# Synthesis of new copper(I) complexes with tris(2-pyridyl) ligands. Applications to carbene and nitrene transfer reactions<sup>†</sup>

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New copper(I) complexes with tris(2-pyridyl)methane (TPC), tris(2-pyridyl)methoxymethane (TPM) and tris(2-pyridyl)amine (TPN) ligands have been synthesized and characterized, including structural determinations by X-ray diffraction of some examples. Their activity as catalysts in carbene and nitrene transfer reactions was studied.

# Introduction

Copper complexes of tridentate tris(pyrazolyl)borates (CuTp) are some of the most useful catalysts for carbene and nitrene transfer (CNT) reactions.<sup>1</sup> Therefore, there is an obvious interest in the exploration of other copper complexes of nitrogen-donor ligands as catalysts for these reactions. Ligands with pyridyl donor groups have been extensively employed in copper coordination chemistry,<sup>2</sup> including the catalysis of CNT reactions.<sup>3</sup> However, tridentate tris(2-pyridyl) ligands (TPy), widely used for complexes of other metals,<sup>4</sup> received little attention in copper chemistry, and their copper complexes were never used as catalysts for CNT reactions.<sup>5</sup>

In CuTp complexes, a correlation was found between catalytic activity and metal center electron deficiency.<sup>6</sup> In turn, the latter can be estimated by the position of the infrared  $v_{co}$  band of the TpCu–CO complex, electron-poor metal centers giving rise to high  $v_{co}$  values. Some of the CuTp complexes that have been found to display a high activity in CNT reactions and the  $v_{co}$  values of their carbonyl adducts are:  $[(Tp^{Br3})CuCO] (2110 \text{ cm}^{-1})^6$  and  $[(Tp^{CF3,CF3})CuCO] (2137 \text{ cm}^{-1})$ .<sup>7</sup> Very recently, Fujii and co-workers<sup>8</sup> reported that  $v_{co}$  values for  $[(TPOH)CuCO]ClO_4$  (TPOH= tris(2-pyridyl)carbinol),  $[(TPM)CuCO]ClO_4$  (TPC = tris(2-pyridyl)methane) and  $[(TPC)CuCO]ClO_4$  (TPC = tris(2-pyridyl)methane) are 2106, 2101 and 2091 cm<sup>-1</sup> respectively. The comparison between these values suggests that CuTPy complexes could be good catalysts for CNT reactions. Here we report our studies in this area.

# **Results and discussion**

Copper(1) complexes of the ligands tris(2-pyridyl)methane (TPC), tris(2-pyridyl)methoxymethane (TPM) and tris(2-pyridyl)amine (TPN) (Chart 1) were chosen for this study.



The reaction of equimolar amounts of CuOTf and TPC in a THF/MeCN mixture afforded a high yield of a white powder. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of its  $CD_2Cl_2$  solution were consistent with a [Cu(TPC)(NCMe)]OTf (1) formulation, and indicate the equivalence at room temperature of the three 2-pyridyl groups. Attempts to isolate a related THF (instead of MeCN) complex, either as a triflate salt or as a salt of the low coordinating BAr'<sub>4</sub> anion (Ar' = 3,5-bis(trifluoromethyl)phenyl) (see below), afforded a material insoluble in dichloromethane or chloroform. Compound 1 was employed as the catalyst for the reaction of ethyldiazoacetate (EDA) and styrene in non-coordinating solvents. The results are displayed in Table 1.

When EDA was added in one portion to a dichloromethane solution of styrene (styrene : EDA ratio = 5 : 1) containing 1% of the [Cu(TPC)(NCMe)]OTf (1) complex as catalyst, a <sup>1</sup>H NMR spectrum taken after two hours showed full conversion of EDA to a mixture of the two diasteromers of 2-phenyl-ethoxycarbonylcyclopropane (82%), ethyl fumarate and ethyl maleate (Scheme 1). When the experiment was repeated using a 1 : 1 mixture of 1 and NaBAr'<sub>4</sub> as catalyst, the yield obtained was the same. This lack of an activating effect of NaBAr'<sub>4</sub> supports our assumption that the triflate anion is not copperbonded in 1 (see below). When EDA was slowly added over 10 hours to minimize the formation of the olefins formally resulting from carbene dimerization, the cyclopropanation was virtually quantitative (entry 1). Applying the same procedure to other olefins also afforded the corresponding cyclopropanes

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<sup>†</sup> Electronic supplementary information (ESI) available: Tables of crystal data of **4** and **5** and references giving the spectroscopic data of the products. CCDC reference numbers 695439 and 695440. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b812604f ‡ Present address: IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

 Table 1
 Yields of cyclopropanes and aziridines in the Cu-catalyzed reactions of EDA with the listed olefins

entry		1	2b	3	4
	Cyclopropanation <sup>a</sup>				
1	Styrene	97 (77,20)	84(62,22)		98 (67, 31)
2	1-Hexene	32	17		21
3	Cyclooctene	94	95		98
4	Cis-stilbene	64	41		84
5	Trans-stilbene	38	32		50
6	1,1-Diphenylethylene	83	76	_	96
	Aziridination <sup>b</sup>				
7	Styrene	70	55	100	
8	1-Hexene	18	16	20	
9	Cyclooctene	77	63	80	
10	Cis-stilbene	28	15	26	
11	Trans-stilbene	15	11	13	
12	1,1-Diphenylethylene	33	26	45	

<sup>*a*</sup> 5 mmol of substrate, 1 mmol EDA (added over 11 h), 1 mol% cat, CH<sub>2</sub>Cl<sub>2</sub> (25 mL), in parentheses, ratio of *trans/cis* products. Yield based on EDA and determined by <sup>1</sup>H-NMR spectroscopy, average of two runs. Mass balance was accounted for by dimethyl maleate and fumarate formation. <sup>*b*</sup> reactions run for 5h with 5 mmol substrate, 1 mmol PhI=NTs, 2 mol% cat, CH<sub>2</sub>Cl<sub>2</sub> (15 mL). Yield based on PhI=NTs and determined by <sup>1</sup>H-NMR spectroscopy, average of two runs.



(entries 2–6), the different yields reflecting the relative reactivity of the olefins.

When furan was used as substrate (Table 2), the reaction afforded not only the cyclopropane, ethyl fumarate and ethyl maleate, but also the two diasteromeric ring-opened dienes (Scheme 2).



#### Scheme 2

In these cyclopropanation reactions, no green or blue color, indicative of an oxidation to a Cu(II) species, was observed. Therefore, we propose that the catalyst resting state is a Cu(I) species. Accordingly, no broadening was observed in the NMR lines in the spectra of the reaction crudes. The same can be said of all the reactions in which EDA serves as carbene source discussed below.

Compound 1 was also active in olefin aziridination<sup>9</sup> employing PhI=NTs as nitrene source (Scheme 3, Table 1, entries 7–12).

 
 Table 2
 Yields of cyclopropane and ring-opened dienes in the Cucatalyzed reactions of furan and EDA

Cat	Addition time	%Cyclopr	ZZ%, ZE%
1	12h	58	2, 14
4	15h	60	12, 12



In this case, addition of the PhI=NTs caused an immediate development of a green color, suggestive of a Cu(II) species as the catalyst resting state.

Next, the known complex [Cu(TPM)(NCMe)]OTf (**2a**) was prepared by reaction of CuOTf and TPM in THF/MeCN, using a slight modification of the method reported by Jonas and Stack.<sup>10</sup> In agreement with these authors, **2a** was found to be quite sensitive to aerobic oxidation. Using **2a** as catalyst in the cyclopropanation of styrene and 1-hexene afforded 57% and 7% respectively of the corresponding cyclopropanes.

Unlike when the tris(pyridyl) methane complex 1 was used as catalyst, now the addition of NaBAr'<sub>4</sub> led to a significant increase of the yield. Such an activation effect has been noted for copper complexes used as catalysts for aziridination reactions by Vedernikov and co-workers.11 These authors found that chloro complexes are poor catalysts for olefin aziridination, and that they can be effectively activated by replacing the chloro ligand by the non-coordinating  $BAr'_4$  anion, because more unsaturated catalysts are so generated. The authors suggest that such species could be tri-coordinated copper(I) complexes. In our case, we have found that the reaction of 2a with NaBAr'<sub>4</sub> afforded [Cu(TPM)(NCMe)]BAr'<sub>4</sub> (2b) which was employed in the cyclopropenation and aziridination reactions (Table 1). In the preparation of 2b from 2a, addition of NaBAr'<sub>4</sub> to a CH<sub>2</sub>Cl<sub>2</sub> solution of 2a causes precipitation of triflate as its sodium salt, insoluble in CH<sub>2</sub>Cl<sub>2</sub>, leaving the triflate-free, more active catalyst 2b.

Interestingly, compound **2b** is more active than **2a**, in spite of the fact that both are tetra-coordinate nitrile-bonded species. The higher activity of **2b** suggests that, although in the case of the tris(pyridyl)methoxymethane compound **2a** the isolated copper complexes feature a nitrile ligand and the triflate is a non-bonded couteranion, in solution, the triflate anion effectively competes with acetonitrile for the copper center, which is rendered more unsaturated in the absence of triflate, that is, in **2b**.

Finally, we explored the activity of the complex [Cu(OTf)(TPN)] (3), previously reported by Marks and Ibers.<sup>12</sup> The presence of acetonitrile in the medium used for the preparation of the tris(pyridyl) amine complex 3 was found to be beneficial, leading to a shorter reaction time and to a more pure compound, free of Cu(II) contamination. However, unlike 1 and 2a, for 3, the isolated product was found to contain no acetonitrile. Therefore, the role of this solvent must be to stabilize and solubilize copper(I) as the cationic tetrakis(acetonitrile) complex, preventing its decomposition in solution before the final TPN complex is formed.

The reaction of styrene with EDA employing **3** (1 mol%) as a catalyst yielded cyclopropane in 49% (ratio *trans* : *cis* 28 : 21). A significant activation was observed upon addition of NaBAr'<sub>4</sub> (98%, ratio *trans* : *cis* 67 : 31), in agreement with the proposal of Marks and Ibers that a copper-bonded triflate is formed. In contrast, in the aziridination of styrene with PhI=NTs as the

nitrene source, a quantitative conversion resulted when **3** was used as catalyst (Table 1, entry 7).

A comparison between the catalytic results of the three families of complexes (TPM, TPC and TPN) shows that, in general, once the Cu-OTf precatalyst was activated by NaBAr'<sub>4</sub>, the latter are the more active. This, and the fact that no previous copper(I) TPN complexes have been structurally characterized, prompted us to isolate and characterize cationic, triflate-free Cu-TPN complexes as BAr'<sub>4</sub> salts. Thus, equimolar amounts of **3** and NaBAr'<sub>4</sub> were allowed to react in THF. After THF evaporation, extraction of the residue in CH<sub>2</sub>Cl<sub>2</sub> and filtration (to eliminate NaOTf) followed by addition of hexane precipitated a white solid. Its <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with a formulation [Cu(TPN)(THF)]BAr'<sub>4</sub> (4), and indicated the equivalence of the three pyridyl groups at room temperature. The chemical shifts of the THF signals in 4 were indistinguishable from those of free THF; however, their intensity, consistent with the presence of one THF molecule per copper atom, did not decrease when 4 was maintained under vacuum several hours. Slow diffusion of hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of 4 afforded crystals, one of which was used for the structural determination by X-ray crystallography. The results, graphically displayed in Fig. 1, indicate that 4 exists in the solid state as the  $[{Cu(TPN)(THF)}_2][BAr'_4]_2$  salt. The dicationic complex is a centrosymmetric dimer, in which each TPN ligand acts as a bidentate chelate towards one of the copper atoms, binding the other in a monodentate manner through the third pyridyl group. Therefore, the TPN ligand acts simultaneously as a chelate and a bridge. A THF molecule completes the pseudotetrahedral coordination environment of each copper atom. Metrical data are unremarkable.

C(14)

N(1)

C(31)

C(15)

Cu(1)

C(4)

C(21)

C(22)

C(23)

C(2)

C(1)

0(1)

N(4) 😡

C(24)

C(13)

C(11)

N(4/

N(2A)

Cu(1A)

N(1A)

O(1A)

C(12)



Since the three pyridyl groups are inequivalent in the solid state structure of **4**, but appear equivalent in the room temperature NMR spectrum, an obvious possibility is the operation of a dynamic process that exchanges the three pyridyl arms. Such dynamic processes are frequent in Cu(I) chemistry. However, the <sup>1</sup>H spectrum of **4** in  $CD_2Cl_2$  did not change when the temperature was lowered to 183 K.

While this does not rule out the possibility of a dynamic process with a very low kinetic barrier, we rather postulate a C<sub>3</sub>-symmetric, monomeric  $[Cu(\kappa^3-TPN)(THF)]^+$  complex as the species in solution for three reasons: (a) its instantaneous structure would be in agreement with the <sup>1</sup>H NMR spectrum, (b) pseudotetrahedral complexes of this type are the ones most often encountered in Cu(I) complexes of tridentate tripodal ligands, and (c) such a complex would be entropically favored over the X-ray characterized dimer. Formation of the latter upon crystallization would be driven by its lower solubility resulting from its higher molecular weight. As a matter of fact, the mononuclear complex  $[Cu(\kappa^3-TPN)(THF)]^+$  was found to be the predominant species in  $CH_2Cl_2$  by ESI-MS (m/z 383). Moreover, in the presence of five equivalents of styrene (the conditions used in catalysis), ESI-MS showed that the monomer  $[Cu(\kappa^3-TPN)(styrene)]^+$  (ESI-MS m/z 415) was the most abundant species in CH<sub>2</sub>Cl<sub>2</sub> solution. The relative intensity of the lines and the separation between them in the signals are consistent with monomeric, monocationic copper complexes.

The catalytic activity of 4 in the reactions mentioned above was the same when the compound was isolated or generated in situ by NaBAr'<sub>4</sub> addition to a solution of **3** in THF. When the catalyst was prepared directly by mixing CuOTf, TPN and NaBAr'<sub>4</sub>, the employment of higher than equimolar amounts of TPN led to a decrease in the yields of cyclopropanes. This fact was attributed to the blocking of labile positions in the copper complex by the excess of ligand, generating a [Cu(TPN)<sub>2</sub>]<sup>+</sup> species. Thus, [Cu(TPN)<sub>2</sub>]OTf was obtained by reaction of [Cu(OTf)], toluene with the equimolar amount of TPN (see Experimental). In the <sup>1</sup>H and <sup>13</sup>C NMR of the product at room temperature, the only signals observable were those of the equivalent pyridyl groups (upon lowering the temperature to 183 K, the signals broadened somewhat but did not split). A structural determination by X-ray diffraction showed that the copper atom was in a tetrahedral geometry (Fig. 2), where each TPN ligand acts as bidentate to the metal center, and the third pyridyl arm remained uncoordinated. This mode of coordination for the TPN was known in some Cu(II) complexes,13 however, 5 is the first example of a Cu(I) complex. As expected, the Cu-N distances in 5 (2.057(3)Å) are longer than in the mentioned Cu(II) complexes (2.020(3)Å in [Cu(TPN)<sub>2</sub>(NCMe)<sub>2</sub>]<sup>2+</sup>, 1.999(3)Å in  $[Cu(OClO_3)_2(TPN)_2])$ .

The reaction of styrene with EDA (added over 15 hours) employing **5** as catalyst (1 mol%) yielded cyclopropanes in 72% (ratio *trans* : *cis* 45 : 27), a yield lower than that obtained with **4**.

Compound **4** was also found to be effective in the cyclopropanation of furan (Table 2), affording, in addition, the two diasteromeric ring-opened dienes.

The addition of a carbene fragment to alkynes affords cyclopropenes, a reaction less studied than cyclopropanation. The first catalysts, based on metallic copper or simple Cu(I) or Cu(II) salts, gave low yields, even at high temperatures.<sup>14</sup> Recently, the group of Pérez (no relation to the present author) reported excellent results with copper(trispyrazolylborate) systems at room temperature.<sup>15</sup> We carried out the catalytic reaction of EDA with alkynes using the



 $\begin{array}{l} \mbox{Fig. 2} \quad \mbox{Thermal ellipsoid plot (30\%) of 5. Selected bond lengths (Å) and angles (°):Cu(1)-N(5) 2.022(3), Cu(1)-N(1) 2.039(3), Cu(1)-N(2) 2.072(3), Cu(1)-N(6) 2.097(3), N(4)-C(11) 1.393(4), N(4)-C(6) 1.420(4), N(4)-C(5) 1.429(4), N(8)-C(31) 1.406(4), N(8)-C(26) 1.429(4), N(8)-C(25) 1.434(4), N(5)-Cu(1)-N(1) 122.31(11), N(5)-Cu(1)-N(2) 122.19(12), N(1)-Cu(1)-N(2) 92.65(11), N(5)-Cu(1)-N(6) 93.60(12), N(1)-Cu(1)-N(6) 117.41(11), N(2)-Cu(1)-N(6) 110.16(11), C(11)-N(4)-C(6) 122.8(3), C(11)-N(4)-C(5) 120.0(3), C(6)-N(4)-C(5) 117.2(3), C(31)-N(8)-C(26) 119.4(2), C(31)-N(8)-C(25) 117.9(3), C(26)-N(8)-C(25) 117.8(3). \end{array}$ 

same methodology than in cyclopropanation, *i.e.* 1 mol% catalyst, room temperature, ratio alkyne : EDA = 5 : 1 in  $CH_2Cl_2$ , and EDA added over 10 hours. The yields are summarized in Table 3.

The performance of **4** in cyclopropanation, aziridination and cyclopropenation reactions prompted us to study its activity for the insertion of carbenes into C–H, O–H and N–H bonds.<sup>16</sup> We explored the C–H insertion reactions of alkanes and ethers (Table 4). Reactions were typically run in neat substrate, except for cyclohexane, hexane and pentane, which required the use of  $CH_2Cl_2$  as a co-solvent in order to solubilize the catalyst. For linear alkanes, secondary C–H bonds were exclusively functionalized with yields similar to those obtained by Pérez.<sup>6</sup> For the aromatic substrates benzene, toluene, and mesitylene, ring-expansion to 7-membered rings (Büchner reaction) occurred exclusively (no insertion took place in the methyl C–H bonds),<sup>17</sup> and mixtures of the different isomers were yielded. For ethylbenzene, carbene insertion at the secondary C–H aliphatic bond was also observed. The yields and distribution of the products are in the range of

 Table 3
 Yields of cyclopropenes in the Cu-catalyzed reactions of listed acetylenes with EDA

Substrate	Yield
Phenylacetylene	27
Diphenylacetylene	31
1-Hexyne	36
3-Hexyne	43
1-Phenyl-1-propyne	26

<sup>*a*</sup> Standard conditions: 5 mmol of substrate, 1 mmol EDA (added over 11 h), 1 mol% **4**, CH<sub>2</sub>Cl<sub>2</sub> (25 mL), a) Yield based on EDA and determined by <sup>1</sup>H-NMR spectroscopy, average of two runs. Mass balance was accounted for by dimethyl maleate and fumarate formation. those of the best copper systems, with a lower charge of catalyst in our case.  $^{\rm 17}$ 

The O–H bonds of alcohols are generally activated preferentially over C–H bonds and insertion is usually preferred over other reactions. Recently Fu<sup>18</sup> and Pérez<sup>19</sup> have reported effective copper-based catalysts. Catalyst **4** was found to be highly active for this reaction, and a low catalyst loading (0.5 mol%) was required. EDA was added in one portion and the alkoxyesters are obtained almost quantitatively (Table 5). To the best of our knowledge, these yields are the highest ever reported.

In the activation of N–H bonds of amines, a problem usually found is the poisoning of the catalyst by amine coordination.<sup>20</sup> We studied the carbene insertion into N–H bonds of primary and secondary amines with **4** as a catalyst (1 mol%) (Table 6). Even when EDA and amine were added in one portion, diethyl fumarate and maleate were not detected. The yields are close to the highest published results.<sup>21</sup> Deactivation of the catalysts due to amine coordination is often a concern in this type of catalysis; in our case, high yields were obtained even for aniline, a primary amine, for which the highest coordinating ability would be expected.

As mentioned above, the position of the  $v_{co}$  bands of  $L_nCu$ -CO complexes has been used to gauge the electronic properties of the L ligands. For TPC and TPM ligands, the LCu– carbonyl complexes have already been synthetized.<sup>8</sup> The compound [Cu(TPN)(CO)]BAr'<sub>4</sub> (6) was prepared by bubbling CO through a solution of 4 (see Experimental). The  $v_{co}$  band appeared at 2108 cm<sup>-1</sup> in KBr, indicating that the copper center in 6 is more electron-deficient than those in the compounds with TPM (2101 cm<sup>-1</sup> in KBr) and TPC (2091 cm<sup>-1</sup> in KBr) ligands. Moreover, the comparison of the  $v_{co}$  values indicates that these cationic compounds with tris(pyridyl) ligands are more electron rich than the neutral complexes with halogenated trispyrazolylborates, probably due to the high electron withdrawing effect of the halogenated substituents in the latter.

## Conclusions

Copper(1) complexes with tris(2-pyridyl)methane, tris(2-pyridyl)methoxymethane and tris(2-pyridyl)amine are efficient catalysts for carbene and nitrene transfer reactions, with activities comparable to those shown by the extensively studied tris(pyrazolyl)borate ligands. Tris(2-pyridyl) amine complexes are the best catalysts, due to a combination of ease of preparation, stability and their susceptibly to activation by  $OTf/BAr'_4$  exchange.

## Experimental

#### General considerations

All experiments were carried out at room temperature under a dinitrogen atmosphere employing Schlenk techniques. The amines and solvents were freshly distilled prior to use.  $CH_2Cl_2$  was dried over  $CaH_2$ . THF and diethyl ether and were dried over Na-benzophenone, and hexane, pentane and toluene were dried over sodium. MeOH, EtOH and <sup>i</sup>PrOH were stored over 4 Å molecular sieves for several hours prior for use as substrates. EDA and the remaining reagents were used as received. PhI=NTs was prepared according to a literature procedure<sup>22</sup> and stored in a Schlenk flask under nitrogen at -20 °C. For slow addition of EDA, a

Substrate <sup>a</sup>	Products	t <sup>b</sup>	Yield
$\bigcirc$	CO <sub>2</sub> Et	5	85%
~~~	CO <sub>2</sub> Et + CO <sub>2</sub> Et	11	45%, 11%
~~~	+ CO <sub>2</sub> Et	11	28%, 34%
	CO <sub>2</sub> Et	20	25%
	$CO_2Et$ $CO_2Et$ $CO_2Et$	20	27%, 14%, 8%
	$CO_2Et$ $CO_2Et$ $CO_2Et$ $CO_2Et$	20	27%, 10%, 12%
	CO <sub>2</sub> Et	20	93%
$\langle \rangle$	CO <sub>2</sub> Et	5	79%
$\sim_0 \sim$	CO <sub>2</sub> Et	5	93%

<sup>*a*</sup> Standard conditions: 20 mL substrate, 1 mol% **4**. Yield based on EDA and determined by <sup>1</sup>H-NMR spectroscopy, average of two runs. Mass balance was accounted for by dimethyl maleate and fumarate formation. <sup>*b*</sup> Time of addition of EDA (hours).

gas-tight syringe mounted on an automatic syringe pump was employed. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AV-400 spectrometer. An internal standard (hexamethylbenzene or 1,3,5-tribromobenzene) was added to each reaction mixture immediately before taking an aliquot. The NMR spectra of all products were consistent with those reported in the literature. Yields were estimated by integration of the <sup>1</sup>H NMR signals of the products relative to the internal standard. TPC,<sup>23</sup> TPM,<sup>10</sup> TPN<sup>24</sup> and NaBAr'<sub>4</sub><sup>25</sup> were prepared according to literature procedures.

**Crystallographic details.** Crystallographic data for **4** and **5** were collected with a Bruker AXS SMART 1000 diffractometer

with graphite monochromatized Mo–K $\alpha$  X-radiation and a CCD area detector. Due to the poor quality of the crystals, data collection was taken only to  $2\theta = 46^{\circ}$ , since the intensity of the reflections was very poor from 40° upwards. Raw frame data were integrated with the SAINT<sup>26</sup> program. A semi-empirical absorption correction was applied with the program SADABS<sup>27</sup> The structure was solved by direct methods and refined against F2 with SHELXTL.<sup>28</sup> All non-hydrogen atoms were refined anisotropically, except for N(1), N(2) and N(4) in the structure of **4**, which had to be kept isotropic since otherwise their ellipsoids went to non-positive-definite during the refinement. An incipient disorder was found to affect some atoms of **4**, which show large

 Table 5
 Results of the 4-catalyzed insertion of the carbene from EDA into O–H bonds of the listed alcohols

Substrate <sup>a</sup>	Product	Yield <sup>t</sup>
МеОН	_OCO2Et	95%
EtOH	CO₂Et	95%
<sup>i</sup> PrOH		88%
Phenol	CO <sub>2</sub> Et	95% <sup>c</sup>

<sup>*a*</sup> standard conditions: 1.1 mmol substrate, 1 mmol EDA added in one portion, 0.5 mmol% **4**, CH<sub>2</sub>Cl<sub>2</sub> (10 mL). <sup>*b*</sup> Yield based on EDA, and determined by <sup>1</sup>H-NMR spectroscopy, average of two runs. Mass balance was accounted for by dimethyl maleate and fumarate formation. <sup>*c*</sup> EDA added over 30 min.

Table 6Results of the 4-catalyzed insertion of the carbene from EDAinto N-H bonds of the listed amines

Substrate <sup>a</sup>	Product	$t_{reac}(h)$	Yield <sup>b</sup>
$\mathbb{NH}_2$	H_N_CO <sub>2</sub> Et	1°	95%
М-н		4	42% <sup>d</sup>
		24	79%
N H H	EtO <sub>2</sub> C	14	95%
N N	↓ ↓	11"	46%
	EtO <sub>2</sub> C		

<sup>*a*</sup> Standard conditions:1 mmol substrate, 1 mmol EDA added in one portion, 0.5 mol% **4**, CH<sub>2</sub>Cl<sub>2</sub> (10 mL). <sup>*b*</sup> Yield determined by <sup>1</sup>H-NMR spectroscopy, average of two runs. Mass balance was accounted for by dimethylmaleate and fumarate formation. <sup>*c*</sup> EDA added over 30 min. <sup>*d*</sup> 1 mol% **4**. <sup>*e*</sup> Time of addition of EDA 11 hours.

ellipsoids. Despite of some attempts of modelling these atoms in split positions, the quality of the results did not improve. This, and the resulting low C–C bond precision, can attributed to the poor quality of the crystal. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter.

Synthesis of [Cu(TPC)(NCMe)]OTf (1). Tris(2-pyridyl)methane<sup>23</sup> (TPC, 0.047 g, 0.193 mmol) was added to a solution of [Cu(OTf)]<sub>2</sub>·toluene (0.050 g, 0.097 mmol) in a mixture of THF/MeCN (20/0.5 mL) causing immediately the precipitation of a white microcrystalline solid, which was washed with hexane  $(3 \times 10 \text{ mL})$  and dried under vacuum. Yield: 0.092 g (93%) <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>): 8.36 [d(4.7) 3H, Hpy], 7.78 [dt (7.7, 1.7), 3H, Hpy], 7.56 [dt (4.7, 1.7), 3H, Hpy], 7.31 [d(7.7), 3H, Hpy], 6.99 [s, 1H, CH] 2.23 [s, 3H, CH<sub>3</sub>CN]. <sup>13</sup>C{1H} NMR(CD<sub>2</sub>Cl<sub>2</sub>): 156.8, 148.8, 146.9, 130.3, 129.2 [s, py], 118.1 [s, CN], 58.6 [s, CH], 2.7 [s, CH<sub>3</sub>CN]. Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>CuF<sub>3</sub>N<sub>4</sub>O<sub>3</sub>S: Calcd.: C, 45.60; H, 3.22; N, 11.20. Found: C, 45.62; H, 3.31; N, 11.23.

Synthesis of [Cu(TPM)(NCMe)]BAr'<sub>4</sub> (2b). To a solution of  $[Cu(OTf)]_2$ ·toluene (0.050 g, 0.097 mmol) in THF (20 mL) tris(2pyridyl)metoxymethane<sup>10</sup> (TPM, 0.053 g, 0.193 mmol) and MeCN (0.5 mL) were added and the mixture was stirred for 30 min. After solvent concentration to *ca.* 2 mL, addition of hexane (10 mL) caused the precipitation of [Cu(TPM)(NCMe)]OTf<sup>10</sup> (2a) as a white solid. 2a was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), NaBAr'<sub>4</sub> (0.171 g, 0.193 mmol) was added, the mixture was stirred for 1 hour and filtered through diatomaceous earth. *In vacuo* concentration to a volume of 2 mL and addition of hexane (10 mL) caused the precipitation of 2b as a white microcrystalline solid, which was washed with hexane (2x 20 mL) and dried under vacuum. Yield: 0.202 g (87%). <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>): 8.65 [s br, 3H, H<sub>py</sub>], 8.10 [s br, 14H, H<sub>o</sub> of Ar'<sub>4</sub> and H<sub>py</sub>], 7.47 [m, 7H, H<sub>p</sub> of Ar'<sub>4</sub> and H<sub>py</sub>], 3.63 [s, 3H, OCH<sub>3</sub>], 2.23 [s, 3H, CH<sub>3</sub>CN].

**Synthesis of [Cu(TPN)(OTf)] (3).** A mixture of  $[Cu(OTf)]_2$ . toluene (0.050 g, 0.097 mmol) and tris(2-pyridyl)amine<sup>24</sup> (TPN, 0.048 g, 0.193 mmol) in THF/MeCN (20/0.5 mL) was stirred until precipitation of a white solid (15 min.), which was washed with hexane and dried in vacuo.<sup>29</sup> Yield: 0.077 g (87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.25 [d(4.9), 3H], 8.10 [dt (8.0, 1.5), 3H], 7.49 [dt (4.9, 1.5), 3H], 7.05 [d (8), 3H]. <sup>13</sup>C{<sup>1</sup>H} NMR(CDCl<sub>3</sub>): 156.8 [s], 153.1 [s], 144.9 [s], 125.4 [s], 123.5 [s]. <sup>19</sup>F NMR (CDCl<sub>3</sub>): -77.19. Anal. Calcd. for C<sub>16</sub>H<sub>12</sub>CuF<sub>3</sub>N<sub>4</sub>O<sub>3</sub>S: Calcd.: C, 41.70; H, 2.62; N, 12.16. Found: C, 41.94; H, 2.78; N, 12.25.

Synthesis of [Cu(TPN)(THF)]<sub>2</sub>(BAr'<sub>4</sub>)<sub>2</sub> (4). A mixture of 3 (0.090 g, 0.193 mmol) and NaBAr'<sub>4</sub> (0.170 g, 0.193 mmol) in THF (20 mL) was stirred for 2 hours and the solvent was removed under vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through diatomaceous earth and concentrated to 2 mL. Addition of hexane caused the precipitation of 4 as a white microcrystalline solid. By slow diffusion of hexane into a concentrated solution of 4 in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C white crystals were obtained, one of which was employed for an X-ray structure determination. Yield: 0.198 g (83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.30–8.05 [m, 3H, H<sub>pv</sub>], 7.80–7.70 [m, 8H, H<sub>o</sub> of Ar'<sub>4</sub>], 7.54–7.39 [m, 7H, H<sub>p</sub> of Ar'<sub>4</sub> and H<sub>py</sub>], 7.25– 7.10 [m, 3H, H<sub>pv</sub>], 6.85–6.60 [m, 3H, H<sub>pv</sub>], 3.77 [m, 4H, CH<sub>2</sub> of THF], 1.87 [m, 4H, CH<sub>2</sub> of THF]. <sup>13</sup>C{<sup>1</sup>H} NMR(CDCl<sub>3</sub>): 162.1  $[c ({}^{1}J_{CB} = 49.9 \text{ Hz}), C_{i} \text{ of } Ar'_{4}], 156.8 [s, C_{py}], 149.1 [s, C_{py}], 135.9$ [s,  $C_{py}$ ], 135.1 [s,  $C_o$  of  $Ar'_4$ ], 129.4 [s,  $C_{py}$ ], 129 [c ( $^2J_{CF}$ = 31.7 Hz),  $C_{\rm m}$  of Ar'<sub>4</sub>], 126.7 [s,  $C_{\rm py}$ ], 123.1 [c ( ${}^{1}J_{\rm CF}$ = 272.4 Hz), CF<sub>3</sub> of Ar'<sub>4</sub>], 117.8 [s, Cp of Ar'<sub>4</sub>], 68.1 [s, C<sub>THF</sub>], 25.9 [s, C<sub>THF</sub>]. Anal. Calcd. for C<sub>51</sub>H<sub>32</sub>BCuF<sub>24</sub>N<sub>4</sub>O: Calcd.: C, 49.12; H, 2.59; N, 4.49. Found: C, 49.24; H, 2.78; N, 4.71.

B) To a solution of  $[Cu(OTf)]_2$ -toluene (0.050 g, 0.097 mmol) in THF (20 mL), TPN (0.048 g, 0.193 mmol) and NaBAr'<sub>4</sub> (0.171 g, 0.193 mmol) were added and the mixture was stirred for 30 min. After removing the solvent, the residue was extracted in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a diatomaceous earth, concentrated to a volume of 2 mL and addition of hexane (10 mL) caused the precipitation of 4 as a white solid. The spectroscopic data matched with that reported above for 4.

Synthesis of  $[Cu(TPN)_2]OTf$  (5). A mixture of  $[Cu(OTf)]_2$ toluene (0.050 g, 0.097 mmol) and tris(2-pyridyl)amine (TPN, 0.096 g, 0.386 mmol) in THF (20 mL) was stirred for 15 min. *In vacuo* concentration to a volume of 5 mL and addition of hexane caused the precipitation of **5** as a yellow solid. Slow diffusion of hexane into a solution of **5** in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C afforded yellow crystals, one of which was employed for an X-ray structure determination. Yield: 0.121 g (89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.61–8.11 [m, 3H], 7.90–7.55 [m, 3H], 7.45–6.85 [m, 6H]. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 154.2 [s br], 148.7 [s br], 139.1 [s br], 121.6 [s br], 120.2 [s br]. Anal. Calcd. for C<sub>31</sub>H<sub>24</sub>CuF<sub>3</sub>N<sub>8</sub>O<sub>3</sub>S: Calcd.: C, 52.54; H, 3.42; N, 15.80. Found: C, 51.23; H, 3.74; N, 16.09.

Synthesis of [Cu(TPN)(CO)]BAr'<sub>4</sub> (6). CO was bubbled through a solution of 4 (0.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) for 30 min. By addition of hexane (20 mL) into this solution, a white microcrystalline solid was obtained, which was washed with hexane and dried under vacuum. This compound decomposed after few hours in CH<sub>2</sub>Cl<sub>2</sub> solution. IR(KBr)  $v_{co}$ (cm<sup>-1</sup>):2108. IR(CH<sub>2</sub>Cl<sub>2</sub>)  $v_{co}$ (cm<sup>-1</sup>):2103. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.10 [d(4.5), 3H], 7.98 [t(7.5), 3H], 7.73 [m, 8H, H<sub>o</sub> of Ar'<sub>4</sub>], 7.56 [m, 4H, H<sub>p</sub> of Ar'<sub>4</sub>], 7.42 [d(8,2), 3H], 7.26 [t(6.2), 3H].

**Cyclopropanation.** A solution of EDA (1 mmol, 0.105 mL) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added over 10 h using a syringe pump to a solution of the corresponding catalyst (0.01 mmol) and the olefin (5 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The solution was stirred for two hours after complete addition of EDA. An internal standard, C<sub>6</sub>Me<sub>6</sub> (0.055 mmol, 9 mg) was added, an aliquot (1 mL) was then filtered through silica gel, and the solution was concentrated to ~0.5 mL. CDCl<sub>3</sub> (0.5 mL) was added and the sample was transferred to an NMR tube. Yields were estimated using <sup>1</sup>H NMR spectroscopy by integration of product resonances relative to the internal standard. Only for the cyclopropane from styrene the signals due to the different diastereomers appeared at sufficiently different chemical shifts so that their integration could be used to obtain an estimation of the *trans/cis* ratio.

Aziridination. To a mixture of the catalyst (0.02 mmol), the olefin (5 mmol), and 4 Å molecular sieves (*ca.* 1 g) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub>, PhI=NTs (1 mmol, 348 mg) was added, and the mixture was stirred until PhI=NTs was completely dissolved (*ca.* 5 hours). An internal standard, C<sub>6</sub>Me<sub>6</sub> (0.055 mmol, 9 mg) was added, an aliquot (1 mL) was filtered through silica gel, and concentrated to ~0.5 mL. CDCl<sub>3</sub> (0.5 mL) was added and the sample was transferred to an NMR tube. Yields were estimated using <sup>1</sup>H NMR spectroscopy by integration of product resonances relative to the internal standard.

**Cyclopropenation.** A solution of EDA (1 mmol, 0.105 mL) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added over 10 h using a syringe pump to a solution containing the catalyst **4** (0.012 g, 0.005 mmol) and the alkyne (5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The solution was stirred for two hours after complete addition of EDA. An internal standard, C<sub>6</sub>Me<sub>6</sub> (0.055 mmol, 9 mg) was added, an aliquot (1 mL) was then filtered through silica gel, and the solution was concentrated to ~0.5 mL, CDCl<sub>3</sub> (0.5 mL) was added and the sample was

transferred to an NMR tube. Yields were estimated using <sup>1</sup>H NMR spectroscopy by integration of product resonances relative to the internal standard.

**Carbene insertion into C–H bonds.** A solution of EDA (1 mmol, 0.105 mL) in substrate (10 mL) was added using a syringe pump over the specified period of time to a Schlenk flask charged with **4** (0.012 g, 0.005 mmol), 10 mL of the substrate and  $CH_2Cl_2$  (10 mL, only for cyclohexane, pentane, and hexane substrates). An internal standard, 1,3,5-tribromobenzene (0.030 mmol, 10 mg) was added, an aliquot (1 mL) was filtered through diatomaceous earth, and the solution was concentrated to ~0.5 mL. CDCl<sub>3</sub> (0.5 mL) was added and the sample was transferred to an NMR tube. Yields were estimated using <sup>1</sup>H NMR spectroscopy by integration of product resonances relative to the internal standard.

**Carbene insertion into O–H bonds.** EDA (1 mmol, 0.105 mL) was added in one portion to a solution of **4** (0.006 g, 0.0025 mmol) and the alcohol (1.1 mmol) in  $CH_2Cl_2$  (10 mL). After 4 hours, an aliquot (0.5 mL) was taken and analyzed as described above, using  $C_6Me_6$  (0.055 mmol, 9 mg) as an internal standard. For phenol, best results were obtained when EDA was added over 30 min.

**Carbene insertion into N–H bonds.** EDA (1 mmol, 0.105 mL) was added in one portion to a solution of **4** (0.012 g, 0.005 mmol) and the amine (1 mmol) in  $CH_2Cl_2$  (10 mL).The mixture was stirred for the specified amount of time, then an aliquot was taken and analyzed as described above using  $C_6Me_6$  (0.055 mmol, 9 mg) as the internal standard for aniline, and 1,3,5-tribromobenzene (0.030 mmol, 10 mg) as the internal standard for the others amines.

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