

Mini Review

The use of polypyrazolylborate copper(I) complexes as catalysts in the conversion of olefins into cyclopropanes, aziridines and epoxides and alkynes into cyclopropenes

M. Mar Díaz-Requejo, Pedro J. Pérez *

Departamento de Química y Ciencia de Materiales, Universidad de Huelva, Carretera de Palos de la Frontera s/n, E-21819 Huelva, Spain

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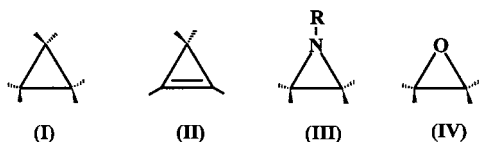
Abstract

Polypyrazolylborate complexes of Cu(I) present catalytic activities towards the carbene, nitrene and oxo transfer reactions to unsaturated substrates to form cyclopropanes, cyclopropenes, aziridines and epoxides. Kinetic studies have led to the proposal of a general mechanism for the cyclopropanation reaction with copper catalysts, a 14-e species being responsible of the catalytic step. Heterogenisation of those complexes on silica gel does not affect their catalytic capabilities under heterogeneous conditions when compared with those in the homogeneous phase. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The transformation of unsaturated substrates into added-value products constitutes one of the main goals in chemistry [1]. Transition metal complexes are very often employed as the catalysts for such reactions, and the development of new, more efficient catalysts attracts the attention of many research groups. One of these reactions is their conversion into three-member rings: cyclopropanes (I), cyclopropenes (II), aziridines (III) and epoxides (IV), compounds that present several properties that make them attractive for their use [2,3]. Thus, the cyclopropane ring appears in natural and non-natural products, and they have importance from a synthetical point of view.

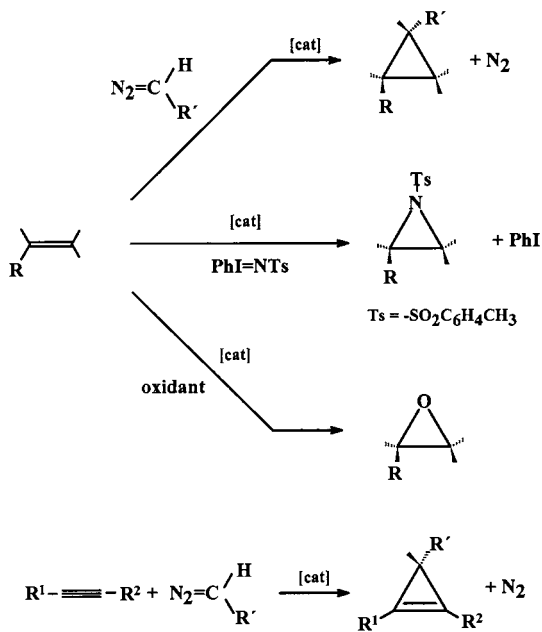


Cyclopropene units are also common in many biomolecules, such as fatty acids and sterols. The aziridines have been employed for years in organic syntheses, and lately the induction of enantiomeric excesses in the formation of this compound has increased the interest in their preparation. The epoxides are known to be starting materials in industry for many other products (ethylenglycol, propylenglycol, chiral diols) [4]. Another recent application has been found in the formation of polymeric materials, in which the oxirane ring is one of the monomers.

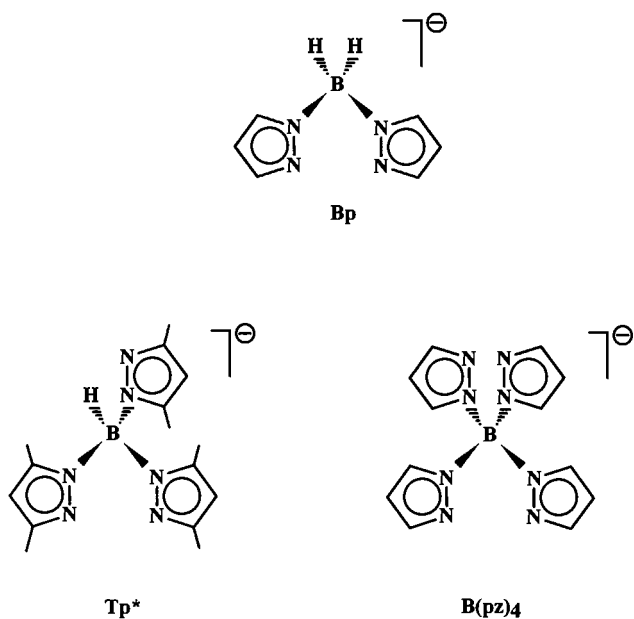
The main routes in the metal-catalyzed conversion of olefins into I–IV are summarised in Scheme 1. Olefin cyclopropanation has been commonly achieved using a diazocompound as the carbene source. Rhodium and copper are the most frequent metals employed, although iron, ruthenium, cobalt and some others are also known to catalyse this reaction. Alkyne cyclopropanation can be performed in a similar way: a diazocompound is employed to generate the carbene moiety that is later transferred to the alkyne via the metal centre, usually with a rhodium-based catalyst. The aziridination of olefins has frequently been compared with the cyclopropanation as similar reactions, in

* Corresponding author.

E-mail address: perez@dqcm.uhu.es (P.J. Pérez).



Scheme 1.



Scheme 2.

Table 1
Styrene cyclopropanation^a with 1–3 as the catalyst precursors

Catalyst precursor	% cyclopropanes ^b	<i>Anti:syn</i> ratio ^b
BpCu (1)	76	75:25
Tp*Cu (2)	80	43:57
(Bpz ₄)Cu (3)	74	78:22

^a [Cu]:[EDA]:[styrene] = 1:50:250.

^b Determined by GC after total consumption of EDA.

the sense that a nitrene group is transferred to the olefin to generate the ring. Copper-based catalysts are among the most effective, and the nitrene source can be an azide (RN₃, that thermally decomposes to give transient nitrene RN groups that further reacts with the metal centre) or alternatively the *p*-(toluenesulfonyl)iminophenyliodinane, PhI=NTs. Finally, the conversion of olefins into epoxides has been described using, among others, titanium, manganese and iron-based catalysts, and with a variety of oxo sources, ranging from hydrogen peroxide to sodium hypochlorite, as well as organic hydroperoxides and peroxosulfates.

The work we present herein constitutes an account of our research [5–10] in the field of olefin and alkyne transformations into three-member rings of the type I–IV, using copper-based catalysts containing polypyrazolylborate ligands [11]. The ligands we have employed in this work (Scheme 2) are the dihydrido-bis(pyrazolyl)borate (Bp), hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) and tetrakispyrazolylborate (Bpz₄). These ligands are anionic, and can act in several co-ordination modes (monohapto, dihapto, trihapto, bisbidentate) [11]. We have tested the catalytic capabilities of their copper(I) complexes towards the conversions of organic substrates into three-member rings. We have dedicated more emphasis to the cyclopropanation reaction, and a complete kinetic study has allowed to propose a reasonable mechanism that could be extended to most of the already reported Cu(I) catalysts. The polypyrazolylborate copper(I) complexes have been supported on silica gel, and the catalytic activities of the heterogenised catalysts have also been studied. The cyclopropanation, aziridination and epoxidation reactions have also been achieved; a comparison between the cyclopropanation and the aziridination reaction in terms of reactive intermediates being also discussed.

2. Olefin cyclopropanation [5–9]

2.1. Olefin cyclopropanation reaction catalysed by BpCu (1), Tp*Cu (2) and (Bpz₄)Cu (3)

The complexes BpCu (1) [12], Tp*Cu (2) [13] and (Bpz₄)Cu (3) [12] were prepared by other groups from direct reaction of copper iodide and the corresponding salt of the polypyrazolylborate ligand. Their structures in solution were described as monomeric, although in the solid state some aggregation may occur. We have tested these complexes as the catalyst precursor for the styrene cyclopropanation reaction, using ethyl diazoacetate as the carbene source. Table 1 displays the results of these experiments, from which we observed that these three copper(I) complexes present catalytic activity towards diazo decomposition and the subsequent

Table 2
Olefin cyclopropanation catalysed by complexes **1** and **5–9**

Catalyst	Styrene ^a		<i>cis</i> -cyclooctene ^b		1-Hexene ^b	
	Yield ^{c d}	<i>Syn:Anti</i> ^d	Yield ^{c d}	<i>Syn:Anti</i> ^d	Yield ^{c d}	<i>Syn:Anti</i> ^d
1	58	25:75	71	20:80	58	26:74
5	60	25:75	60	20:80	41	26:74
6	60	25:75	41	18:82	32	26:74
7	64	25:75	67	20:80	41	28:72
8	65	25:75	74	22:78	54	28:72
9	64	25:75	54	20:80	42	26:74

^a [Cu]:EDA:olefin ratio of 1:100:500.

^b [Cu]:EDA:olefin ratio of 1:25:150.

^c Based in ethyldiazoacetate.

^d Determined by GC after total consumption of EDA.

cyclopropane formation. The yields appeared in the range 75–80% of cyclopropanes relative to the final mixture of products (diethyl fumarate and maleate accounted for the total amount of EDA used). It is worth to mention that these experiments were carried out upon adding in one portion the entire EDA reagent, thus avoiding the use of slow addition devices.

The diastereoselectivity is very similar for **1** and **3**, nearly 3:1 favouring the anti isomer. In the case of **2**, a 43:57 ratio was observed. When the ethylene complex $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ (**4**) [14] was employed as the catalyst precursor, the same yield and diastereoselectivity were observed. NMR experiments showed that when **4** is dissolved under a nitrogen atmosphere, loss of ethylene to give **2** was observed, in good accord with previous reports [14]. In the presence of styrene, both complexes gave rise to a new pattern of signals that were assigned to $\text{Tp}^*\text{Cu}(\text{PhCH}=\text{CH}_2)_n$ [5]. This highly fluxional species could not be fully characterised in situ. Thus, **2** and **4** could be alternatively employed as the catalyst precursor.

Since complexes **1–3** were employed as the precatalyst, we decided to study the possible similarities between them during the catalytic reaction. The BpCu complex had been proposed to display a 14-e structure, probably oligomeric, since the Bp_2^{Me} and $\text{Bp}^{\text{t-Bu}}$ analogues have been described and structurally characterised by Tolman and co-workers as oligomeric and dimeric, respectively [15]. The Tp^*Cu complex has also been characterised by X-ray in the solid state [13]: a dimer had been proposed to explain its geometry. The structure of the tetrakispyrazolylborate complex has not been reported, although a tetrameric unit has been proposed based on molecular weight in solution [12]. In our hands, the NMR spectra of complexes **1–4** in the presence of styrene showed the co-ordination of the olefin to the metal centre, and the formation of fluxional species as the result of fast exchange of styrene. This is in agreement with seminal work by Kochi et al. [16] that assessed the role of the olefin co-ordination to

the copper centre in the metal-catalysed diazodecomposition reaction. It is clear for us that these olefin complexes constitute the catalyst resting state in this system. But the parallelism between the three catalysts is quite complicated to be established. If we assume that an 18-e structure could be reached upon olefin co-ordination, there is only one possibility for **1** if the Bp ligand is acting in a dihapto fashion. However, the cases of Tp^* and Bp_z are not that simple. They could act as trihapto or as dihapto, and the number of olefin ligands could, respectively, be one or two. In fact, there is still one more possibility: the non-coordinated pyrazolyl rings in the latter could be bounded to another copper centre, this ligand acting in a bisbidentate mode. Nevertheless, considering the large excess of olefin employed, this option can be discarded.

2.2. Olefin cyclopropanation reaction catalysed by BpCuL ($L = \text{phosphine, amine}$)

In order to obtain information with comparable ligands, thus avoiding the dissimilarities between the mentioned polypyrazolylborate complexes, we prepared a series of BpCu-derived complexes with P- or N-donor atoms. The addition of one molar equivalent of 1,2-bis(diphenylphosphino)ethane (dppe) or bipyridine (bipy) to BpCu afforded the 18-e complexes $\text{BpCu}(L)$ ($L = \text{bipy}$, (**5**); $L = \text{dppe}$, (**6**)). The addition of a bulkier phosphine such as PCy_3 only gave the 16-e product, $\text{BpCu}(\text{PCy}_3)$ (**7**). Finally, the addition of two equivalents of monodentate PPh_3 or pyridine gave the 18-e complexes $\text{BpCu}(L)_2$ ($L = \text{PPh}_3$, (**8**); $L = \text{py}$, (**9**)). We employed these complexes as the catalyst precursor for the general olefin cyclopropanation reaction, and the results are displayed in Table 2.

These Cu(I) complexes displayed a moderate catalytic activity. However, the important information stands of the similarities found with all the precatalysts regarding the yield and the diastereoselectivity. For each olefin, it seems that complexes **1** and **5–9** induced

the same degree of transformation as well as a similar diastereoselection, despite the differences in the electronic and steric effects of the ligands attached to the BpCu moiety. However, it is a well-known feature that the steric effect is not very pronounced in this reaction for copper-based catalysts [1]. Because of this, we carried out competition experiments with *p*-substituted styrenes, as a probe for the existence of noticeable electronic effects during the catalytic transformation. An equimolar mixture of styrene and a *p*-substituted styrene was reacted with EDA in the presence of catalytic amounts of **1** and **5–9**. Fig. 1 shows the Hammett's plot for the results obtained with **1**. The presence of electron-donating groups in the olefin reagent favoured the formation of the corresponding cyclopropane, whereas electron-withdrawing groups induced the opposite effect. This was in accord with the already proposed, by other authors, existence of an electrophilic metal–carbene intermediate resulting from the interaction of the metal centre and the diazocarbene.

But the important information came out of the results obtained with complexes **5–9**: a set of very close values of ρ (-1.10 ± 0.13 (**5**), -1.03 ± 0.12 (**6**), -0.99 ± 0.09 (**7**), -1.23 ± 0.19 (**8**) and -1.14 ± 0.4 (**9**)) can be interpreted as a consequence of an almost non-existent electronic effect in this reaction. In addition, this is quite difficult to explain if we consider the strong differences in electronics between the ligands **5–9**. An alternative explanation could invoke the existence of a common active species that would account for this similarity in the ρ values. This common fragment is the BpCu complex, that could be independently employed or in addition to the referred P- and N-ligands. Thus, pre-equilibrium dissociation between the BpCu fragment and the corresponding ligand must occur previously to the metal–carbene intermediate formation. This is in accord

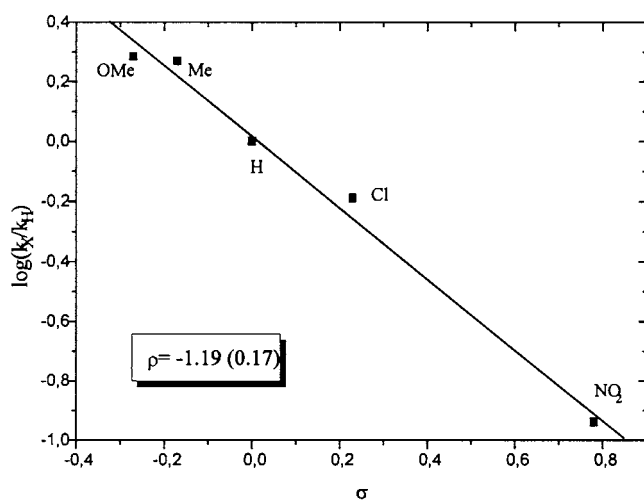
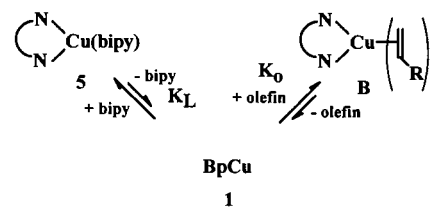


Fig. 1. Hammett $\sigma\rho$ correlation for the relative rates of cyclopropanation with BpCu (**1**) as the precatalyst ($\rho = -1.19(0.17)$). Errors are given at 95% confidence limits.

with the observation of free bipy ligand in the methylene chloride solutions of BpCu(bipy) (**5**). When solutions of this complex were analysed by GC, it was possible to quantify the exact amount of bipy ligand in solution, and the dissociation equilibrium constant for **5** was calculated as 4.5×10^{-4} [8].

With the collected data, it was possible to propose the existence of pre-equilibria before the catalytic reaction occurs (Scheme 3). Thus, if complex **1** was employed as the cyclopropanation catalyst, some of it existed as an olefin–copper complex (**B**). On the other hand, when complexes **5–9** were employed as the catalyst precursors, then a dissociation equilibrium took place, and only a portion of the initially added amount of copper was doing the real catalysis, depending of the value of the equilibrium constant. This scheme provided also a route to obtain the value of K_O [8]. When a solution of **5** was treated with 300 equivalents of styrene and the system was stirred for several hours to reach the equilibrium position, free bipy was detected and quantified by GC. From this, and with the above value of K_L , it was possible to estimate the value of K_O as 56 [8].

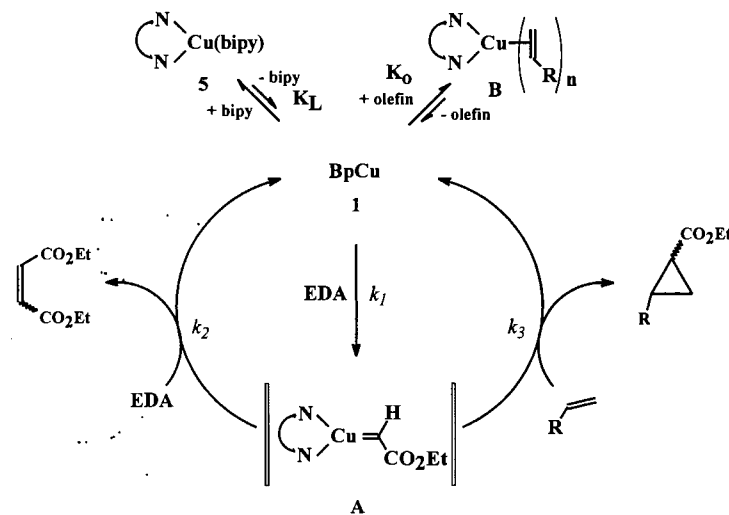


Scheme 3.

2.3. Kinetic studies [8]

The proposed pre-equilibria supposed the existence of constants K_L and K_O . In addition, the conversion of EDA and olefin into cyclopropanes or alternatively in diethyl fumarate and maleate depended of kinetic constants that were yet unknown. Scheme 4 summarises an overall reaction pathway that includes both those equilibria as well as the EDA decomposition reactions: its dimerisation and the cyclopropane formation.

A complete kinetic study [8], that cannot be explained here in detail, have led to the knowledge of k_1 ($51.9 \pm 5.4 \text{ M}^{-1} \text{ min}^{-1}$), k_2/k_3 (1.51 ± 0.12), K_L (3.43×10^{-4}) and K_O (77 ± 29). However, more interesting is the reinforcement of the proposal of a 14-e complex, BpCu, as the real catalyst. This constituted a crucial point in this work, due to further applications in enantioselective cyclopropanation reaction. If a 14-e species is responsible for the catalytic transformation, the enantioselection could be due only to one bidentate ligand. This had also been proposed by Pfaltz and co-workers [17], that had discovered that a (semicorrine) Cu(I) complex displayed identical catalytic activity (yield, ee) that the Cu(II) precursor containing two semicorrine ligands per copper centre.



Scheme 4.

A kinetic study was also carried out with the complex $[\text{Cu}(\text{bipy})_2\text{X}]$ ($\text{X} = \text{I}$, **10a**, $\text{X} = \text{OTf}$, **10b**) as a model for the in situ generated catalyst by Evans' method [18]: CuOTf was reacted with two equivalents of the chiral ligand (bisoxazoline, bipyridine, etc.) previous to the catalytic reaction. GC studies showed that at least 95% of complex **10a** dissociated in solution to one bipy ligand. This complex catalysed the EDA decomposition reaction, a transformation that was dramatically retarded upon adding free iodide. These data were interpreted in the following manner, as depicted in Scheme 5. The 18-e complex **10a** equilibrates with two complexes with one bipy ligands: *C* (iodide bonded to copper) and *D* (iodide as the counter ion). Iodide inhibition supported the formulation of *D* as the catalytic species to react with EDA, the copper complex $[\text{Cu}(\text{bipy})]^+$ (*D*) being isoelectronic with BpCu (**1**).

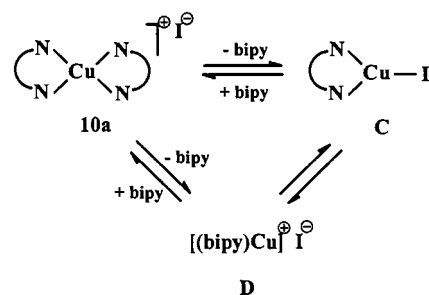
The final test came out from the direct use of a bisoxazoline ligand and Evans' method. We monitored the consumption of EDA with time using mixtures of CuOTf and the corresponding ligand (bipy, bisoxazoline) in different ratios, as shown in Table 3.

The fastest conversions correspond to CuOTf ('naked' copper) and the addition of ligand retarded the process. Only when two equivalents of ligand per Cu were added, the reaction rate diminished considerably, meaning that no more free CuOTf was available. The obtained values for the reaction rate constants with bipy and bisoxazoline are nearly identical. Thus, we proposed that the ligand dissociation equilibria explained for the bipy system also applied for the chiral system, and therefore the induction of enantioselectivity could be due to a 14-e species of type $[(\text{bisoxazoline})\text{Cu}]^+$. Schemes 6 and 7 display the general reaction pathways for the copper-mediated cyclopropanation of olefins. The former corresponds to anionic ligands (providing neutral Cu complexes) whereas the latter

finds application with neutral ligands (affording cationic intermediates).

2.4. Olefin cyclopropanation under heterogeneous conditions [9]

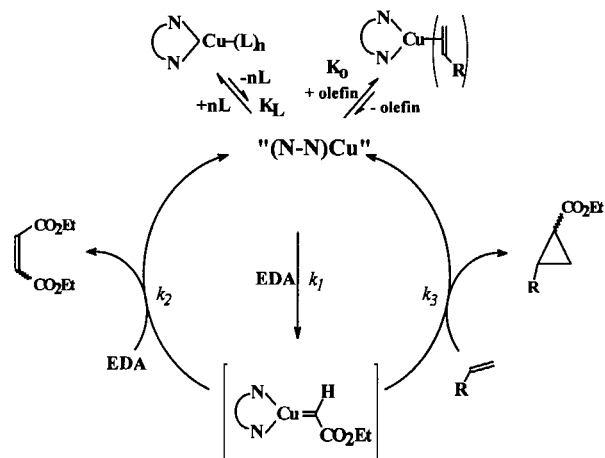
The complexes **1–3** could be supported on silica-gel using the common impregnation technique. Air-sensitive solids were obtained, and their catalytic activities towards the cyclopropanation reaction were tested. Table 4 shows the results of these experiments, that



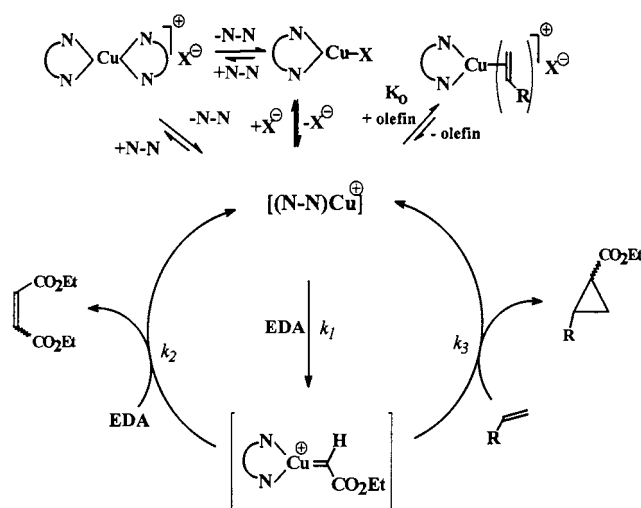
Scheme 5.

Table 3
Observed rate constants for the styrene cyclopropanation reaction in the presence of mixture of CuOTf and bidentate ligands

Equivalent of ligand/equivalent of CuOTf	k_{obs} (min^{-1})	
	Bipy	Bis(oxazoline)
0	2.16	2.16
0.5	1.22	1.24
1	0.989	1.12
1.5	0.254	0.220
2	0.0135	0.0138



Scheme 6. Reaction pathway with anionic ligands



Scheme 7. Reaction pathway with neutral ligands

Table 4
Styrene cyclopropanation^a using 1–3 supported on silica gel

Catalyst precursor (SiO ₂ supported)	% cyclopropanes ^{b,c}	<i>Anti:syn</i> ratio ^c
BpCu (1)	90	54:46
Tp*Cu (2)	80	46:54
(Bpz ₄)Cu (3)	80	64:36

^a Petroleum ether was employed as the solvent reaction.^b [Cu]:[EDA]:[styrene] = 1:50:250.^c Determined by GC after total consumption of EDA.

should be compared with those exposed in Table 1. Petroleum ether was the preferred solvent since metal-leaching studies revealed that Cu loss is minimised in this solvent. The heterogeneous system provided slightly higher yields and similar diastereoselectivities than the homogeneous case. However, perhaps more interesting could be the recycling and reuse of the

catalyst that can be easily separated from the reaction mixture by filtration. We have performed consecutive catalytic cycles in which the same catalyst was recovered and reused for five or ten cycles. The observed activity and diastereoselectivity were constant along this study. Fig. 2 shows the variation of these parameters for the conversion of styrene in the corresponding cyclopropanes, using supported **2** as the catalyst precursor. Each cycle consisted of a ca 1:1000:5000 Cu:EDA:styrene ratio, the total conversion after five cycles being of 5000 equivalents of EDA relative to Cu supported. Further studies have revealed that these complexes can be supported in other solids such basic or acid alumina, magnesium dichloride or titanium dioxide, and they all present catalytic activity in this carbene transfer reaction, although the reaction rates are much lower than those in silica gel [19].

One important feature in these transformations stands on the complex–support interaction. Since the adsorption of metal complexes usually involves the existence of a certain metal–surface linkage, this fact could affect the catalytic activity. However, the similarities between the homogeneous and the heterogeneous systems with these copper complexes called our attention on the possibility of a copper centre free of such interaction, at least during the catalytic cycle. In order to obtain information about the electronic effects that a Cu–surface interaction could induce, we have run competition experiments with *p*-substituted styrenes, with supported complexes, and with different solvents. Fig. 3 shows the Hammett's plot of two experiments carried out with supported **2** using methylene chloride and petroleum ether as the solvent, as well as a third experiment in the homogeneous phase with **2** as the catalyst. The variation was nearly identical, and followed a trend similar to the already commented experiment with BpCu (**1**). Thus, we could conclude that (i) an electrophilic carbene was involved in these transfor-

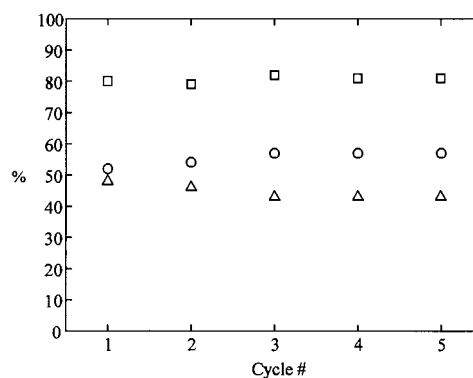


Fig. 2. Styrene cyclopropanation using silica gel-absorbed complex **2**, recovering and reusing the supported catalyst: (□) yield of cyclopropanes (*syn* + *anti*); (○) percentage of the *anti* isomer in the mixture of cyclopropanes; (△) percentage of the *syn* isomer in the mixture of cyclopropanes.

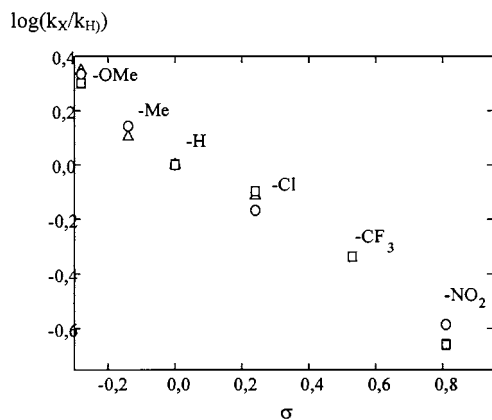


Fig. 3. Hammett plot for the competition experiments with para-substituted styrenes using **2** as the catalyst: (O) heterogeneous conditions, with petroleum ether as solvent; (Δ) heterogeneous conditions, with methylene chloride as solvent; (\square) homogeneous conditions, with methylene chloride as solvent.

Table 5
Alkyne cyclopropanation catalysed by $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ ^a

Alkyne ^b	% cyclopropene ^c
1-Hexyne	47
3-Hexyne	41
1-Phenyl-1-propyne	64

^a 1 mol % of catalyst used, relative to EDA.

^b Alkynes were distilled before use. A fivefold excess relative to EDA was used.

^c Products were characterised by NMR spectroscopy and determined by ¹H-NMR analyses at the end of the reactions.

Table 6
Olefin aziridination catalysed by $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ ^a

Olefin ^b	% yield ^c
Styrene	90
cis-cyclooctene	75
1-Hexene	40

^a 5 mol % of catalyst used, relative to PhI=NTs.

^b A ten-fold excess of the olefine was employed.

^c Products were characterised by NMR spectroscopy. Isolated yields after crystallization.

mations in the heterogeneous phase; and (ii) the copper centre environment in both cases are quite similar, thus avoiding the proposal of any Cu–surface interaction at least during the catalytic reaction. Work currently under progress in our laboratory seems to favour the existence of a possible interaction that does not affect the catalytic conversion but regulates the reaction rate [20].

3. Alkyne cyclopropanation [5]

The catalytic capabilities of these polypyrazolylborate complexes towards the carbene transfer reaction could also be used for the conversion of alkynes into the corresponding cyclopropenes. Thus, the complexes Tp^*Cu (**2**) or alternatively $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ (**4**) were employed as the catalyst precursor in the reaction of 1-hexyne, 3-hexyne or 1-phenyl-1-propyne with EDA. The results are shown in Table 5. Although the yields could appear to be moderate to low, it is worth to mention that previous copper-based catalysts for these transformations required the use of higher temperatures (90–140°C) for conversion in the range of 30–75% for disubstituted alkynes and 20% for terminal alkynes [21].

The use of complexes **1** and **3** as catalysts precursors has also been tested, the yields being similar to those obtained with **2**, but the reaction rate in the case of **1** being considerably slower than with the Tp^* ligand [22].

4. Olefin aziridination [5,6]

The catalytic activity of the aforementioned complexes were not restricted to carbene–transfer reactions. Similarly to other copper-based catalysts, we tested the possibilities of complex $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ (or alternatively Tp^*Cu) in the olefin aziridination reaction, using the reagent PhINTs ((*p*-toluensulfonyl)iminophenyliodine) [23] as the nitrene source. Styrene, *cis*-cyclooctene and 1-hexene were converted in the corresponding aziridines in different yields, ranging from 90% (styrene) to 40% (1-hexene), referred as isolated crystalline materials (Table 6).

This system gave us the possibility of studying the use of the same precatalyst Tp^*Cu or its ethylene adduct $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ for both transformations: the cyclopropanation and the aziridination reactions. In addition to the already commented competition experiments with *p*-substituted styrenes in the former, we also carried out similar experiments in the latter. The differences between both processes appeared immediately. In the cyclopropanation reaction, electron-donating groups favoured the transformation, the opposite effect being observed with electron-withdrawing groups. Nevertheless, for the aziridination case, every *p*-substituted styrene favoured the reaction compared with the styrene. Fig. 4 shows these results, only the cyclopropanation data being fitted into a Hammett's linear correlation, with a ρ value of -0.85 ± 0.07 . This was in accord with the proposition of an electrophilic metal–carbene complex intermediate [24].

The observed trend in the aziridination reaction required a different approach. Despite the proposed analogy between these two reactions, some differences could

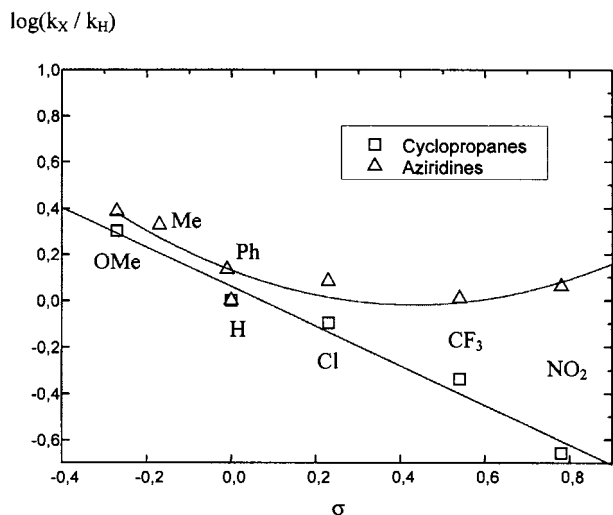
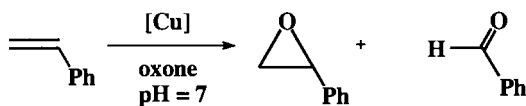


Fig. 4. Hammett plot for the competition experiments with *para*-substituted styrenes using **2** as the catalyst: (□) cyclopropanation reaction; (△) aziridination reaction.



Scheme 8.

Table 7
Epoxidation of styrene catalysed by complexes **1** and **2**

Catalyst	Styrene oxide ^a	PhCHO ^a	Yield ^b
BpCu	> 85	< 5	70
Tp*Cu	> 90	< 5	60

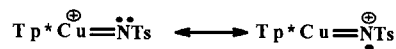
^a Quantified after 18 h by GC, % mol of the products.

^b Based in oxidant.

be observed. For example, UV–vis studies provided data about the existence of Cu(II) in the reaction mixture for the aziridination case whereas no oxidation from Cu(I) was detected in the cyclopropanation reaction. The appearance of this paramagnetic species in the former led us to think about the involvement of radical intermediates. Since no fit was possible with different, simple Hammett-type σ scales, we tried a dual-parameter equation that involved polar and radical contributions [25]:

$$\log(k_X/k_H) = \rho^+ \sigma^+ + \rho^\bullet \sigma^\bullet \quad (1)$$

The experimental data could be fitted to that equation upon iteration of the ρ^+ and ρ^\bullet , that led to the best values of $\rho^+ = -0.28$ and $\rho^\bullet = +0.34$. Thus, polar and radical effects must be considered when proposing an intermediate. Based on Jacobsen's work [26], we proposed the following electrophilic, as well as radical nitrene, as the species responsible of the nitrene group transfer from the metal to the olefin.



5. Olefin epoxidation [10]

Despite the noticeable number of copper-based catalysts reported in the literature for the already-commented transformations, there are only few known copper catalyst for the oxidation of olefins into the corresponding epoxides. We have tested the catalytic capabilities of the complexes **1** and **2** in the reaction of styrene with oxone, a well-known oxo transfer agent Scheme 8. The results are shown in Table 7. Phenylacetaldehyde was also formed in addition to styrene oxide, and the overall yield, based in oxidant, accounted for ca 70%. It is worth to mention the biphasic character of this transformation, since the water–acetonitrile–olefin gave two separate phases. However, catalysis was performed without any phase-transfer catalyst.

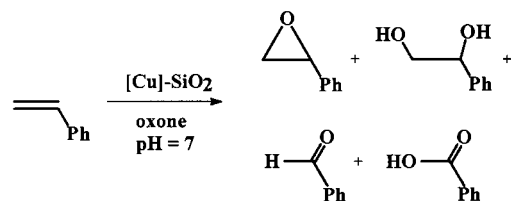
As mentioned above, complexes **1** and **2** are easily supported on silica gel. We have also carried out the catalytic epoxidation reaction with these solid catalysts, the results being shown in Table 8. In this case, after 6 h stirring, four different products were identified from the reaction mixture: styrene oxide, 1-phenylethanediol, benzaldehyde and benzoic acid (Scheme 9). The appearance of 1-phenylethanediol was a consequence of the epoxide ring opening reaction due to the acidic nature of the silica gel. This reaction was inhibited in the homogeneous system using a neutralised reaction medium. This means that the amount of epoxide and epoxide-derived formed was in the range 75–85%, close to the values under homogeneous conditions. Again, the heterogenisation of the homogeneous system does not considerably affect the catalytic capabilities of the copper centre.

Table 8
Epoxidation of styrene catalysed by complexes **1** and **2** supported on silica gel

Catalyst	Styrene oxide ^a	1-Phenyl-ethanediol ^a	PhCHO ^a	PhCOOH ^a	Yield ^b
BpCu	28	38	22	11	57
Tp*Cu	17	70	3	10	68

^a Quantified after 6 h by GC, % mol of the products. Average of three cycles.

^b Based in oxidant.



Scheme 9.

Thus, copper(I) complexes containing polypyrazolylborate ligands presented catalytic activity towards the epoxidation reaction, as they did with the olefin cyclopropanation and aziridination reaction. These catalysts can operate under both homogeneous and heterogeneous conditions, with no significant differences when moving from the former to the latter, and thus achieving the well-known advantages of the recycling and reuse of the catalyst in the heterogeneous system.

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