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# Copper-catalyzed selective pyrrole functionalization by carbene transfer reaction

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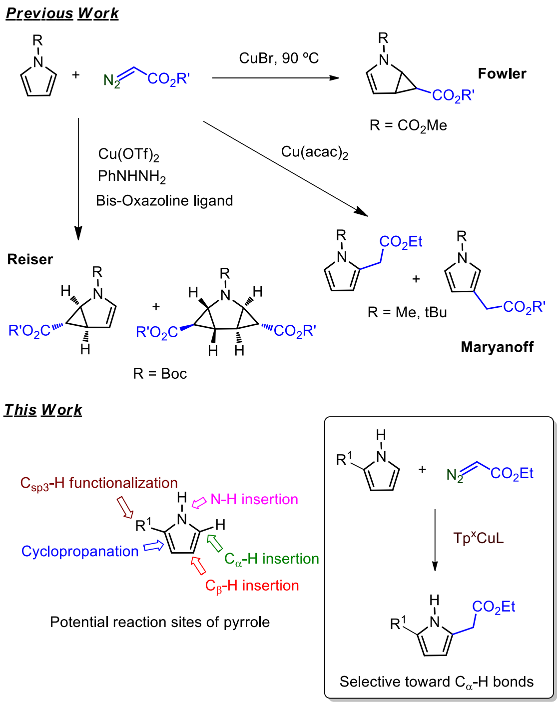
**Abstract.** 1H-Pyrroles can be directly functionalized by means of the incorporation of carbene groups from diazo compounds, in a process catalyzed by $Tp^xCu$ complexes ($Tp^x$ = hydrotrispyrazolylborate ligand). The reactions take place with a complete selectivity toward the formal insertion of the carbene into the $C_\alpha$-H bond, leading to alkylated pyrroles, with no modification of the $C_\beta$-H, N-H or C=C bonds of the pyrrole unit. Alkyl substituents at C-ring as well as alkyl, aryl, allyl or alkyne substitution at N atom are tolerated, the strategy affording 20 new pyrrole derivatives. The observance of partial deuteration at the methylene group when the reaction is carried out with added $D_2O$ serves to discard the direct insertion of the carbene group into the $C_{sp2}$-H bond, the alternative electrophilic attack to the pyrrole ring being feasible.

**Keywords:** Pyrrole functionalization, copper catalysis, carbene transfer, diazo compounds, C-H functionalization, selectivity;

## Introduction

The metal-catalyzed carbene transfer reactions from diazo compounds constitutes a useful tool in organic synthesis,[1] incorporating such moiety to the structure of many compounds either by addition to unsaturated C-X (X = C, N) bonds or by insertion into saturated C-Y bonds (Y = H, halide). Thus, many substrates have been modified following this strategy, including alkanes, alkenes, alkynes, arenes, alcohols or amines, among others.[1] Heterocycles such as furans,[2] indoles[2] or pyrroles[3] have also been employed as substrates, where the carbene group can be incorporated to several saturated or unsaturated moieties, catalyst design becoming crucial toward the control of the selectivity.

Following our previous work[4] on the use of group 11 metal-based catalysts for carbene transfer reactions from diazo compounds, we have now focused in pyrroles as substrates. Albeit a number of transformations have been described involving the incorporation of a carbene group to pyrrole skeleton, in an area mainly dominated by rhodium-based catalysts,[5] we noticed that there is not any example of 1H-pyrroles being modified by this metal-induced methodology, only N-protected pyrroles being



**Scheme 1.** Early examples of pyrrole functionalization by carbene incorporation and the selective functionalization of Cα–H bonds work described herein.

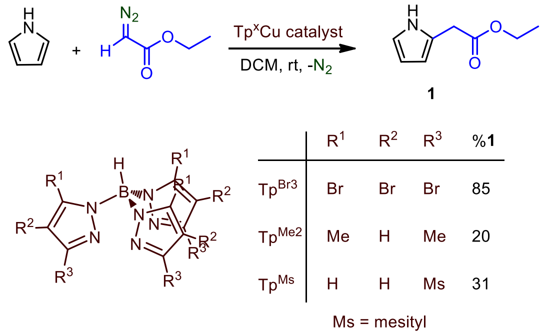
employed as substrates. Also, the chemoselectivity of this transformation is highly dependent on the N-substituent: electron withdrawing groups favor C=C cyclopropanation whereas N-alkyl-substituted pyrroles often result in C-H insertion products. Fowler first described[6] the cyclopropanation of a pyrrole (Scheme 1), using CuBr as the catalyst, and ethyl diazoacetate as the carbene source. Maryanoff later reported the insertion into C-H bonds with $Cu(acac)_2$.[7] Reiser introduced the chiral version using Cu-bis(oxazoline), thus inducing enantiomeric excesses in the mono- and bis-cyclopropane products.[5d,8]

To the best our knowledge, there are no examples of the selective functionalization of the C-H bonds of N-H unprotected pyrroles by carbene incorporation from a diazo compound. This is a quite challenging transformation, in view of the potential reaction sites at a given pyrrole (Scheme 1), where the carbene group can be transfer to N-H, $C_{sp2}$-H, $C_{sp3}$-H or C=C bonds. Herein we report the excellent activity of several $Tp^xCu$ complexes as catalysts for the selective functionalization of pyrroles, with a noticeable degree of tolerance to other functional groups. For the $C_{sp2}$-H functionalization cases the products correspond to the formal insertion of the carbene group in such bonds, albeit this is not the actual case from a mechanistic point of view.

## Results and Discussion

### Pyrrole and unprotected N-H pyrroles as substrates.

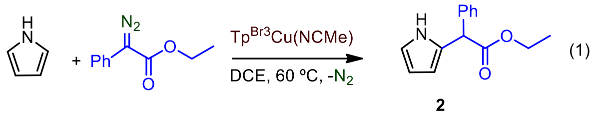
We first targeted the challenging pyrrole as the substrate, using $Tp^{Br3}Cu(NCMe)$ as the catalyst in view of its outstanding performance in carbene transfer reactions to saturated and unsaturated substrates.[4b] With ethyl diazoacetate (EDA) as the carbene source, the reaction proceeded at room temperature in 1.5 h using 0.01 mmol of catalyst, 20 equiv of EDA and 100 equiv of pyrrole (Scheme 2), resulting in the selective formation of compound **1**, where the carbene group has formally inserted into the $C_\alpha$-H bond in 85% yield (EDA-based). Compound **1** was fully characterized by NMR spectroscopy (see SI): it is worth mentioning the observation of a broad singlet at 8.74 ppm corresponding to the N-*H*. The remaining 15% of the initial EDA was converted into a mixture of diethyl fumarate and maleate. Other $Tp^xCu$-based catalysts were also tested for this transformation, such as $[Tp^{Me2}Cu(NCMe)]$ or $Tp^{Ms}Cu(THF)$, their activities being moderate compared with that of the $Tp^{Br3}$-containing catalyst. The $[Tp^{*,Br}Ag]_2$ complex[9] was also tested, yielding a successful 75% yield into **1**, in the first example of a silver-based catalyst for pyrrole functionalization by this methodology. We also evaluated a series of IPrMCl catalysts (M = Cu, Ag, Au; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazo-2-ylidene) in view of the previously reported activity for carbene transfer reactions.[10] The yields into **1** were lower (Cu, 53%; Ag, 15%; Au, 42%) than those obtained with the $Tp^{Br3}M$-based catalysts (M = Cu, Ag).



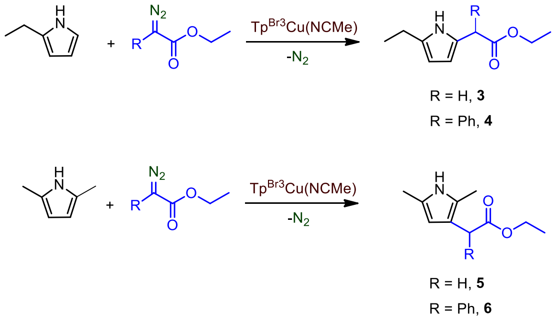
| | R1 | R2 | R3 | %1 |
|---|---|---|---|---|
| $Tp^{Br3}$ | Br | Br | Br | 85 |
| $Tp^{Me2}$ | Me | H | Me | 20 |
| $Tp^{Ms}$ | H | H | Ms | 31 |

Ms = mesityl

**Scheme 2.** $Tp^xCu$-catalyzed functionalization of pyrrole.



Ethyl 2-phenyldiazopropionate (PheDA) was chosen as the model for a disubstituted carbene group. The reaction barely proceeded at room temperature, but heating at 60 ºC in DCE induced the complete consumption of the diazo compound. Compound **2** was formed in 80 % yield, derived from the functionalization of the $C_\alpha$-H bond (eq 1).

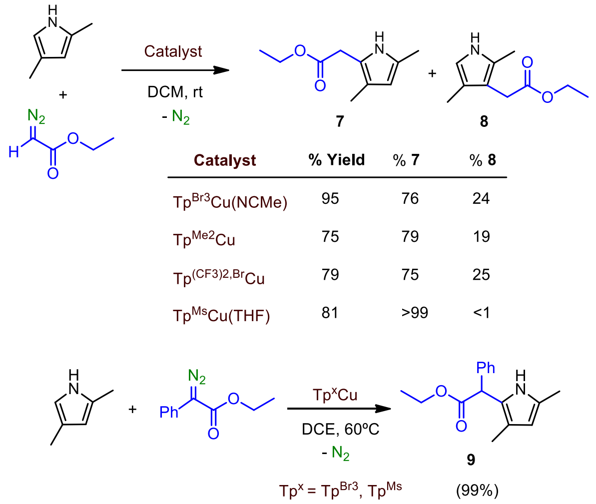


**Scheme 3**. Alkyl-substituted pyrroles as substrates.

The syntheses of compounds **1** and **2** constitute the first examples of the direct functionalization of 1H-pyrrole by carbene insertion, with such high conversions and selectivity. At variance with the examples described by Maryanoff,[7] where $C_\beta$-H bonds were also altered, in our case only the insertion into the $C_\alpha$-H bonds is observed. In an effort to push the reaction toward the former, we employed 2-ethyl-1H-pyrrole as the substrate, under the standard catalytic conditions (see Scheme 2 and eq 1), with $Tp^{Br3}Cu(NCMe)$ as the catalyst. The products **3** and **4** were obtained in high yields, as inferred from NMR studies with the reaction crudes (> 95%), showing the exclusive functionalization of the $C_\alpha$-H bond (Scheme 3). Only when 2,5-dimethyl-1-H-pyrrole was employed, the reaction proceeded at the $C_\beta$-H bond, leading to the formation of compounds **5** and **6**

(Scheme 3, see SI for full description of novel compounds **3-6**).

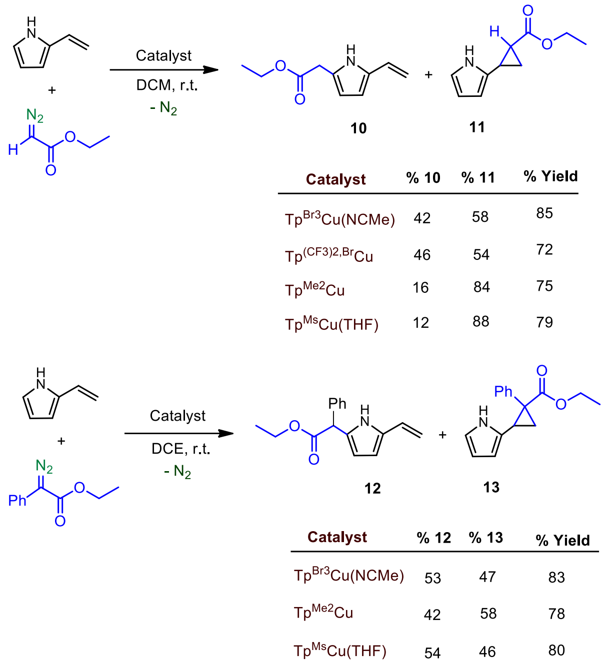
The use of 2,4-dimethyl-1H-pyrrole brought some additional information to this catalytic system (Scheme 4). With EDA as the carbene source and Tp$^{Br3}$Cu(NCMe) as the catalyst, a mixture of two compounds was obtained, derived from carbene incorporation into both C-H bonds (**7**, **8**), in a ca. 3:1 ratio, favoring that of the insertion into the C$_{\alpha}$-H bond. Interestingly, the use of other Tp$^{x}$Cu catalysts showed the effect of the catalyst structure in the reaction outcome. Thus, those bearing Tp$^{Me2}$ or Tp$^{(CF3)2,Br}$ ligands (with similar steric hindrance but different electronic density at metal)[11,12] provide a similar ratio, whereas the bulkier Tp$^{Ms}$-containing catalyst exclusively provided compound **6**. Moving to PheDA as the diazo compound showed the exclusive formation of **9** with both Tp$^{Br3}$- or Tp$^{Ms}$-based catalysts. These data demonstrate that the carbene transfer is mainly influenced by the steric pressure of the Tp$^{x}$ ligand, the β position being more hindered than the α counterpart in this substrate.



| Catalyst | % Yield | % 7 | % 8 |
|---|---|---|---|
| Tp$^{Br3}$Cu(NCMe) | 95 | 76 | 24 |
| Tp$^{Me2}$Cu | 75 | 79 | 19 |
| Tp$^{(CF3)2,Br}$Cu | 79 | 75 | 25 |
| Tp$^{Ms}$Cu(THF) | 81 | >99 | <1 |

**Scheme 4.** Functionalization of C$_{\beta}$-H bond using 2,4-dimethyl-1H-pyrrole as substrate.

The collected results demonstrate the preferential incorporation of the carbene group into the C$_{sp2}$-H bonds of pyrrole ring, with no modification of the N-H or the C=C bonds neither the alkyl substituents. To evaluate an intramolecular competition for the carbene group, we synthesize 2-vinyl-1H-pyrrole. Scheme 5 shows the results obtained using different Tp$^{x}$Cu-based catalysts and two diazo compounds. In the case of the EDA, products derived from the insertion into the C$_{\alpha}$-H bond (**10**) as well as from the addition to the vinyl C=C bond (**11**) are observed. Electron-poor metal catalysts (containing Tp$^{Br3}$ or Tp$^{(CF3)2,Br}$ ligands) provide distribution of products **10:11** close to equimolar (42:58, 46:54) whereas the sterically similar, more electron rich Tp$^{Me2}$Cu clearly favors the formation of **11** (16:84). Steric factors appear prominent when the very bulky Tp$^{Ms}$Cu catalyst is employed, leading to a 12:88 ratio for **10**:**11**. Unlike with EDA, no significant changes in the regioselectivity can be observed in the case of PheDA as the diazo reagent for the selected catalysts with different electronic and steric characteristics, obtaining a nearly equimolar mixture of both products **12** and **13**.



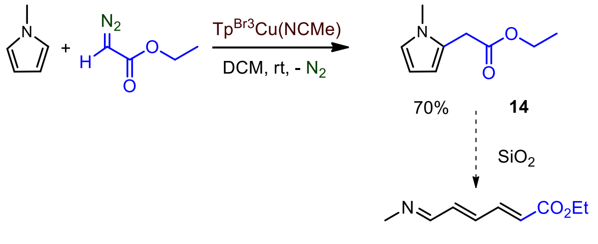
| Catalyst | % 10 | % 11 | % Yield |
|---|---|---|---|
| Tp$^{Br3}$Cu(NCMe) | 42 | 58 | 85 |
| Tp$^{(CF3)2,Br}$Cu | 46 | 54 | 72 |
| Tp$^{Me2}$Cu | 16 | 84 | 75 |
| Tp$^{Ms}$Cu(THF) | 12 | 88 | 79 |

| Catalyst | % 12 | % 13 | % Yield |
|---|---|---|---|
| Tp$^{Br3}$Cu(NCMe) | 53 | 47 | 83 |
| Tp$^{Me2}$Cu | 42 | 58 | 78 |
| Tp$^{Ms}$Cu(THF) | 54 | 46 | 80 |

**Scheme 5.** Intramolecular competition for carbene incorporation in 2-vinyl-1H-pyrrole as the substrate.

## N-substituted pyrroles as substrates: tolerance to diverse functional groups.

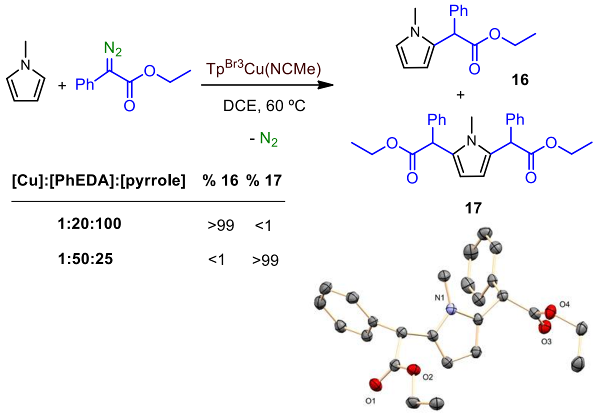
Once investigated the catalytic behavior of N-H unprotected pyrroles, we moved onto N-methyl-pyrrole as the substrate. With Tp$^{Br3}$Cu(NCMe) as the catalyst and EDA as the carbene source, the room temperature transformation led to the formation of the product **14** in 70 % yield (by NMR quantification of the reaction crude, diethyl fumarate and maleate accounting for 100% of the initial EDA) formed upon incorporation of the carbene unit into the C$_{\alpha}$-H bond (Scheme 6). During the purification of the reaction mixture by column chromatography, compound **15** (Scheme 6) was also obtained, in addition to **14**, albeit it was not detected at the end of the reaction, thus forming due to partial decomposition during purification. The use of Tp$^{Me2}$Cu(NCMe) and Tp$^{Ms}$Cu(THF) did not improve the results with the



**Scheme 6.** Reaction of 1-methyl-1H-pyrrole with ethyl diazoacetate using Tp$^{Br3}$Cu(NCMe) as the catalyst.

perbromo catalyst, the amount of **15** remaining as minor in all cases after column chromatography.

When PheDA was used as the carbene source, heating at 60 ºC was required to accomplish the consumption of the diazo compound, employing $Tp^{Br3}Cu(NCMe)$ as catalyst, and using a [Cu]:[PhEDA]:[N-Methyl-pyrrole] ratio of 1:20:100. After 4h of reaction time, compound **16** (Scheme 7). The use of two equiv of PheDA led to the quantitative formation of compound **17**, as the result of the double functionalization of the pyrrole at both $C_{\alpha}$-H bonds (see SI for detailed description of the products, including X-ray characterization for **17**). As expected, the double activation is favored when using a two-fold excess of PheDA with respect to the pyrrole



**Scheme 7.** Mono- and disubstituted functionalization of N-methyl pyrrole with ethyl 2-phenyldiazopropionate.

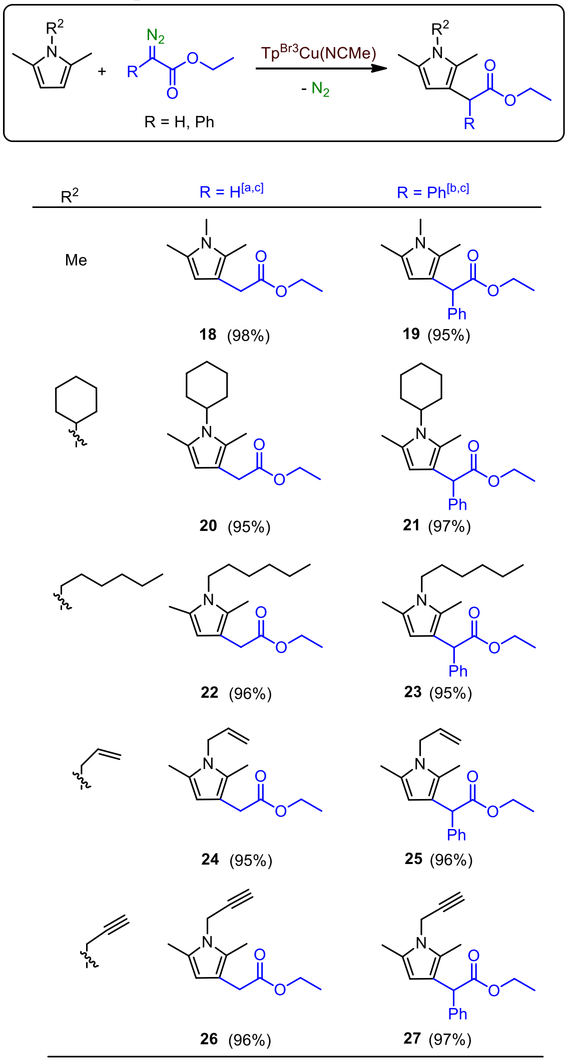
Next we studied the scope of this transformation regarding the substitution at nitrogen, with a series of 2,5-dimethyl-N-substituted pyrroles. Table 1 shows the results obtained, for both EDA and PheDA as carbene sources. In all cases the insertion of the carbene unit into the $C_{\beta}$-H bond was observed, in spite of the presence of alkene or alkyne functionalities attached to the N atom. Alkyl and cycloalkyl $C_{sp3}$-H bonds were also tolerated, in spite of the capabilities of the $Tp^{Br3}Cu(NCMe)$ catalyst to transfer the carbene group to those bonds. N-Boc and N-Ph 1H pyrroles constitute the limit of the system, seems they do not provide the expected products, whereas 1,5-dimethyl-1H-pyrrole-2-carbonitrile only gives minor yields (10-15%) of the insertion product.

The methodology presented herein provides a series of 26 functionalized pyrroles, from which only three have been previously reported using carbene transfer reactions from diazo compounds (**5**,[13] **7**[14] and **14**[6]), assessing the potential of this catalytic system as a synthetic tool.

## Mechanistic interpretation.

The reaction outcome of the catalytic system reported herein corresponds to the formation of compounds which can be formally considered as the result of the metal-mediated transfer and insertion of a carbene group into a $C_{sp2}$-H bond. To shed light on this issue, the reaction of 2-ethyl-1H-pyrrole with EDA was carried out in the presence of added $D_2O$, with $Tp^{Br3}Cu(NCMe)$ as the catalyst. Figure 1 shows the NMR spectra of these experiments, as well as that in the absence of $D_2O$. Partial deuteration of the methylene group attached to the pyrrole ring was observed, as inferred from the appearance of a 1:1:1 triplet due to the -CHD- group (Figure 1). Noteworthy, the degree of deuteration increased when augmenting the amount of added $D_2O$. We interpret this observation as a proof of the absence of a direct insertion of the carbene into the $C_{sp2}$-H. A similar behavior was observed using pyrrole or 2,5-dimethylpyrrole as the starting materials (see SI). These observations demonstrate that the

**Table 1.** N-substituted pyrroles as substrates for carbene incorporation.



[a] Reactions carried out at room temperature with 0.01 mmol of catalyst, 20 equiv of EDA and 100 equiv of the corresponding pyrrole in 6 mL of $CH_2Cl_2$. Reaction time: 2 h.

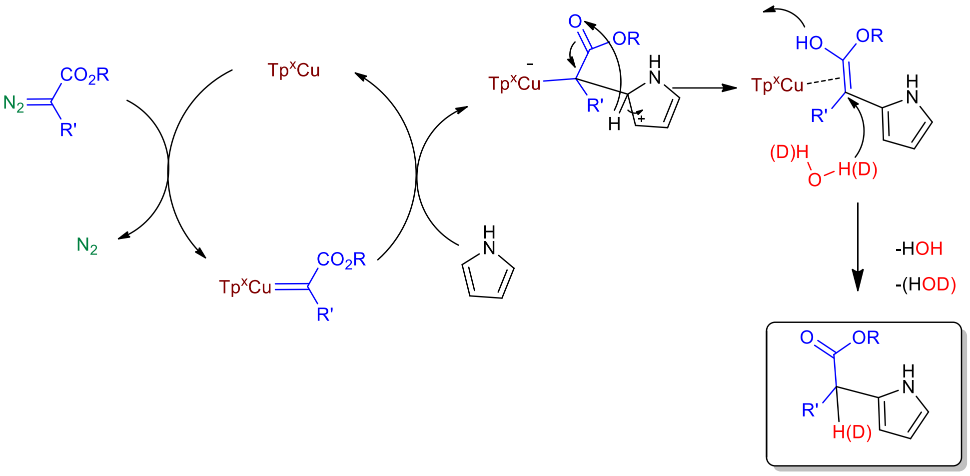
[b] Reactions carried out at 60 ºC with 0.01 mmol of catalyst, 20 equiv of PheDA and 100 equiv of the corresponding pyrrole in 6 mL of $CH_2Cl_2$. Reaction time: 4 h.

[c] Yields determined by NMR using 1,3,5-trimethoxybenzene as internal standard. Diethyl fumarate and maleate accounted for 100% of initial diazo compound.

**Scheme 5.** Scope reaction with N-substituted pyrroles.

aforementioned direct insertion is not possible, since otherwise no deuteration would take place.

The alternative should be based on an aromatic electrophilic substitution. This is in agreement with the lack of reactivity observed with pyrroles bearing substituents such as Boc or Ph at the N or CN at the C-ring. It is well established that such substituents reduce the electronic density at the heterocycle.



**Scheme 8**: Mechanistic proposal for the carbene transfer to pyrroles catalyzed by $Tp^xCu$.

Based on the experimental data available and literature precedents, Scheme 8 shows a mechanistic proposal for this transformation. The carbene group is added to the aromatic ring generating a zwitterionic species.[15] A similar behavior has been recently reported for the arene functionalization by carbene insertion using group 11 metal-based catalysts.[10] Following the same pathway, a hydrogen atom is transferred to the ester moiety, leading to an enolate intermediate, which undergoes protonation/deprotonation processes involving adventitious water or added $D_2O$, thus providing the final product.

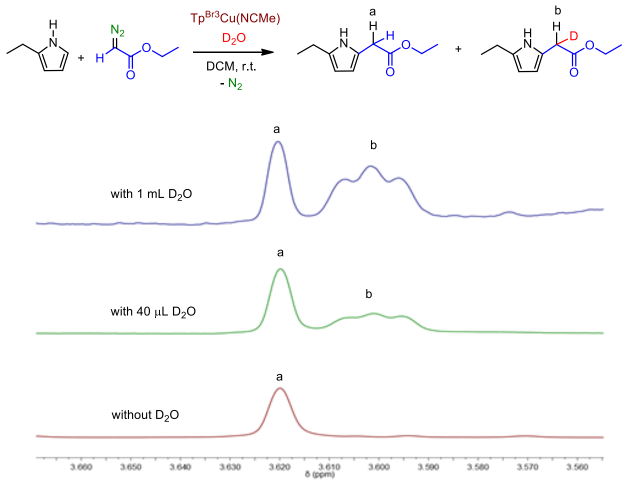


**Figure 1**. Methylene region of the $^1H$ NMR spectra of the crude of the reactions of 2-ethyl-1H-pyrrole with EDA in the absence and presence of $D_2O$.

## Conclusions

We have found that complexes $Tp^xCu$ ($Tp^x$ = trispyrazolylborate ligand) catalyze the transfer of carbene units from diazo compounds to 1H-pyrroles promoting the selective modification of the $C_\alpha$-H bonds affording the formal insertion products, leaving the other potential reaction sites such as NH, C=C or other substituents at C (alkyl) or N (alkene, alkyne, alkyl) undisturbed. Only in the case of vinylic substitution at the $C_\alpha$ induces a certain loss of selectivity. The reaction takesplace through an electrophilic attack of the copper-carbene intermediate with the formation of ylidic species en route to the final formal insertion product.

## Experimental Section

All air– and moisture–sensitive manipulations were carried out with standard Schlenck techniques under nitrogen atmosphere or in a glovebox (MBRAUN UNILAB). Solvents were purchased from commercial sources, dried by distillation under nitrogen atmosphere using the suitable drying agent and deoxygenated immediately before their use. Reagents were acquired from Aldrich and used without any further purification. Commercially unavailable pyrroles were obtained following synthetic routes previously described in the literature, and which are detailed in the supporting information. The copper catalysts were synthesized by literature procedures. NMR spectra were recorded on the Agilent 400MR and Agilent 500DD2 spectrometers. X-ray studies were performed in a Bruker D8 QUEST ECO. High resolution mass spectroscopy experiments were carried out at the Centre of Research Technology and Innovation of the University of Seville (CITIUS).

**General Catalytic Procedure: Reaction of ethyl acetate and pyrroles catalyzed by Tp$^{Br3}$Cu(MeCN).** In a Schlenk tube, under inert atmosphere, the catalyst (0.01 mmol) was dissolved in deoxygenated DCM (6 mL) and the pyrrole was added (1 mmol). EDA (0.2 mmol) was added in three portions (3x8.33 µL), every 15 min, and the mixture was stirred at room temperature for 2 hours. The solvent was removed under reduced pressure and the reaction crude was investigated by NMR spectroscopy using trimethoxybenzene as internal standard. Purification can be done by column chromatography (petroleum ether:EtOAc 1:1).

**Reaction of ethyl diazophenylacetate and pyrroles catalyzed by Tp$^{Br3}$Cu(MeCN).** Following the same previous protocol, the catalyst (0.01 mmol) was dissolved in DCE (6 mL) and the pyrrole was added (1 mmol). PhEDA (0.2 mmol) was added in one portion, and the mixture was stirred at 60 ºC for 4 hours. The solvent was evaporated by reduced pressure and the residue was purified through a column of silica gel (eluent: petroleum ether:EtOAc, 1:1).

Experimental procedures, spectroscopic and analytical data of compounds **1**-**27**, are provided in the Supporting Information. CCDC-1978196 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgements

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**FULL PAPER**

# Copper-catalyzed selective pyrrole functionalization by carbene transfer reaction

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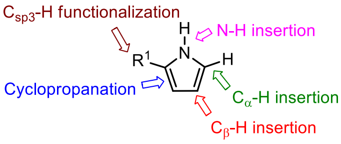
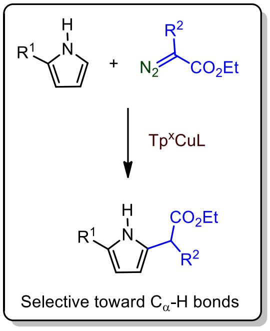


Potential reaction sites of pyrrole



Selective toward $C_{\alpha}$-H bonds