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Phosphine ligands stabilized Cu(I) catalysts for carbene insertion

into the N-H bond

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Graphical abstract

 $R \stackrel{H_2}{\stackrel{H_2}}\stackrel{H_1}{\stackrel{H_2}{\stackrel{H_2}}\stackrel{H_1}{\stackrel{H_2}}\stackrel{H_1}{\stackrel{H_1}{\stackrel{H_2}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}\\{H_1}}\stackrel{H_1}{\stackrel{H_1}\\{H_1}}\stackrel{H_1}{\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}}\stackrel{H_1}{\stackrel{H_1}\\{H_1}}\stackrel{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H_1}\\{H$

38 examples

HN

R

Graphical synopsis

Cu(I)-phosphine complexes as catalysts for carbene insertion into the N-H bond of different anilines

Keywords: Cu(I) catalyst, phosphine ligands, carbene, insertion reaction, C-N bond formation.

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Abstract

Phosphine ligands have been successfully used along with Cu(I) for several catalytic reactions, nevertheless these ligands were less explored relatively for carbene involved reactions owing to the formation of carbene-phosphine ylides. In this report we successfully used three different phosphine stabilized Cu(I) complexes (1-3) as catalysts for chemoselective carbene insertion into the N-H bond of different aromatic amines over the formation of olefin (carbene dimerized product). In order to understand the substrate scope, different α -diazo esters have been reacted with large number of amines and all the reactions produced reasonably good yields under normal experimental conditions (38 examples). All the carbene inserted products have been isolated by column chromatography and fully characterized using standard spectroscopic techniques without any ambiguities. Several control reactions have been conducted in order to understand the importance of the type of phosphine ligands used in the catalysts 1-3 and found that without these catalysts we observed less selectivity (more of olefin as the product over N-H inserted product) and low yield. From this present study, it can be noted that the rigid framework phosphine ligands would be the better choice for carbene chemistry. The results obtained from the current studies would inspire chemists to develop more novel Cu(I)-phosphine catalysts for carbene related reactions including asymmetric versions in the near future.

1. INTRODUCTION

The C-N bond has the significant place in both synthetic and nature made molecules. There are many methods known in the literature to form C-N bonds,[1–3] however the most studied methods are simple nucleophilic substitution and coupling reactions. Apart from these widespread methods, carbene insertion into the N-H bond catalyzed by metals or metal salts is also found to be a useful method.[4–6] Nevertheless from the commercial point of view, catalytic methods are more economic than the simple stoichiometric nucleophilic substitution methods. Carbene insertion into the N-H bond is one of the fast growing research areas in the last decade. Thus far only Cu,[7–22] Rh[23–27] and Fe[28–36] based catalysts have been widely used with nitrogen and carbene type ligands respectively.



Scheme 1. Some known catalysts for carbene insertion into the N-H bond.

Apart from these metal based catalysts, Ru,[33,37–40] Pd,[41] Ir,[42] Au,[43,44] Re[45] and Ag[10] have also been developed for carbene insertion into the N-H bond. Thus far mostly N, O and C based ligands have been used to stabilize the desired oxidation states of the above mentioned transition metal ions (Scheme 1). However, phosphine based ligands have been neglected for carbene chemistry mainly owing to the formation of carbene-phosphine ylides when the phosphine ligands are not tightly linked with the metal ions.[11,41] Therefore only few Cu(I) phosphine complexes are known for this carbene chemistry (Scheme 2).





Scheme 2. Widely used phosphine ligands stabilized Cu(I) catalysts for carbene insertion reaction.

On the other hand phosphine ligands based catalysts have been used successfully for the C-C coupling reactions, C-H activation and many other organic reactions.[46–50] Nevertheless if the phosphine ligands exist only in the complex form during the course of the reaction, one can avoid the formation of carbene-phosphine ylides. Prudently by choosing the right substituents and scaffold, one can develop catalysts with phosphine ligands for carbene chemistry. In this regard, continuation of our research upon carbene insertion reaction,[21] we herein report three phosphine based copper catalysts (Scheme 3) for carbene insertion reactions and demonstrate the substrate scope (38 examples). These results perhaps useful to develop large number of

phosphine stabilized cooper catalysts for similar chemistry including for asymmetric version in the near future.



Scheme 3. Cu(I) catalysts used in the present study.

2. RESULTS AND DISCUSSION

We started our investigation with simple aniline and α -phenyl diazoacetate using 2 mol % of catalyst **1** in DCM (Scheme 4). The reaction was completed within 4 hours and furnished an excellent yield 97%. This result prompted us to optimize the reaction conditions.



Scheme 4. Carbene insertion into the N-H bond using catalyst 1.

For optimizing the reaction conditions, we screened commonly used organic solvents and catalyst load as well. First of all we screened the catalyst load, we observed the best yield with 2 mol % of catalyst. In case of solvents, we observed excellent yields with DCM solvent. In case of coordinating solvent THF (Table 1, entry 2), the reaction was found to be slow and given 76%

yield in 10 h. In acetonitrile solvent (Table 1, entry 3), the rate of the reaction was very slow and given only 67% yield in 36 h, however we have not observed carbene dimerized product but recovered unreacted diazo and aniline. This could be owing to the difference in the rate of carbene formation versus acetonitrile binding. In water (Table 1, entry 6), we have isolated 32% yield in 48 h, although in toluene the reaction mixture was happened to be heterogeneous, surprisingly this carbene insertion reaction furnished 92% yield (Table 1, entry 7) (catalyst **1** is insoluble in toluene, throughout the reaction we observed solid particles). After completion of the reaction in toluene, we reused the catalyst **1** for two more runs and observed that the yield was reduced for second and third runs (74% and 49% respectively).

 Table 1. Optimization of reaction conditions.

Entry ^a	Solvent	<i>t</i> [h] ^b	Yield [%] ^c
1	DCM	4	97
2	THF	10	76
3 ^d	MeCN	36	67
4	DMF	48	45
5	MeOH	6	93
6	Water	48	32
7	Toluene	5	92

^aAll the reactions are carried out with 0.5 mmol (with respect to aniline) in 5 mL of solvent with 2 mol % of catalyst and 0.55 mmol of diazo compound in a 25 mL Schlenk flask under nitrogen atmosphere. ^bDiazo compound (1.1 equiv.) added at 0°C followed by warming to rt. ^cIsolated product yield. ^dWe have not observed any homo coupling product of diazo compound.

In order to understand the role of catalyst **1**, we screened various copper sources as catalysts, when we used Cu(I) complex of commercially available bis-phosphine ligands such as xantphos (xantphos = 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene) and dppf (dppf = 1,1'-Ferrocenediyl-bis(diphenylphosphine)) (Table 2, entry 2 and 3), we observed good yields 91% and 90%. In case of PPh₃-Cu(I) complex (Table 2, entry 6), we observed only 38% yield and in case of dppe (Table 2, entry 7), we observed 69% yield in 8 h, with simple [Cu(CH₃CN)₄]ClO₄ salt (Table 2, entry 4), we observed 76% yield in 5 h. In the presence of nitrogen based donor

ligand (1, 10-Phenanthroline) (Table 2, entry 5), we observed 71% yield in 4 h. In order to gain more insight to understand the importance of Cu(I) ion in dppf-Cu(I) complex, we screened simple ferrocene and FeCl₂.4H₂O (Table 2, entry 8 and 9) as catalysts for carbene insertion into the N-H bond and we observed less than 10% yield in 48 h.

Table 2. Carbene insertion into the N-H bond using various copper sources as catalysts.

	H₂ 〕 + 〔	N ₂	O <u>catalyst (2 mol %</u> DCM, rt		
_	Entry ^a	Solvent	Catalyst	<i>t</i> [h]	Yield [%] ^b
	1	DCM	1	4	97
	2	DCM	2	5	91
	3	DCM	3	5	90
	4	DCM	(CH ₃ CN) ₄ CuClO ₄	5	76
	$5^{\rm c}$	DCM	CH ₃ CN) ₄ CuClO ₄	4	71
			+ 1, 10-Phenanthroline		
	6	DCM	$(CH_3CN)_4CuClO_4 + 2PPh_3$	8	38
	7	DCM	$(CH_3CN)_4CuClO_4 + dppe$	8	69
	8	DCM	Ferrocene	48	<10
	9	DCM	FeCl ₂ .4H ₂ O	48	<10
	10	DCM	1 (1 mol %)	6	89

^aAll the reactions are carried out with 0.5 mmol (with respect to aniline) in 5 mL dichloromethane with 2 mol % of catalyst and 0.55 mmol of diazo compound in a 25 mL Schlenk flask under nitrogen atmosphere. ^bIsolated product yield. ^cWe observed 8% of unidentified product.

From the above observation we found that the complex **1** is the best choice catalyst for carbene insertion into the N-H bond of aniline. After optimizing the reaction conditions, we focused our investigation on the scope of different diazo compounds. We have screened reaction of various diazo derivatives with simple aniline using catalyst **1** (2 mol %) in DCM solvent. All the diazo compounds smoothly reacted with the aniline and given good to excellent yields. We observed highest yield in case of simple α -phenyl diazoacetates 97% (Table 3, entry 1) and we observed lowest yield (82%) with *o*-Cl-phenyl diazoacetates (Table 3, entry 4). These results

prompted us to study the electronic effects of various substituents on aryl part of diazo compounds and observed good correlations with yields and reaction times. In case of electronic withdrawing groups, we observed lower yields and less reaction time. On the other hand insertion reaction has taken more time to complete the reaction when the electronic donating groups were used, nevertheless given more yields. Changing of ester groups also affected the yields, isopropylate and benzylate (Table 3, entry 2 and 3) were given 94% and 89% yields in 4 hours respectively. These results prompted us to examine the substrate scope with various anilines.



	$NH_2 + Ar^1 V_2$	O cata	alyst 1 (2 mol %) rt, DCM	HN Ar ¹	,O. _R	
4a - 4j 5a - 5j						
Entry ^a	Ar	R	<i>t</i> [h]	5	Yield [%] ^b	
1	Ph	Et	4	а	97	
2	Ph	iPr	4	b	94	
3	Ph	Bn	4	с	89	
4	$o-\mathrm{ClC}_6\mathrm{H}_4$	Et	3	d	82	
5	m-ClC ₆ H ₄	Et	4	e	91	
6	p-ClC ₆ H ₄	Et	3	f	86	
7	p-BrC ₆ H ₄	Et	3	g	85	
8	o-OMeC ₆ H ₄	Et	5	ĥ	92	
9	<i>p</i> -OMeC ₆ H ₄	Et	4	i	89	
10	<i>o</i> -OMe, <i>p</i> -OMeC ₆ H ₃	Et	6	j	93	

^aAll the reactions are carried out with 0.5 mmol (with respect to aniline) in 5 mL dichloromethane with 2 mol % of catalyst and 0.55 mmol of diazo compound in a 25 mL Schlenk flask under nitrogen atmosphere. ^bIsolated product yield.

We have screened various aniline derivatives containing electron donating groups on the aryl part (Scheme 5). All the anilines reacted smoothly with α -aryl diazoesters and given very good yields, we observed highest yield with *p*-toludine (90%). We observed lowest yield with *o*-methoxyaniline (77%) in 16 h, this might be owing to the formation of Cu(I) complex with the

subtrate in a η^2 fashion and reducing the possibility of forming carbene complex. In case of electron donating groups substituted anilines, the steric factor not reflected on the yields and reaction times. For an instant, sterically bulky 2, 6-diisopropyl aniline also given good yield 85% in 6 h.





Scheme 5. Scope of anilines with electron donating groups.

Scheme 6. Scope of anilines with electron withdrawing groups.

Furthere we have also screnned various anilines with electron withdrawing groups on the aryl group (Scheme 6). All the anilines smoothly reacted with α -phenyl diazoacetates and given good to excellent yields. We also observed faster reaction rates when compared to the electron donating anilines. We observed highest yield when the modarate electron withdrawing groups present on the aryl part of aniline, observed hightest yield 99% and 97% with 4-iodoaniline and 4-bromoaniline respectively. In case of 2-aminonitrile, we observed 72% yield in 8 h, it has taken reasonably longer time when compared to other subtrates and this might be owing to the complexation of nitrile group with copper and diminshed the rate of carbene formation. We observed lowest yields 39% and 47% with 4-nitroaniline and 2,4-dinitro aniline respectively. Sterically bulky anilines have also given good to excellent yields, in case 2,4,6-tribromoaniline given 78% in 3 h. In order to gain more evidence for carbene insertion into the N–H bond, two of the products **5a** and **7q** (Figure 1) were subjected to the single-crystal XRD studies, and the molecular solid-state structure clearly revealed that the carbene is inserted into the N–H bond of aninlines.



Figure 1. Molecular structure of ethyl 2-phenyl-2-(phenylamino)acetate (5a) and ethyl 2-((2-bromo-4-methylphenyl)amino)-2-phenylacetate (7q); thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

In order to understand how the electronic factors of aniline affecting the yields, we have screened series of para substituted anilines towards carbene insertion into the N-H bond using

catalysts **1**, **2** and **3**. We ploted the isolated yields versus para substitued groups (Figure 2), in case of catalyst **1**, we observed lowering the yields while increasing or decreasing the electron density. We observed best yields with moderate electron withdrawing group 4-iodo aniline. In case of catalysts **2** and **3**, we have not observed any particular trends in yields while increasing or decreasing the electron density. In case of catalyst **2** we observed best yields with simple aniline and 4-nitroaniline, whereas with catalyst **1**, we observed 39% yield with 4-nitroaniline. In case of 4-acetylaniline we observed lowest yield 26%, however in this case we observed 32% of unidentified product. In case of catalyst **3**, we observed best yield 97% with 4-iodoaniline and lowest yield 69% with 4-chloroaniline.



$$X = -OCH_3$$
, $-CH_3$, $-H$, $-I$, $-Br$, $-CI$, $-F$, $-CN$, $-COCH_3$ or NO_2

Scheme 7. Carbene insertion into *para*-substituted anilines using catalysts 1-3.





It is important to mention here that the rigid ligand fromwork is seems to be one of the important creaters for observed reactivity pattern over the formation of phophine-carbene ylide. The rigid frmaework is one of the general features that present in the catalysts **1-3**, when compared to other phosphine lingands which are used in the current study (Table 2, entry 6 and 7). It is well known in the litarature that depending upon the solvent medium, the Cu(I) complexes of PPh₃ and dppe are in equilibrium with more than one complex form as described by *A.G.Samuelson et. al.*[51,52] And therefore perhaps rigid framework is more important for the stability of catalysts **1-3** in the solution during the course of the reaction.

Plausible mechanism for carbene insertion into N-H bond of different anilines by Cu(I) catalysts is given in Scheme 8, two acetonitrile molecules can be replaced by aniline and carbene to give four coordinate Cu(I) complexes **II** and **III** respectively as key intermediates, subsequently these intermediates can form ylide **IV** by the attack of nitrogen lone pair of electrons as proposed and proved by the DFT calculations.in the literature.[53] Eventually the ylide (**IV**) can undergo subsequent proton transfer to offer the final product. Nevertheless more

specific experiments are to be conducted to gain more insights to understand the reaction mechanism in the near future.

3. CONCLUSSIONS

In this report, we successfully demonstrated three different Cu(I)-phosphine complexes as catalysts for carbene insertion into the N-H bond of different anilines under normal experimental conditions. Unlike previously reported Cu(I) catalysts, the catalysts **1** and **3** are air stable while catalyst **2** is relatively less stable. All the carbene inserted products were fully characterized using standard spectroscopic techniques without any ambiguities. We have also studied the effects of electronic factor upon yield and reaction time while using catalysts **1**-**3**. From the observed results, it can be noted that the rigid scaffold phosphine ligands are important to stabilize the Cu(I) ion in solution during the course of the reaction which prevents the formation of phosphine-carbene ylide. These results would inspire chemists to develop more phosphine based Cu(I) catalysts for carbene related reactions. The mechanistic studies and other related work is underway in our laboratory.



Scheme 8. Plausible mechanism for carbene insertion into the N-H bond promoted by catalysts 1-3.

Appendix A. Supplementary material

Contains analytical data, NMR spectra. X-ray crystallographic data CCDC 1420257 (5a) and

CCDC 1420258 (**7q**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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4. EXPERIMENTAL SECTION

4.1. General information

Unless otherwise stated all the reactions were performed under dry nitrogen or argon atmosphere using oven dried glassware and standard Schlenk techniques. All the solvents were distilled prior to use and stored in solvent storage flasks under nitrogen atmosphere. THF and Et₂O were distilled from sodium and benzophenone, all other solvents were distilled from the CaH₂ and used. Commercially available chemicals were obtained from Sigma-Aldrich and Loba Chemie, and used as received, unless otherwise mentioned. Ligand (L1)[54], complex 1[21] and all diazo compounds were prepared by following the standard literature procedures.[55,56] The [Cu(CH₃CN)₄]ClO₄ is explosive in nature therefore minimum quantity was prepared and used

whenever is needed by following adequate safety measures. TLC was performed on pre coated silica gel 60 GF₂₅₄ on aluminum plates and UV light (254 nm). Column chromatography was performed on silica gel 100-200 mesh size. ¹H, ¹³C and ³¹P NMR recorded on Bruker Avance II 400 MHz (¹H), 100 MHz (¹³C) and 162 MHz (³¹P), Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references for ¹H and ¹³C, ³¹P NMR spectra recorded using 85% H₃PO₄ as an external standard, ESI-MS was recorded on Agilent 6540 UHD Q-TOF mass spectrometer.

4.2. Typical procedures of Cu(I) catalyzed carbene insertion into N-H bond

Oven dried 25 mL Schlenk flask was charged with aniline (0.5 mmol.) and catalyst (2 mol %), then 4 mL of solvent was added, the diazo compound (0.55 mmol.) was dissolved in 1 mL of solvent and added to the reaction flask at 0°C, then allowed to room temperature and stirred for required time. The progress of the reactions were monitored by TLC experiment using appropriate mixture of hexane and ethyl acetate as an eluent. After completion of reaction, the solvent was evaporated under reduced pressure and the crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate to give analytically pure compound.

4.3. Experimental procedure for preparation (P-P)CU(I) complexes

The catalyst **1** was reported recently by our group. [17] Catalysts **2** and **3** were prepared by following standard literature procedures.[57–59] Catalysts **1-3** were prepared from an equimolar mixture of respective ligands and $[Cu(CH_3CN)_4]ClO_4$ in acetonitrile.

4.3a. Preparation of xantphos-Cu(I) complex (catalyst 2):

A 50 mL Schlenk flask was loaded with ligand (L2) (4,5-bis(diphenylphosphino)-9,9dimethylxanthene) (xantphos) (1 mmol, 0.57 g) and [Cu(CH₃CN)₄]ClO₄ (1 mmol, 0.32 g) and acetonitrile. The reaction mixture was stirred for 3 h at room temperature. Then filtered through the pad of celite, the filtrate was concentrated under reduced pressure and diethyl ether was added to yield complex **2** as a white solid. Yield: 91%. Complex **2** was further purified by crystallization (DCM/diethyl ether) to yield analytically pure compound. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 6.8 Hz, 2 H, Ar-H), 7.30 – 7.05 (m, 22 H, Ar-H), 6.54 (d, *J* = 3.6 Hz, 2 H, Ar-H), 2.06 (s, 6 H, CH₃CN), 1.60 (s, 6 H, -CH(CH₃)₂). ³¹P (162 MHz, CDCl₃) δ -14.65.

4.3b. Preparation of dppf-Cu(I) complex (catalyst 3):

A 50 mL Schlenk flask was loaded with ligand (L3) (1,1'-ferrocenediyl-bis(diphenylphosphine (dppf) (1 mmol, 0.55 g), [Cu(CH₃CN)₄]ClO₄ (1 mmol, 0.32 g) and acetonitrile. The reaction mixture was stirred for 3 h at room temperature. Then filtered through the pad of celite, the filtrate was concentrated under reduced pressure and diethyl ether was added to yield complex **3** as a white solid. Yield: 83%. Complex **3** was further purified by crystallization (CH₃CN/diethyl ether) to yield analytically pure compound. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (m, 20 H, Ar-H), 4.28 (s, 4 H, *H*_{Cp}), 4.08 (s, 4 H, *H*_{Cp}), 2.0 (s, 6 H, CH₃CN); ³¹P (162 MHz, CDCl₃) δ -13.91.

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Phosphine ligands stabilized Cu(I) catalysts for carbene insertion

into the N-H bond

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Highlights

- Have been used phosphine stabilized Cu(I) complexes for carbene reactions
- Carbene inserted into the N-H bond of anilines under mild experimental conditions
- Wide scope of diazo and aniline derivatives
- Studied electronic effects on yields of carbene inserted products
- Wide range α -aryl amino esters were synthesized and characterized