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Role of substituents present in bidentate ligand frame of Cu(I) catalysts on Sonogashira cross coupling reactions

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Keywords Bidentate ligands; Cu(I) complexes; DFT studies; Sonogashira coupling; Single X- ray crystal.

Abstract

Cu(I) catalysts {[Cu(L¹⁻⁴)Cl(PPh₃)] where L¹⁻⁴ = condensed product of 2-(1phenylhydrazinyl)-pyridine with different benzaldehydes} were synthesized, characterized by ¹H, ³¹P NMR, UV-Vis and IR techniques. Complex **2** structure was authenticated by single crystal X-ray method. Different electron donating and withdrawing substituents are present in the ligand frame of Cu(I) catalysts and their role on Sonogashira reaction was investigated. The efficiency order of catalysts for the coupling reaction was found to be 2>1>3>4, clearly indicated the role of substituents present in the ligand frame was useful to effectively catalyze the Sonogashira reaction. The products were characterized using ¹H and ¹³C NMR.

Introduction

Carbon-carbon bond formation using transition metal complexes received considerable current attention and was developed as a resourceful device for the synthesis of important molecules utilised in the pharmaceutical and agriculture industries. The reaction between sp²-carbon of alkyl halides and sp- carbon of terminal alkynes was examined by Sonogashira, Heck and Cassar back in the year 1975. [1-3] Heck and Cassar utilised palladium transition metal to couple sp²-carbon of haloarenes and sp-carbon of terminal ethynes whereas Sonogashira involved both palladium and copper metal based catalyst to couple haloarenes and terminal ethynes. Sonogashira cross coupling reaction mainly requires base, Pd as

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catalyst and CuI as co-catalyst. [4-8] 1-10 mol% of palladium catalyst generally consumed for Sonogashira reaction. As Pd metal is very costly so its usage at higher gage in industries is circumscribed.[9] However, among all transition metals copper was found to be best choice for such reactions as Cu metal is cheap, easily available and biologically relevant. [14] In 1964, Weingarten and other researchers, published that if copper salts have good solubility at moderate temperature, output of the reaction will be high. [10-15] Several additives were utilized in the coupling reactions so as to enrich the output of the reaction. [16-22] Varous reports in the literature described Sonogashira reaction catalysed by copper based catalyst supported by different bidentate ligands depicted in Scheme 1.



Scheme 1. Ligands used in the literature.

The C-C coupling reactions are performed using different catalytic systems. In 2001, Venkataraman and coworkers, reported coupling of haloarenes and terminal alkynes using 1, 10 phenanthroline ligand. The reaction was catalyzed by $[Cu(phen)(PPh_3)Br]$ catalyst in presence of K₂CO₃ and toluene solvent. [23] Guo et al. utilized ethylene diamine as a ligand and CuI for the Sonogashira reactions. [24] Fuo and his coworkers developed global friendly method for Sonogashira reactions using CuBr, 1,10-phenanthroline as a ligand, TBAB as phase transfer catalyst. [25] Li's group used DABCO (1,4-Diazabicyclo[2.2.2]octane) as a ligand in combination with CuI, Cs₂CO₃ to perform coupling reaction between terminal phenylethynes and haloarenes.[26] Coupling reaction between terminal ethynes and alkyl

Journal Pre-proot

halides was also achieved by Sekar and his group employing N,N'-dibenzyl BINAM and CuI as a catalyst. [27] Bolm's group performed Sonogashira coupling reaction in presence of dioxane solvent and Cs₂CO₃ base using [Cu(DMEDA)₂]Cl₂.H₂O as a catalyst. [28] Various researchers have utilised different ligands such as triphenylphosphine [23, 29-30], 1,3-diphenylpropane-1,3-dione [31], rac-BINOL [32], N, N-dimethylglycine [33] with Cu(I) metal salts to perform coupling reactions.

To our best knowledge, a single report by Venkataraman and co-workers depicted the formation of Cu(I) complex which was derived from 1,10 phenanthroline ligand and utilised 10 mol% of catalyst to perform Sonogashira reaction. [23] Bolm and coworkers clearly mentioned that electron donating group containing complex are more stable compared to electron withdrawing group. The electron donating group containing complex increase the reactivity of coupling reactions by stabilizing intermediate species.[34] Inspired from literature, we synthesized Cu(I) complexes{ $[Cu(L^{1-4})PPh_3Cl]$, where L are bidentate ligands} from the bidentate Schiff bases which contains electron donating and withdrawing groups at benzaldehyde part shown in Scheme 2. All mentioned complexes were well characterized by different spectral techniques and utilised for Sonogashira coupling reactions. Most of the research groups performed the reaction with 10 mol% of catalyst whereas 8 mol% of catalyst is utilised in the present work. Electron donating and withdrawing substituents present in ligand frame of Cu(I) complexes effect the rate of reaction. The order of efficiency of catalysts for the coupling reaction was found to be 2>1>3>4. This is due to stabilisation of intermediate species more by electron donating substituents present in ligand frame of Cu(I) catalysts compared to withdrawing groups. This order clearly indicated the role of substituents present in the ligand frame was useful to effectively catalyze the Sonogashira coupling reaction. The formation of isolated products were characterized using ${}^{1}\text{H}$ and ${}^{13}\text{C}$ NMR spectral techniques.



Scheme 2: Cu(I) complexes used in the present work.

Results and Discussion

Syntheses

The bidentate ligands L^1 , L^2 , L^3 , L^4 were formed by treating 2-(1-phenylhydrazinyl)-pyridine [35] with benzaldehyde, 2,2-dimethylaminobenzaldehyde, 4-chloro benzaldehyde, 4-nitro benzaldehyde. The obtained Schiff bases were treated with CuCl in one step and in another step equimolar solution of triphenylphosphine was added and it resulted in formation of yellow green compound. These compounds were recrystallized using dichloromethane.

The structure of complex **2** is displayed in Figure 1. The bond angles and lengths are shown in Table 1. The –NN donor atoms present in bidentate ligand binds to CuCl and on other side phosphorous atom of triphenylphosphine get attached to metal centre offered tetrahedral geometry to complex.



Figure 1. ORTEP diagram of complex 2. Hydrogen atoms are omitted for lucidity.

Bond distance (Å)

Cu(1)-N(1)	2.057(3)	Cu(1)-P(1)	2.2026(10)					
Cu(1)-N(3)	2.199(3)	P(1)-C(1)	1.823(4)					
Cu(1)-Cl(1)	2.2905(11)	P(1)-C(2)	1.829(4)					
N(2)-N(3)	1.406(4)	P(1)-C(3)	1.830(4)					
N(3)-C(4)	1.290(5)	C(4)-C(5)	1.437(5)					
N(4)-C(6)	1.437(6)	N(4)-C(7)	1.450(6)					
N(1)-Cu(1)-N(3)	76.59(12)	N(3)-Cu(1)-P(1)	117.14(8)					
N(1)-Cu(1)-Cl(1)	100.45(9)	N(1)-Cu(1)-P(1)	125.88(9)					
Cl(1)-Cu(1)-P(1)	116.30(4)	C(1)-P(1)-Cu(1)	115.35(13)					

Table 1. Bond lengths (Å) and angles (°) of complex 2.

The crystal evidences and structural factors related to complex 2 is prescribed in Table S3. The crystal structure of complex 2 comprised of one copper metal centre attached to one pyridine nitrogen (N1), one imine nitrogen (N3), one phosphorus atom P(1) of triphenylphosphine and one chlorine (C11) atom. All donor atoms attached to central metal offered tetrahedral geometry to the complex.

Electronic properties

The ¹H and ¹³C NMR of ligands ($L^{1}-L^{4}$) were recorded in CDCl₃ solvent. Cu(I) complexes are diamagnetic as these contains d¹⁰ configuration. The ¹H NMR spectra of all four complexes (1-4) were taken in deuterated DMSO solvent and their related NMR plots are placed in supporting file. Crystal structure of complex 2 clearly showed that the complexes consist of one phosphine group which can give ³¹P NMR. So, ³¹P NMR plot for PPh₃ molecule attached to metal centre is located in supporting file. The IR spectra was collected between 400-4000 cm⁻¹ range for all four ligands and their complexes placed in supporting information. The UV-Visible spectra of all mentioned ligands and their complexes were done in acetonitrile solvent. The UV-Visible plots and the molar absorption coefficient values of ligands as well as complexes is given in Figures S17-S18 and Table S2 of supporting file. The ESI-MS spectra of all complexes were taken in acetonitrile solvent and the relevant plots of complexes **1-4** are given in supplementary file (Figure S72-S75).

Theoretical calculations

All the theoretical data correlated to complexes (1-4) are depicted in the Figure S71 and Table S4 of supplementary file.

Catalytic studies

Sonogashira coupling was done using Cu(I) catalyst. To carry out the coupling reaction, Scheme 3 was followed. Catalyst and K_2CO_3 were dissolved in toluene solvent. Substituted phenylacetylenes and the haloarenes was poured to above solution. Now, the solution was heated under nitrogen environment for 20 h at 110°C temperature



Scheme 3. Schematic drawing of Sonogashira reaction using catalyst 1-4.

Sonogashira coupling reaction was carried out using CuCl metal salt. When catalyst was replaced by CuCl metal salt for coupling of iodobenzene and phenylacetylene in presence of K_2CO_3 and toluene at 110°C, no reaction was observed.

Catalyst effect was studied for Sonogashira reaction. Optimisation was done with all the complexes and it was observed that **2** complex is more effective compared to other complexes and the isolated yields obtained for all four complexes is depicted in Figure 2.



Figure 2. Effect of catalyst (1-4) on coupling of iodobenzene and phenylacetylene.

Solvents and bases effect were studied using complex 2 shown in Figures 3 and 4. Reactions were carried out in different solvents and bases. Using K_2CO_3 , toluene as a base and solvent, isolated yields for desired product is high compared to other solvents and bases.



Figure 3. Effect of solvents during coupling of iodobenzene and phenylacetylene using catalyst 2.



Figure 4. Effect of bases during coupling of iodobenzene and phenylacetylene using catalyst **2**.



Figure 5 Effect of catalyst 2 loading on Sonogashira coupling reaction.

Different mol% of catalyst **2** such as 2, 4, 6 and 8 mol% were employed to study the reactivity of Sonogashira coupling reaction. The obtained % yield with each mol% is shown in Figure 5. The yield increases with increase in mol% of catalyst **2**. With 2, 4, 6 and 8 mol% of catalyst **2**, % yield are 19%, 43%, 59% and 85%. Maximum yield was obtained when 8 mol% of catalyst was used. We also examined the catalytic activity of other copper based catalyst in this reaction. When Cu(I) complex having 1,10 phenanthroline ligand i,e. [Cu(phen)(PPh₃)Cl] [36] was employed for the coupling of iodobenzene and phenylacetylene under optimized reaction conditions, 58% yield was obtained. Maximum amount of coupled product was gained in 20h, when 8 mol% of catalyst was employed during the reaction. Sonogashira reaction was studied with different substituents of phenylacetylene and haloarenes. The attained product was characterized using ¹H and ¹³C NMR spectral studies. The NMR plots and the spectral data of the desired products are deposited in the supporting file. The isolated yields obtained with different substituents of phenylacetylene and aryl halides consuming catalyst **2** are shown in Table 2.

During the reaction electron donating groups present in the metal complex will help in stabilization of Cu(III) intermediate shown in the mechanism. The lone pair of $-NMe_2$ group can interacts with p orbitals of benzene ring that further donates its electron to p orbital of - imine group due to which electron donating tendency of ligand increases and form stable Cu(III) intermediate during progress of the reaction, but such type of interactions are not possible in case of electron withdrawing groups. That's why isolated yields obtained for all the complexes follows the order 2>1>3>4. In complex 2, the electron donating power of – NMe₂ is more than –H, Cl, NO₂. That's why ended up with better isolated yields. The reason behind it is stabilization of Cu(III) intermediate during the mechanism.

S.No	Phenylacetylenes	Haloarenes	Products	% Yield ^a
1.	И———И		(P1)	85
2.	И———И		(P2)	92
3.	М———н	I-OCH3	(P3) OCH3	83
4.	Кн		(P4) - NO ₂	87
5.	Кн		$(P5) \qquad \qquad$	79
6.	И———н		(P6)	86
7.	—	I	(P7)	83
8.			(P8)	81
9.	н		(P9)	73
10.	нн		(P10)	86
11.	н———н		(P11)	69
12.			(P12)	82
13.	н		(P13)	70
14.	н		(P14)	79
	н			

Table 2: Reactions of phenylacetylenes with haloarenes using catalyst 2.



Reaction conditions: Phenylacetylenes (2.5 mmol), Haloarenes (2.0 mmol), catalyst (8 mol%), base (2.0 mmol), Toulene. Temperature (110° C) under inert atmosphere for 20h. (^a) represents the isolated yields.

2.5 Mechanistic Pathway



Figure 6. Proposed mechanism for Sonogashira coupling. [34]

Mechanistic pathway for Sonogashira coupling reaction is given in Figure 6. In the first step of mechanism, base deprotonated the terminal alkyne. The Cu(I) metal complex bound to deprotonated phenylacetylene and gave rise to (b) step. In the next step, alkyl halide attached to (b) intermediate and gave rise to (c) step. The oxidation state of Cu(I) altered to Cu(III). At last, reductive elimination occurred and formed desired products.

Conclusions

To study a new methodology for Sonogashira coupling reaction, four new mononuclear copper complexes were synthesized and characterized. These complexes have different substituents on the ligand frame. Molecular structure of representative complex 2 was determined by single crystal X-ray diffraction. These complexes were utilised as catalysts for Sonogashira coupling reactions. The order of efficiency of catalysts for the coupling reaction was found to be 2>1>3>4. This order clearly indicated -NMe₂ group present in the ligand frame was useful to effectively catalyze the Sonogashira coupling reaction.

Experimental Section

Materials and Measurements

The quality of all chemicals were of high standard. The solvents utilized during reactions were purified by distillation. Reagents such as substituted benzaldehydes, CuCl, triphenylphosphine were consumed as obtained.

Methods and instrumentation

IR spectra were analysed using KBr pellets with Thermo Nikolet Nexus FT-IR spectrometer. The UV-Vis spectra were obtained from Thermo Scientific UV-Visible spectrophotometer. ¹H, ¹³C and ³¹P NMR spectral data were collected by Jeol, 400 MHz spectrometer using deuterated solvents. All synthesis was done at room temperature and the catalytic reactions were performed under inert atmosphere at 110°C. ESI-MS spectra of all **1-4** compounds were taken using Brüker microTOF-Q II mass spectrometer.

Syntheses of ligands

The bidentate ligands L^1 , L^2 , L^3 , L^4 were produced by the reaction of 2-(1-phenylhydrazinyl)-pyridine [35, 37] with benzaldehyde, 2, 2- dimethylaminobenzaldehyde, 4-chloro benzaldehyde, 4-nitro benzaldehyde. The synthesized ligands were given in the scheme 2. The ¹H, ¹³C NMR, IR, UV-Visible plots and their relevant data are placed in the supporting file for all ligands (L^1 - L^4).

Syntheses of metal complexes: $[Cu(L^{1-4})Cl(PPh_3)]$ complexes were prepared using the resulting method given below.

[Cu(L¹)(PPh₃)Cl] (1): L¹ and CuCl was dissolved in acetonitrile and ligand L¹ was poured to metal solution under inert environment. After half an hour of stirring, same equivalent of triphenylphosphine was added to it. The solution was stirred for one day. Yellow colored compound was precipitated out. The compound was recrystallized using dichloromethane. Yield (76%). Theoretical. calcd. for C₃₆H₃₀ClCuN₃P (634.61): C, 68.13; H, 4.76; Cl, 5.59; Cu, 10.01; N, 6.62; P, 4.48. IR (KBr pellet, v_{max} / cm^{-1}): 1590 ($v_{C=N}$), 507, 694, 755(v_{PPh3}). UV-Vis (Acetonitrile; $\lambda max / nm$ (ε , M⁻¹cm⁻¹)): 228(65000), 277(25500), 327(45000). ³¹P NMR (400 MHz, (CD₃)₂SO): δ 30.17 ppm.¹H NMR (400 MHz, (CD₃)₂SO): δ 7.92 (bs, 3H), 7.83-7.80(m, 6H), 7.59-7.39 (m, 21H) ppm. {HRMS: [1-Cl⁻] (C₃₆H₃₀CuN₃P m/z =598.1223)}

[Cu(L²)(PPh₃)Cl] (2): Same procedure was followed as given for complex 1 but L² was used instead of L¹. Yield (74%). Theoretical. calcd. for C₃₈H₃₅ClCuN₄P (677.68): C, 67.35; H, 5.21; Cl, 5.23; Cu, 9.38; N, 8.27; P, 4.57. IR (KBr pellet, v_{max} /cm⁻¹): 1587($v_{C=N}$), 510, 696, 758(v_{PPh3}).UV-Vis (Acetonitrile; λ_{max} /nm (ε, M⁻¹cm⁻¹)): 254(29330), 323(32830), 354(48350). ³¹P NMR (400 MHz, (CD₃)₂SO): δ 30.82 ppm.¹H NMR (400 MHz, (CD₃)₂SO): δ 8.42 (s, 1H), 8.08-7.83(m, 13H), 7.63-7.56 (m, 9H), 7.33 (s, 3H), 7.16 (s, 1H), 6.61(s, 2H), 3.06(s, 6H) ppm. {HRMS: [2-Cl⁻] (C₃₈H₃₅CuN₄P m/z =641.1836)}

[Cu(L³)(PPh₃)Cl] (3): Above procedure was followed but L³ was used instead of L¹. Yield (71%). Theoretical. calcd. for C₃₆H₂₉Cl₂CuN₃P (669.061): C, 66.86; H, 4.85; Cl, 5.33; Cu, 9.56; N, 6.32; O, 2.41; P, 4.67. IR (KBr pellet, $vmax / cm^{-1}$): 1588 ($v_{C=N}$), 508, 694, 752(v_{PPh3}). UV-Vis (Acetonitrile; $\lambda max/nm$ (ε , M⁻¹cm⁻¹)): 231(43000), 274(17500), 333(37600). ³¹P NMR (400 MHz, (CD₃)₂SO): δ 30.97 ppm.¹H NMR (400 MHz, (CD₃)₂SO): δ 7.99 (s, 2H), 7.60-7.41(m, 8H), 7.28-7.19 (m, 16H), 7.05 (d, 2H), 6.25 (bs, 1H) ppm. {HRMS: [**3**-Cl⁻] (C₃₆H₂₉ClCuN₃P m/z =632.1044)}

[Cu(L⁴)(PPh₃)Cl] (4): Same procedure was followed as given for complex 1 but L⁴ was used instead of L¹. Yield (72%). Theoretical. calcd. for C₃₇H₃₂ClCuN₄O₂P (679.61): C, 64.63; H, 4.37; Cl, 10.60; Cu, 9.50; N, 6.28; P, 4.63. IR (KBr pellet, $vmax / cm^{-1}$): 1587 ($v_{C=N}$), 505, 694, 742 (v_{PPh3}). UV-Vis (Acetonitrile; $\lambda max/nm$ (ε , M⁻¹cm⁻¹)): 262(32830), 389(36500). ³¹P NMR (400 MHz, (CD₃)₂SO): δ 30.35 ppm.¹H NMR (400 MHz, (CD₃)₂SO): δ 8.08 (s, 5H), 7.79(s, 2H), 7.67-7.53 (m, 9H), 7.38-7.25 (m, 12H), 7.15-7.11 (m, 1H) ppm. {HRMS: [4-Cl⁻] (C₃₇H₃₂ClCuN₄O₂P m/z =643.1164)}

Single X-ray Crystallography

Crystal of complex 2 was attained by gentle vaporization of dichloromethane solvent. The data was collected on a Bruker Kappa Apex-II CCD diffractometer by using graphite monochromated Mo-K α radiation (λ = 0.71073 Å) at 293 K. The structure was solved using WinGX software. ORTEP structure was attained using MERCURY software.

Catalytic studies

In a round bottom flask, 8% mole percent of catalyst, K_2CO_3 (2.0 mmol), phenylacetylene (2.5 mmol), aryl halide (2.0 mmol), and 20ml toluene was taken. The whole solution was heated at 110-120°C for 20 h under N₂ atmosphere. The solution was cooled to room temperature and filtered to remove insoluble impurities. Filterate was evaporated and the solid was then passed through column. The desired compound was characterized by ¹H and ¹³C NMR.

DFT studies

The DFT studies were performed using Gaussian 03 software. HOMO and LUMO plots were drawn using Chemcraft software. The time dependent DFT studies were performed to analyse the electronic transitions.

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Journal Pre-proo

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Highlights:

- Sonogashira coupling reactions were performed using Cu(I) complexes. •
- All four Cu(I) complexes were supported by bidentate ligands. The ligands contain ٠ electron donating and withdrawing group at the benzaldehyde part.
- The structure of complex 2 was determined by single crystal X-ray technique.
- The electron donating group in the complex helps in stabilization of Cu(III) • intermediate during coupling reaction. The Cu(I) complex having electron donating groups will provide better efficiency of the reaction compared to electron withdrawing groups.
- Catalytic efficiency of complex 2 was found to be the best among the complexes. ٠