, 130.7 (d, $J = 6.8$ Hz), 126.4 (d, $J = 33.0$ Hz), 119.4, 114.7, 39.0 (d, $J = 16$ Hz), 37.5, 34.7, 30.4, 23.9, 23.8, 20.8. Anal. Calcd. for $\text{C}_{64}\text{H}_{88}\text{N}_2\text{P}_2\text{Br}_2\text{Cu}_2$: C, 62.28; H, 7.19; N, 2.27. Found: C, 61.90; H, 7.14; N, 2.29.

Catalysis

A mixture of phenylacetylene (0.137 mL, 1.25 mmol), aryl halide (1 mmol), K_2CO_3 (0.18 g, 1 mmol), and catalyst (0.1 mmol) in toluene (10 mL) was heated to reflux for 24 h under nitrogen atmosphere. Upon concentration, the reaction mixture was analyzed by ^1H nmr and GC. In some cases, the products were isolated by column chromatography. Results are summarized in Table 2.

X-ray Crystallographic Analysis

Crystal suitable for X-ray determination was obtained for **1** by re-crystallization at room temperature. Cell parameters were determined by a Siemens SMART CCD diffractometer. Crystal data of the complex X: $\text{C}_{32}\text{H}_{44}\text{BrCuNP}$, $F_w = 617.10$, monoclinic, $\text{P}2_1/\text{n}$, $a = 13.1390(2)$ Å, $b = 15.0160(2)$ Å, $c = 17.1110(2)$ Å, $\alpha = 90^\circ$, $\beta = 105.272(1)^\circ$, $\gamma = 90^\circ$, $V = 3256.70(8)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.259$ Mg/m³, $F(000) = 1288$, $0.30 \times 0.25 \times 0.20$ mm, 2θ range = $2.21\text{--}27.49^\circ$, 7460 independent refln. ($R_{\text{int}} = 0.0520$) out of 36271 refln collected, Full-matrix least square on F^2 , $R1 = 0.592$, $wR2 = 0.1553$ [$I > 2(I)$], Goodness-of-fit on F^2 1.066. Other crystallographic data have been deposited with the Cambridge Crystallographic Data Center: CCDC-236306 for **1**. Copies of this information can be obtained free of charge and by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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