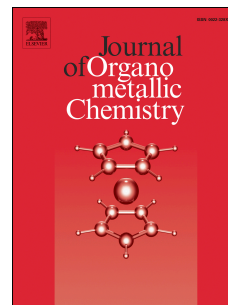


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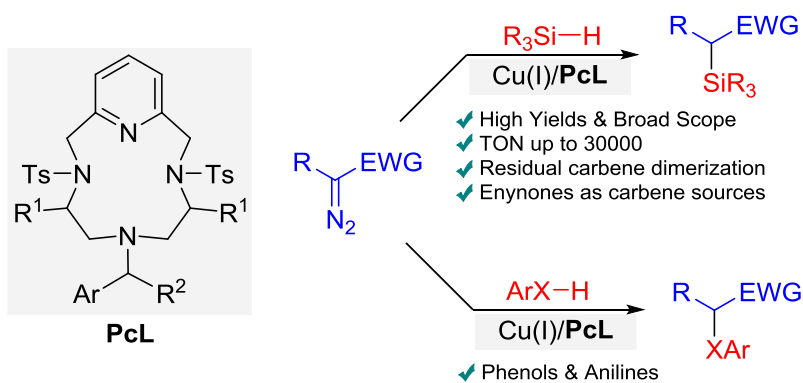
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Carbene X–H Bond Insertions Catalyzed by Copper(I) Macrocyclic Pyridine-Containing Ligand (PcL) Complexes

Giorgio Tseberlidis,^{1,2} Alessandro Caselli*² and Rubén Vicente*¹

¹Departamento de Química Orgánica e Inorgánica, and Instituto Universitario de Química Organometálica “Enrique Moles”, Universidad de Oviedo, c/ Julián Clavería 8, 33007, Oviedo (Spain) and ² Dipartimento di Chimica, Università degli Studi di Milano and ISTM-CNR, Via Golgi 19, 20133 Milano (Italy)

* Corresponding author. Email: Rubén Vicente - vicenteruben@uniovi.es and Alessandro Caselli - alessandro.caselli@unimi.it

Abstract

A catalytic system comprising copper(I) and macrocyclic pyridine-containing ligands (Pc-L) proves capable of promoting carbene Si-H bond insertions using diazo compounds as the carbene source. This catalytic system showed broad scope and a remarkable robustness as indicated by high TON numbers (up to 30000). Moreover, the use of enynones as carbene sources proved also feasible in hydrosilane insertion using this catalytic system. Finally, the insertion in O-H and N-H bonds of phenols and anilines, respectively, has been also demonstrated.

Keywords

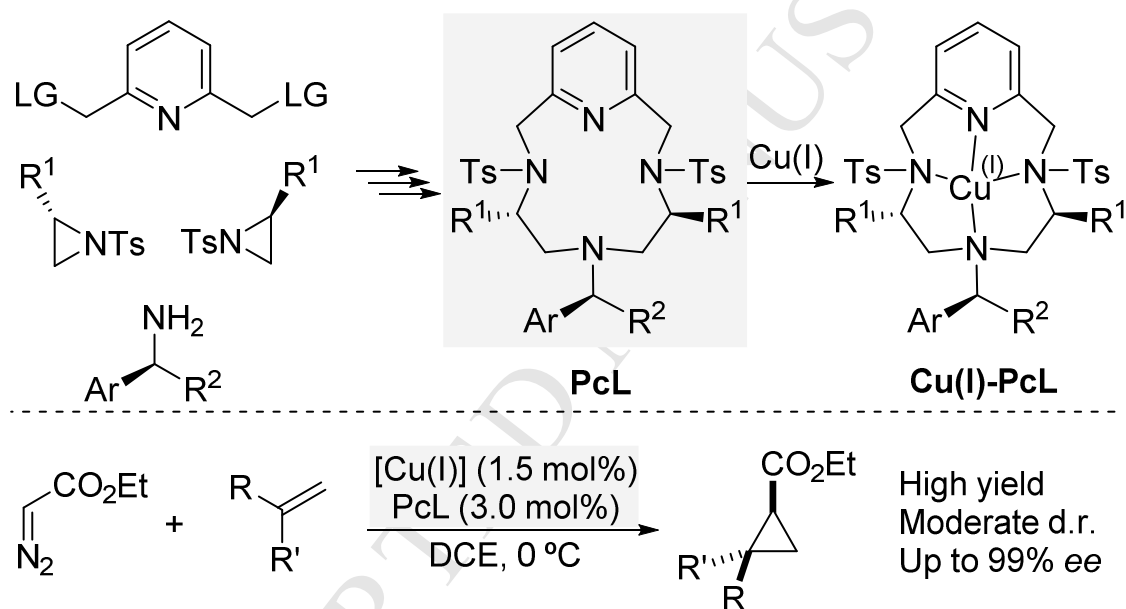
Si–H bond insertions, diazoalkanes, macrocyclic ligands, copper complexes, Pyridine-containing ligands

Introduction

Macrocycles constitutes an important class of ligands in transition metal chemistry since they can mimic the biological environment of various metalloenzymes or can provide beneficial thermodynamic and kinetic properties to their metal complexes^[1-6]. 1,4,7,10-Tetraazacyclododecane scaffolds, normally referred as *cyclen*-type ligands, have been widely employed as ligands for a variety of metals and applied in different reactions^[7-14]. By introducing a pyridine at one of the coordinating positions, flexibility of the ligand can be altered affecting the coordination properties and the activity of a given metal complex. In this sense, we have recently reported a flexible, scalable and high-yielding synthesis of pyridine-containing cyclen-type ligands, including chiral non racemic ones, starting from inexpensive materials (PcL, Scheme 1)^[15-18]. The macrocyclic skeleton is obtained by the sequential assembly of an (enantiopure) aziridine, an (enantiopure) primary amine and a 2,6-disubstituted pyridine derivative. Enantiopure aziridines are easily prepared in two steps using natural aminoacids as chiral pool^[19]. Consequently, we have also studied their coordination chemistry and catalytic activity with copper(I)^[20-23], among other metals^[24-27]. Due to the relevance in synthesis of reactions involving metal-promoted carbene transfer using diazo compounds^[28,29], a series of Cu(I)-PcL complexes was evaluated to assess their catalytic competence in alkene cyclopropanation reactions. Indeed, various Cu(I)-PcL complexes proved capable of promoting cyclopropanations in high yields and, in some cases, high enantioselectivities, yet in moderate diastereoselectivity (Scheme 1).

Besides, the selective functionalization of X-H bonds, particularly those with high bonding energies, constitutes appealing transformations with interest from synthetic and theoretical perspectives. Electrophilic metal-carbene intermediates generated

from diazocompounds enable the functionalization of strong X–H bonds under very mild reaction conditions^[30,31]. With the aim to expand the scope and selectivity of Cu(I)-PcL complexes in carbene transfer reactions, we decide to evaluate them in archetypal X–H bond functionalization reactions. Considering the relevance of silicon-containing compounds^[32-35], which can be used as versatile synthetic intermediates, we selected the metal-promoted carbene insertion into Si–H bonds^[36] to test the activity and selectivity of the Cu(I)-PcL catalytic system. Herein, we disclose our findings.



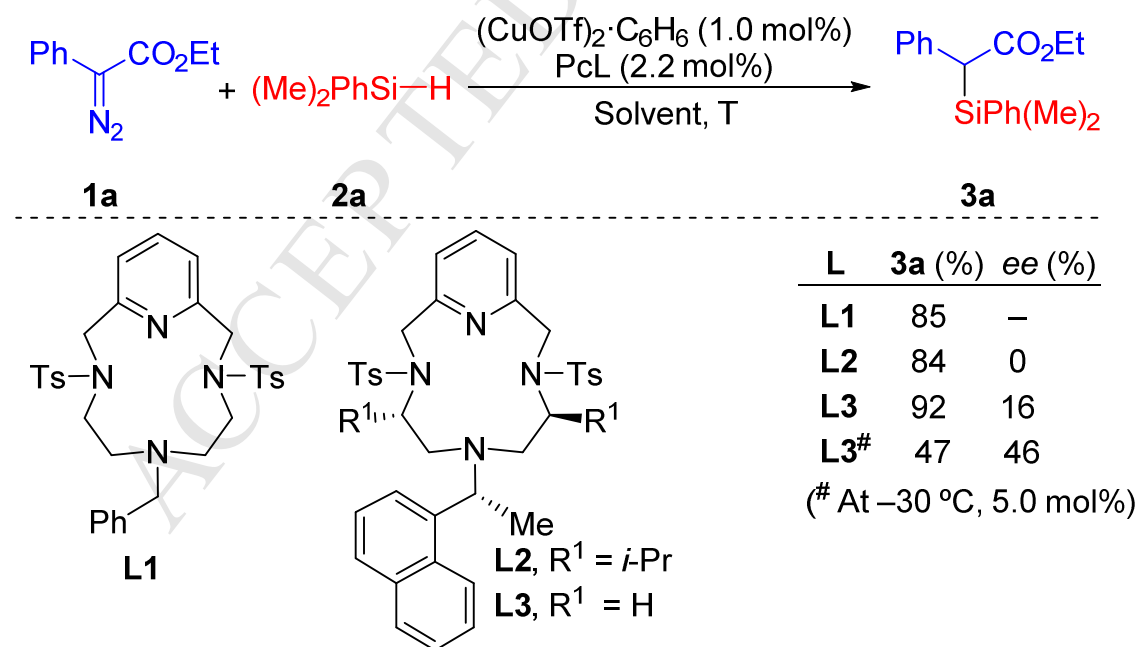
Scheme 1: Synthesis of pyridine-containing ligands (PcL) and their applications in copper(I)-catalyzed cyclopropanations with diazo compounds (Ref. 22). ([Cu(I)] = (CuOTf)₂·C₆H₆)

Results and Discussion

At the outset, ethyl 2-diazo-2-phenylacetate (**1a**) and dimethyl(phenyl)silane (**2a**, 3.0 equiv.) served as benchmark substrates for the study of the reaction (Scheme 2). The catalytic system comprising (CuOTf)₂·C₆H₆ and ligand **L1**^[20] showed

competence to promote efficiently Si–H bond insertion under mild reaction conditions (r.t, DCE, 18 h, slow addition of **1a** over **2a** during 1.5 h, see the Supporting Information for details), affording compound **3a** in 85% isolated yield and a remarkably high product selectivity, since only residual amounts of alkenes arising from dimerization of the carbene were detected. Heterogeneous system employing bare $(\text{CuOTf})_2 \cdot \text{C}_6\text{H}_6$ in the absence of the ligand led to the formation of **3a** (75%, ^1H NMR yield) along with alkenes by-products derived from diazo homocoupling (ca. 25%, ^1H NMR yield). It should be noticed that the formation of these by-products deleteriously impacts the practicality of the reaction since product isolation and purification by standard techniques becomes unrealizable.

With this result in hands and based on our previous studies,^[21-23] *pseudo-C*₂-symmetrical **L2** ligand was used to assess the ability for a stereoselective Si–H insertion^[37-45]. Even though **L2** kept similar yield efficiency, **3a** was disappointingly obtained as a racemate.



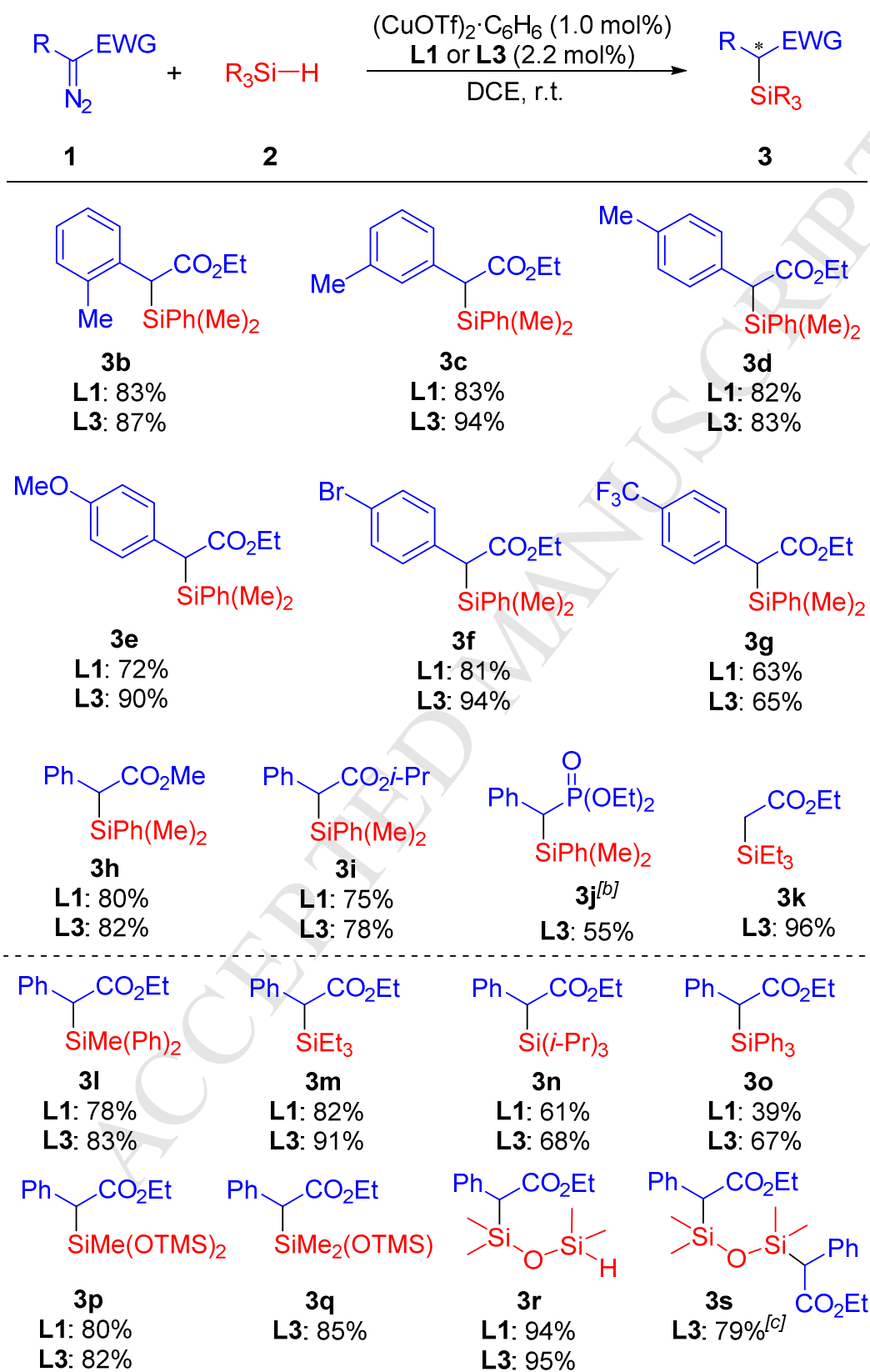
Scheme 2: Cu(I)/PcL-catalyzed carbene insertion in Si–H bonds: initial findings and ligand evaluation. Isolated yields.

As we earlier showed in cyclopropanation reactions^[22], we believe that the enantioselective outcome of the reaction is imposed preferentially by the presence of the stereogenic carbon provided by the amine fragment (position 13, see Experimental Section for numbering). Moreover, an overcrowded environment around the metal might likely be detrimental for the selectivity of the carbene transfer^[46].

In fact, unsubstituted enantiopure ligand **L3** provided **3a** as a single reaction product in excellent yield (92%) and with a promising 16% of ee. Noteworthy, ligand **L3** provides complete product selectivity since dimers arising from diazo compounds **1a** were not detected in the reaction crude as judged by ¹H NMR. Disappointingly, among various modifications on the reaction conditions, the asymmetric induction could be increased only to 46% ee at low temperature (−30 °C) with a 5.0 mol% catalyst loading (based on metal, for details on the screening, see the Supporting Information).^[14] It is worth mentioning that the corresponding catalytic system using AgOTf as the metal source did not provide silane **3a**^[47].

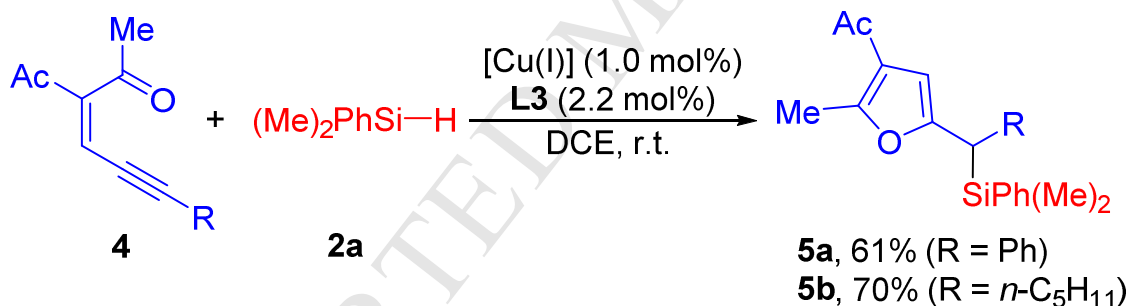
Despite the modest values of ee obtained, we also tried to assess the scope of the transformation using ligands **L1** and **L3**. Thus, various diazo compounds were subsequently tested, as depicted in Table 1. Indeed, various 2-aryl diazo compounds could be employed to obtain the corresponding functionalized silanes **3a–g** in good yields. Neither the electronic properties nor the steric hindrance of the arene influenced the yield. Modification on the ester of the diazo could be also accomplished as demonstrated with the synthesis of silanes **3h–i**. Noteworthy, a diazo phosphonate could also be employed, yet higher temperature was required to reach a useful yield preparing **3j**. Unfortunately, the use of alkyl- or vinyl-substituted diazo compounds seemed to be incompatible with this protocol. Commercially

available ethyl diazoacetate was also employed in the reaction with triethylsilane, leading to compound **3k** almost quantitatively (96% yield) and, importantly, avoiding the undesired homodimerization. With respect to the silane reagent, commonly employed silanes, such as diphenylmethylsilane or triethylsilane were functionalized in generally good yields (compounds **3l–m**). It should be noticed that sterically hindered silanes, as triphenylsilane or triisopropylsilane were well tolerated (compounds **3n–o**). The preparation in good yields of **3p–q** by means of using various hydrosiloxanes, which can be further modified, demonstrated the broad scope of the transformation. Interestingly, by tuning the stoichiometry of diazo **1a** and 1,1,3,3-tetramethyldisiloxane (TMDS, **2h**) we were able to prepare mono- and difunctionalized silanes **3r** and **3s** with very good overall yield and complete product selectivity. It should be noticed that ligand **L3** provided, in general, better yields of **3** than analogous **L1**, minimizing the formation of carbene dimerization side-products (see below). As already noted before, copper(I) triflate in the absence of the ligand is a competent catalyst for the diazoalkane activation but, especially with more hindered substrates such as triphenylsilane, the carbene dimerization side-products are formed preferentially. Neither the modifications on the arene of the diazo compounds nor the substituents on the silane showed a decisive influence in the stereochemical outcome of the reaction when **L3** was used, providing low ee values (0-36% ee, see Supporting Information for details).

Table 1: Cu(I)/PcL-catalyzed Si–H bond carbene insertion: Scope.^a

^a See Supporting Information for detailed reaction conditions. Isolated yields. ^b T = 70 °C. ^c Diazo/silane ratio 5:1. **3s** was obtained as a mixture of diastereoisomers.

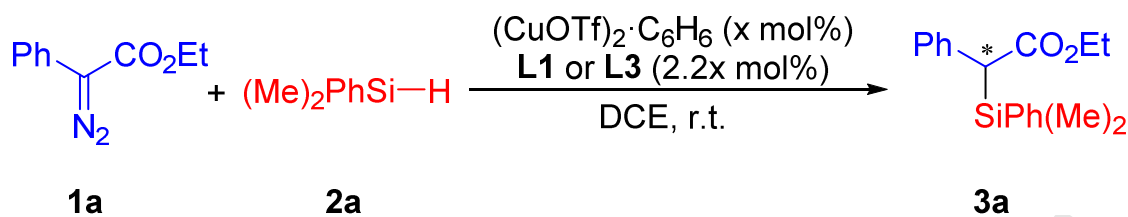
In the recent years, the use of conjugated enynones as precursors of furyl carbene intermediates has been fruitfully exploited by means of transition metal catalysis^[48-50]. We wondered if the Cu(I)-PcL catalytic system could be used with this type of carbenes for the Si-H insertion reaction. Indeed, when enynones **4** were treated with silane **2a** under the standard conditions, the corresponding 2-furylmethylsilanes **5a-b** were obtained in good yields, confirming the capability of the catalyst (Scheme 3). Noteworthy, the formation of furyl-carbene dimerization products was also minimized by using this catalytic system. Regrettably, no stereoselection was observed under the conditions tested.



Scheme 3: Cu(I)/PcL-catalyzed Si-H bond carbene insertions using conjugated enynones **4** as the carbene source. ([Cu(I)] = (CuOTf)₂·C₆H₆).

In addition to the scope in Si-H bond insertion reactions, we also tested the robustness of the catalytic system Cu(I)-PcL using **L1** and **L3** by performing the model reaction at lower catalyst loadings (Scheme 4). Interestingly, a 100-fold decrease in the catalyst loading with **L1** ((CuOTf)₂·C₆H₆ : 0.01 mol%; **L1**: 0.022 mol%), under otherwise identical reaction conditions (r.t, DCE, 18 h, slow addition of **1a** over **2a** during 1.5 h, see the Supporting Information for details), led to the

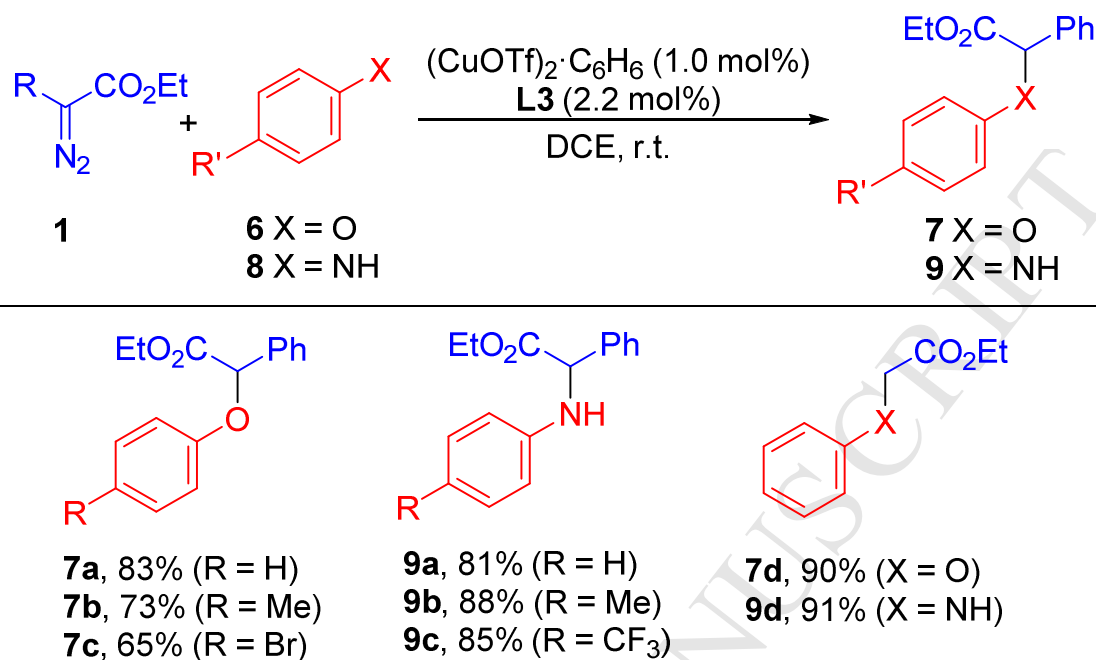
formation of **3a** in a useful 64% yield (68% conversion of **1a** by $^1\text{H-NMR}$, 94% selectivity). It should be pointed out at this stage that the same reaction in the absence of added ligand resulted in a lower conversion (35% $^1\text{H NMR}$ yield) and product selectivity (a 3:1 ratio of **3a** with respect to alkenes arising from carbene dimerization was observed). A slow addition of the **1a** was still required in order to avoid the formation of dimerization products. A one order of magnitude diminution of the catalyst loading revealed the formation of **3a** in lower yield (27% yield, 36% conv.). Moreover, the use of **L3** at low catalyst loadings was also feasible. Indeed, silane **3a** was obtained in 85% yield by using 0.02 mol% of catalyst loading after 48 h (>95% conv.). Further decrease in the loading to 0.002 mol%, resulted in a slower reaction, nevertheless, a remarkable 60% yield of **3a** was obtained after 84 h (70% conv.), meaning a respectable TON number of 30000. At lower catalyst loading ee values were also low (ca. 5%). Further decrease in the catalyst loading (0.0002 mol%) led to the formation of carbene dimerization products (20% NMR yield; 24% conv.) without the observation of **3a**. It is important to highlight the high product selectivity of both catalytic systems, since small amounts of alkenes arising from diazo homocouplings were detected in the reaction mixture. The remarkable stability of the Cu(I) complex with ligand **L3** can be ascribed to the macrocyclic structure of the ligand and to the presence of a pendant naphthyl group, which can coordinate (η^2) the copper(I) atom.^[22]



	Yield (Conv.)		TON
L1 , x = 0.01 mol%	64%	(68%)	3400
L1 , x = 0.001 mol%	27%	(36%)	13500
L3 , x = 0.01 mol%	85%	(>95%)	4250
L3 , x = 0.001 mol%	60%	(70%)	30000

Scheme 4: Robustness of the catalytic system Cu(I)/PcL in Si-H bond carbene insertions at low catalyst loadings.

Finally, we wondered if the present catalytic system could be able to promote other typical X-H bond insertion reactions (Table 2)^[30,31]. For instance, under the standard reaction conditions (with **L3**), the reaction of diazo compound **2a** with phenol (**6a**) afforded the corresponding insertion product **7a** in a good isolated yield of 83%, albeit almost as a racemic mixture^[51,52]. The catalytic system proved active both with electron rich and electron poor phenols, leading to the corresponding ethers **7b-c** in reasonable yields. Additionally, the analogous transformation using aniline (**7a**) led to the formation of secondary amine **9a** in 81% isolated yield. In this case, EDG- or EWG-substituted anilines were used to yield **9b-c** in good yields^[53-57]. Besides, with ethyl diazoacetate the reaction proceeds smoothly and the O-H or the N-H inserted products **7d** or **9d** were isolated in good yields. Unfortunately, aliphatic alcohols and amines were unreactive when using this catalytic system.

Table 2: Cu(I)/PcL-catalyzed X–H bond carbene insertion: Scope.^a

^a See Supporting Information for detailed reaction conditions. Isolated yields.

Conclusion

In summary, we have demonstrated the ability of the catalytic system comprising Cu(I) and pyridine-containing ligands (PcL) to promote the insertion of carbene intermediates into Si–H bonds. This catalytic system, comprised of an economic metal source and an easy to assemble macrocyclic ligand, demonstrated a remarkable ample scope and product selectivity. Moreover, the catalytic system is quite robust and the remarkable TON of 30000 could be achieved. On the contrary, the level of stereoselection of the ligand was modest. As bonus features, this catalytic system enabled the use of alternative carbene sources as conjugated enynones, yielded to only very modest amounts of side products derived from diazo-homocoupling, including those examples with less reactive substrates, and could be employed for the insertions onto O–H and N–H bonds. The chemoselective insertion

into N-H vs O-H bond has also been shown, despite the fact that a good reactivity of the catalyst towards phenols has been observed. Studies towards the implementation in the ligand structure with the aim to extend synthetic applications and increase the stereoselection capacity are currently ongoing in our labs.

Experimental

General Experimental Details

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. 1,2-Dichloroethane (DCE) was distilled from CaH_2 under nitrogen atmosphere. Solvents for column chromatography were obtained from commercial supplier and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). $^1\text{H-NMR}$ (300, 400 MHz) and $^{13}\text{C-NMR}$ (75.5 and 100 MHz) spectra were recorded at room temperature in CDCl_3 on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts (δ) are given in ppm relative to TMS (^1H , 0.0 ppm) or CDCl_3 (^{13}C , 77.0 ppm). Carbon multiplicities were assigned by DEPT experiments. High-resolution mass spectra were recorded in with a VG AutoSpec M mass spectrometer. IR spectra were recorded at a Bruker Alpha-T IR spectrometer. Diazo compounds **1**^[58], enynones **4**^[59], $[\text{Cu}(\text{OTf})_2 \cdot \text{C}_6\text{H}_6]$ ^[60] and PcL-type ligands **L1**, **L2** and **L3** were prepared according to literature procedures.^[22] The rest of the compounds were commercially available.

Representative procedure for the Cu(I) catalyzed Si-H bond carbene insertion using diazocompounds

Under Ar atmosphere, a solution of **L1** or **L3** (0.0044 mmol) and [(CuOTf)₂·C₆H₆] (0.002 mmol) in 1,2-dichloroethane (1.0 mL) was stirred for 1h at rt. The silane **2** (0.6 mmol) was added, followed by the slow addition during 1.5 h of a solution of the diazocompound **1** (0.2 mmol) in 1,2-dichloroethane (1.0 mL) using a syringe pump. The resulting mixture was stirred at this temperature until disappearance of the starting material (checked by TLC analysis). The solvent was removed under vacuum. The resulting residue was purified by flash column chromatography (SiO₂, hexanes:ethyl acetate) to afford **3**.

Representative Procedure for the Cu(I) catalyzed Si-H bond carbene insertion using enynones

Under Ar atmosphere, a solution of **L3** (0.0044 mmoles) and [(CuOTf)₂·C₆H₆] (0.002 mmoles) in 1,2-dichloroethane (1.0 mL) was stirred for 1h at rt. Silane **2a** (0.6 mmoles) was added, followed by the slow addition during 1.5 h of a solution of the enynone **4** (0.2 mmoles) in 1,2-dichloroethane (1.0 mL) using a syringe pump. The resulting mixture was stirred at this temperature until disappearance of the starting material (checked by TLC analysis). The solvent was removed under vacuum. The resulting residue was purified by flash column chromatography (SiO₂, hexanes:ethyl acetate) to afford **5**.

Representative procedure for the Cu(I) catalyzed X-H bond carbene insertion using diazocompounds.

Under N₂ atmosphere, a solution of **L3** (0.0044 mmol) and [(CuOTf)₂·C₆H₆] (0.002 mmol) in 1,2-dichloroethane (1.0 mL) was stirred for 1h at rt. The phenol **6** or the aniline **8** (0.6 mmol) was added, followed by the slow addition during 1.5 h of a

solution of the diazocompound **1** (0.2 mmol) in 1,2-dichloroethane (1.0 mL) using a syringe pump. The resulting mixture was stirred at this temperature until disappearance of the starting material (checked by TLC analysis). The solvent was removed under vacuum. The resulting residue was purified by flash column chromatography (SiO₂, hexanes:ethyl acetate) to afford **7** or **9**, respectively.

Supporting Information

Detailed experimental procedures, text, figures and tables reporting full NMR spectra for all compounds This material is available free of charge via the Internet.

Supporting Information File 1: Detailed experimental procedures, text, figures and tables reporting full NMR spectra for all compounds This material is available free of charge via the Internet.

File Name: Supporting Information

File Format: pdf

Title: Carbene X–H Bond Insertions Catalyzed by Copper(I) Macrocyclic Pyridine-Containing Ligand (PcL) Complexes

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- * Cu(I)-PcL complexes promote carbene insertion in Si-H bonds.
- * Cu-PcL catalytic system shows broad scope and a notable robustness (up to 30000 TON).
- * Cu-PcL promotes carbene insertions in O-H or N-H bonds of phenols and anilines.

ACCEPTED MANUSCRIPT