BpCu-Catalyzed Cyclopropanation of Olefins: A Simple System That Operates under Homogeneous and Heterogeneous Conditions (Bp = Dihydridobis(pyrazolyl)borate)†

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The complexes BpCu (**1**), BpCuL (L = bipy, **2**; L = $Ph_2PCH_2CH_2PPh_2$, **3**; L = PCy_3, **4**) and $BpCuL_2$ (L = py, **5**; L = PPh_3, **6**) catalyze the cyclopropanation of olefins in moderate to high yields in the homogeneous phase. These compounds can also be used under heterogeneous conditions, when supported on silica gel. Complex **1** converts an equimolar mixture of an olefin (styrene, *cis*-cyclooctene, 1-hexene) and ethyl diazoacetate in the corresponding cyclopropanes in high yield with no excess of olefin employed. For the heterogeneous system, the catalysts can be recovered and reused several times (6−12 cycles) up to ca. 1000 turnovers. The data available suggest the existence of a common active species: the 14-electron BpCu fragment **1**. These data consist of competition experiments with para-substituted styrenes as well as kinetic studies carried out in the presence and in the absence of the alkene.

Introduction

Metal-catalyzed cyclopropanation of olefins, using diazo compounds as the carbene source, seems to be restricted to a few transition-metal-based systems:[1−3] among them, rhodium and copper appear as the elements of choice for this type of transformation. Several systems with both high diastereo- and enantioselectivities have been reported in the past decade using those metals.[2] Although rhodium-based systems have been extensively studied and usually afford cyclopropanes in better yields and selectivities, those of copper present the incentive of a low cost for potential use in industry. Copper-bronze is employed in the production of permethric acid, whereas copper(II) complexes containing Schiff bases are used in the commercial synthesis of cilastatin, an antibiotic precursor.[4] A general problem in metal-catalyzed olefin cyclopropanation is the need for a large excess of the olefin to avoid the formation of undesired products due to decomposition of the diazo compound. In addition to this, catalyst recycling from the reaction mixture is difficult to achieve. We herein report an inexpensive, copper-based system for olefin cyclopropanation that avoids the outlined drawbacks. It provides cyclopropanes in moderate to high yields with small olefin excess, and it is usable under both homogeneous and heterogeneous conditions. In the heterogeneous case, the catalyst can be reused several times with no loss of activity or stereoselectivity being observed.

Results and Discussion

A. Synthesis of the Catalyst Precursors BpCu (1), BpCuL (2−4), and $BpCuL_2$ (5, 6). Very recently, Tolman et al. have reported[5] the synthesis and structural characterization of 14-electron complexes of composition Bp′Cu (Bp′ = dihydridobis(3,5-dimethyl-1-pyrazolyl)borate, Bp^{Me_2}; Bp′ = dihydridobis(3-*tert*-butyl-1-pyrazolyl)borate, Bp^{t-Bu}). Following this preparation, we have synthesized the related complex BpCu (**1**; Bp = dihydridobis(pyrazolyl)borate), by direct reaction of copper(I) iodide and the potassium salt of the dihydridobis(pyrazolyl)borate ligand (Bp). The NMR spectra of complex **1** show the typical resonances for the coordinated bis(pyrazolyl)borate group. Tolman has reported the X-ray structure of the aforementioned Bp′Cu complexes,[5] showing a dimeric nature for the *tert*-butyl derivative and an oligomeric structure for the dimethyl derivative. Attempts to crystallize complex **1** as single crystals have failed: it decomposes with time

† Dedicated to Professor Ernesto Carmona on the occasion of his 50th birthday.

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(3) Other metals such as iron, palladium, or ruthenium have also been found to promote the addition of a carbene moiety to the carbon−carbon double bond. See for example: (a) Wolf, J. R.; Hamaker, C. G.; Djukic, J.-P.; Kodadek, T.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 9124. (b) Galardon, E.; Le Maux, P.; Simonneaux, G. *Chem. Commun.* **1997**, 927. (c) Lo, W.-Ch.; Che, Ch.-M.; Cheng, K.-F.; Mak, T. C. W. *Chem. Commun.* **1997**, 1205. (d) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1987.

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to give bluish solutions, even at −30 °C. This compound is somewhat unstable in solution compared with the related substituted-pyrazolyl complexes. In the presence of excess olefin, their solutions are stable enough to be employed for days without any observable decomposition. NMR studies have shown the existence of a highly fluxional Cu−olefin species, but the structure of this compound remains unclear.

The addition of Lewis bases to acetonitrile solutions of complex **1** leads to the isolation of 18-electron species of general formula BpCuL (L = bipyridine (bipy), **2**; L = $Ph_2PCH_2CH_2PPh_2$, **3**) and $BpCuL_2$ (L = pyridine (py), **5**; L = PPh_3, **6**). Only in the case of the tricyclohexylphosphine, has a 16 electron complex of composition $BpCu(PCy_3)$ (**4**) been obtained (eqs 1 and 2).

$$\mathrm{BpCu} + \mathrm{L} \rightarrow \underset{\mathbf{2-4}}{\mathrm{BpCuL}} \qquad (1)$$

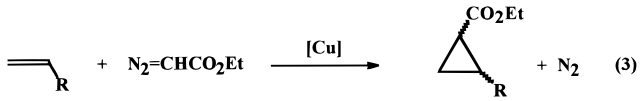
L = bipy (**2**), dppe (**3**), PCy_3 (**4**)

$$\mathrm{BpCu} + 2\mathrm{L} \rightarrow \underset{\mathbf{5,6}}{\mathrm{BpCuL_2}} \qquad (2)$$

L = py (**5**), PPh_3 (**6**)

Complexes **2**−**6** have been spectroscopically and analytically characterized, their NMR spectra showing the resonances for the Bp group as well as those for the corresponding ligand L (see Experimental Section). The proposal of an 18-electron structure for complex **3**, BpCu(dppe), stems from the fact that the triphenylphosphine derivative $BpCu(PPh_3)_2$ (**6**) contains two phosphine groups per copper center. This assumption can also be extended to the bipy adduct (**3**). However, the collected spectroscopic and analytical data for compound **4**, $BpCu(PCy_3)$, are only in accord with the incorporation of one phosphine group per copper atom, probably due to the well-known steric requirements of that ligand.

B. Olefin Cyclopropanation Catalyzed by Complexes 1−6 under Homogeneous Conditions. We have studied the catalytic capabilities of the complexes **1**−**6** toward the olefin cyclopropanation reaction (eq 3).



This transformation is usually accomplished by slow addition of a solution of the diazo compound to the catalyst-containing olefin solution. To avoid this inconvenience, we have performed these reactions by simultaneous addition of the ethyl diazoacetate and the corresponding olefin to the solutions of complexes **1**−**6**. Results are displayed in Table 1. The activities of these compounds as cyclopropanation catalysts have been measured by comparing these results with those obtained for other reported catalytic systems under the same conditions. A 1:5 EDA−styrene mixture was added in one portion to a solution with the corresponding catalyst precursor: rhodium, copper, and palladium were used as described in the Experimental Section. The results are shown in Table 2. The well-known catalysts $Rh_2(OOCCH_3)_4$ and $PdCl_2(PPh_3)_2$ provided higher yields than **1**, this Bp derivative leading to more cyclopropane products than other copper(I) catalysts such as CuOTf and $[Cu(NCMe)_4]^+$. Moreover, the highest *anti*/*syn* stereoselectivity has been achieved with the copper derivatives **1**−**6** and $[Cu(NCMe)_4]^+$.

Table 1. Homogeneous Olefin Cyclopropanation Catalyzed by Complexes 1−6[a]

entry no.	catalyst	styrene[b] yield[d,e]	styrene[b] *syn*:*anti*[e]	*cis*-cyclooctene[c] yield[d,e]	*cis*-cyclooctene[c] *syn*:*anti*[e]	1-hexene[c] yield[d,e]	1-hexene[c] *syn*:*anti*[e]
1	**1**	58	25:75	71	20:80	58	26:74
2	**2**	60	25:75	60	20:80	41	26:74
3	**3**	60	25:75	41	18:82	32	26:74
4	**4**	64	25:75	67	20:80	41	28:72
5	**5**	65	25:75	74	22:78	54	28:72
6	**6**	64	25:75	54	20:80	42	26:74

[a] See Experimental Section for details. [b] [Cu]:EDA:olefin ratio of 1:100:500. [c] [Cu]:EDA:olefin ratio of 1:25:150. [d] Based on ethyl diazoacetate. [e] Determined by GC after total consumption of EDA.

Table 2. Styrene Cyclopropanation[a] Catalyzed by Several Transition-Metal Complexes

catalyst	amt of cyclopropane (%)[b]	EDA-based yield (%)[b]	stereoselectivity (*anti*/*syn*)[b]
$Rh_2(OOCCH_3)_4$	84	72	1.56
$PdCl_2(PPh_3)_2$	84	72	1.40
CuOTf	74	58	1.90
$[Cu(NCMe)_4]^+$	56	38	3.0
$Tp'Cu(C_2H_4)$	80	66	0.90
BpCu	76	61	3.0

[a] 1 mol % of the catalyst referred to EDA; 1:5 EDA:styrene ratio employed. See Experimental Section for details. [b] Determined by GC after total consumption of EDA.

We have also carried out this transformation by following the common procedure of EDA slow addition. As expected, the yields are higher in this case (Table 3), the improvement being dependent on the addition time. Thus, styrene is converted into the corresponding cyclopropanes in 64% yield (relative to EDA, i.e., 78% cyclopropanes + 22% of diethyl fumarate and maleate) for a total reaction time of 20 h and with a 5-fold excess of olefin with respect to EDA. More interesting is the use of equimolar amounts of the diazo compound and the olefin. With complex **1** as the precatalyst (Table 3), the olefins are converted into cyclopropanes in higher yields: 79, 80, and 56% for styrene, *cis*-cyclooctene, and 1-hexene. It is worth noting that these yields are referred to EDA consumed, i.e., the amounts of cyclopropanes in the final mixture are 88, 89, and 72%, respectively, for those olefins.

C. Olefin Cyclopropanation Catalyzed by Complexes 1−6 under Heterogeneous Conditions. We have also investigated the interaction of dichloroethane solutions of **1** or **2** with silica gel. In the case of complex **2**, loss of the red color of the initial solution is observed 10 min after the silica gel was added. Once the Cu derivative is adsorbed, we have tested those silica gel−copper mixtures as the catalyst precursors for olefin cyclopropanation. Table 3 shows the results obtained for the cyclopropanation of styrene, *cis*-cyclooctene, and 1-hexene using **1** as the catalyst either in the homogeneous phase or under heterogeneous conditions. In all cases, the heterogeneous system provides, under the same conditions (1:5 for the EDA:olefin ratio and 1 mol % of catalyst relative to EDA), higher yields of cyclopropanes. We presume that this fact could be related

Table 3. Homogeneous *vs* Heterogeneous Olefin Cyclopropanation Catalyzed by 1[a]

	olefin-EDA mixing [Cu]:[EDA]:[olefin] 1:100:500		slow addition of EDA [Cu]:[EDA]:[olefin] 1:100:500[b]		slow addition of EDA [Cu]:[EDA]:[olefin] 1:100:100[c]	
	homog[d]	heterog[e]	homog[f]	heterog[g]	homog[f]	heterog[g]
styrene	58	64	65	84	79	96
cis-coe	61	74	55	76	80	87
1-hexene	42	53	44	71	56	83

[a] Yields are based on ethyl diazoacetate and determined by GC after total consumption of EDA. [b] Addition time 20 h. [c] Addition time 120 h. [d−g] See Experimental Section.

Table 4. Heterogeneous Styrene Cyclopropanation Catalyzed by BpCu (1) and BpCu(bipy) (2) Supported on Silica-gel[a]

entry no.	catalyst	[Cu]:EDA:styrene	yield (%)[b,c]	syn:anti[c]
1	**1**	1:20:400	77	43:57
2	**1**	1:20:400	82	48:52
3	**1**	1:20:400	83	44:56
4	**1**	1:20:400	85	44:56
5	**1**	1:20:400	85	43:57
6	**1**	1:20:400	85	43:57
7	**1**	1:20:400	85	42:58
8	**1**	1:20:400	85	42:58
9	**1**	1:20:400	85	40:60
10	**1**	1:100:2000	85	40:60
11	**1**	1:120:2400	86	38:62
12	**2**	1:100:500	60	38:62
13	**2**	1:100:500	67	38:62
14	**2**	1:100:500	74	37:63
15	**2**	1:100:500	74	36:64
16	**2**	1:400:2000	75	35:65
17	**2**	1:200:1000	69	35:65

[a] For experimental details, see the Experimental Section. [b] Based on ethyl diazoacetate. [c] Determined by GC after total consumption of EDA.

to the real concentrations of both EDA and olefin on the support surface, which might differ from those in the surrounding solution.

As expected, a slow addition of the carbene precursor enhances the olefin cyclopropanation. Analogously to the homogeneous system, we have carried out the experiments with equimolar amounts of olefin and EDA. Despite the long time employed for these experiments (120 h), the observed yields are significantly high to be taken into account when working with valuable olefins. An alternative approach to improve the yields without excess olefin would be the use of an excess of the diazo compound,[2d,6] the disadvantage being the explosive nature of these reagents.

We have also investigated the recovery and reuse of the copper-supported catalyst (Table 4). For **1**, nine cycles of 20 equiv of EDA/equiv of copper were run, with yields and selectivity remaining within the same range for all the experiments (entries 1−9). The 10th cycle (entry 10) was run with 100 equiv of EDA, and for the 11th cycle (entry 11), 120 equiv of EDA was transformed. In the case of **2**, 4 cycles each of 100 equiv of EDA were run (entries 12−15), and the 5th (entry 16) consisted of the conversion of 400 more equiv of EDA. After this experiment, the supported catalyst was filtered and stored at −5 °C for 1 week and then reused with 200 equiv of EDA. Again, yields and selectivities were consistent after this cycle (entry 17). These results show a remarkable catalytic activity for complexes **1** and **2**: olefins were converted into cyclopropanes with moderate to high yields, whereas the recovery of the catalyst under heterogeneous conditions was achieved with no detectable loss of activity for ca. 1000 turnovers. Although these data would suggest the existence of a strong metal−support interaction, we have not at this stage performed studies to ascertain the nature of this interaction. A recent study by Mayoral and co-workers[7] has shown that copper(II)-exchanged clays and zeolites catalyze olefin cyclopropanation reactions. The yields and selectivities reported are within the same range as those obtained for **1** and **2**, although no data about the catalyst recovery and reuse have been addressed. Iglesias *et al*. have also reported[6] a heterogeneous rhodium-based system for enantioselective cyclopropanation using excess EDA.

D. Competition Experiments with Para-Substituted Styrenes. Data in Table 1 show similar *syn:anti* ratios for the mixture of cyclopropanes obtained with complexes **1**−**6** as the precatalysts when using the same olefin (i.e. 25:75 for styrene; 20:80 for *cis*-cyclooctene). The use of these $BpCu(L)_n$ catalyst precursors does not seem to produce any change in the *syn:anti* ratio, given the variety in basicities and steric requirements of the L ligands. On the other hand, the *syn:anti* ratio values for the heterogeneous system vary from those observed under homogeneous conditions. In the case of styrene, the already mentioned 25:75 *syn*:*anti* ratio moves up to 40:60, increasing the sterically less favored isomer. This behavior, also observed for *cis*-cyclooctene (20:80, homogeneous; 35:65, heterogeneous) and 1-hexene (25:75, homogeneous; 45:55, heterogeneous), could be related to the existence of a different geometry around the metal center when supported on silica gel. The consistency in the values of the isomer ratio for each olefin under the same conditions along with the lack of influence of the ligand bonded to copper in complexes **1**−**6** could suggest the existence of a common active catalytic species. However, it is also common in copper-catalyzed cyclopropanation that the *syn:anti* ratio is fairly independent of the catalyst, with the exception of bulky catalysts. The four copper(I) precatalysts shown in Table 2 display different stereoselectivities, the complexes **1** and $[Cu(NCMe)_4]^+$ leading to the same *anti*/*syn* ratio (3.0). Despite the fact that the steric requirements for complexes **1**−**6** are quite different from each other due to the nature of the L ligand, and the observed similar stereoselectivity could be difficult to explain under those terms, we have performed competition experiments with para-substituted styrenes to obtain some information about the electronic effects of such ligands in the cyclopropanation reaction.

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(7) Fraile, J. M.; García, J. I.; Mayoral, J. A. *Chem. Commun*. **1996**, 1319.

Table 5. Competition Experiments with Para-Substituted Styrenes Using 1−6 as the Catalyst Precursors

	ratio of products ([8a + 8b]/[7a + 7b])			
precatalyst	*p*-OMe/H	*p*-Me/H	*p*-Cl/H	*p*-NO_2/H
1	1.925	1.859	0.647	0.115
2	1.965	1.572	0.678	0.133
3	1.933	1.482	0.696	0.151
4	1.858	1.539	0.679	0.165
5	1.921	1.641	0.662	0.099
6	1.698	1.502	0.967	0.103

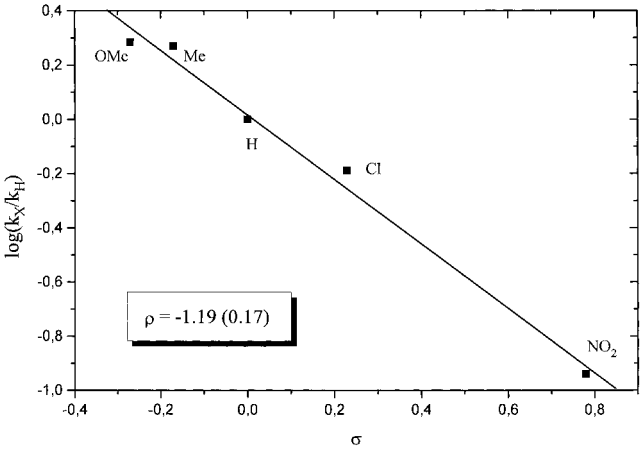
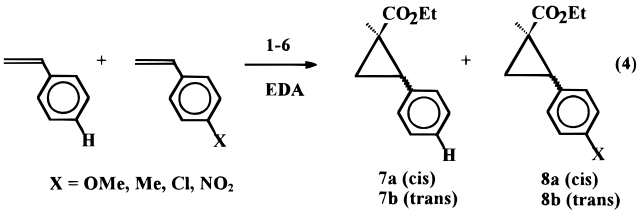


Figure 1. Hammett $\sigma\rho$ correlation for relative rates of cyclopropanation with BpCu (**1**) as the precatalyst ($\rho = -1.19 \pm 0.17$). Errors are given at 95% confidence limits.

Complexes **1**−**6** have been employed as the precatalyst in the cyclopropanation of an equimolar mixture of two styrenes, the nonsubstituted $C_6H_5CH{=}CH_2$ and a para-substituted styrene of general formula XC_6H_4-$CH{=}CH_2$ (eq 4). In all cases (Table 5), the reaction is



favored toward the electron-donating substituted derivatives, i.e., the *p*-methoxy- and *p*-methylstyrenes, whereas the electron-withdrawing groups such as Cl and NO_2 clearly disfavor this transformation. A Hammett plot for the data obtained with complex **1** as the precatalyst is shown in Figure 1. The resulting ρ value of -1.19 ± 0.17 is similar to that recently reported for the complex Tp′Cu(C_2H_4) ($\rho = -0.89$),[8a] a pyrazolyl−borate−copper complex with catalytic capabilities in carbene transfer reactions to unsaturated substrates.[8b] A series of ρ values has been obtained for complexes **2**−**6** as the catalyst precursor: -1.10 ± 0.13 for **2**, -1.03 ± 0.12 for **3**, -0.99 ± 0.09 for **4**, -1.23 ± 0.19 for **5**, and -1.14 ± 0.4 for **6**, leading to an average value of -1.11. The small differences between these values compared with the relatively different nature of the ligands

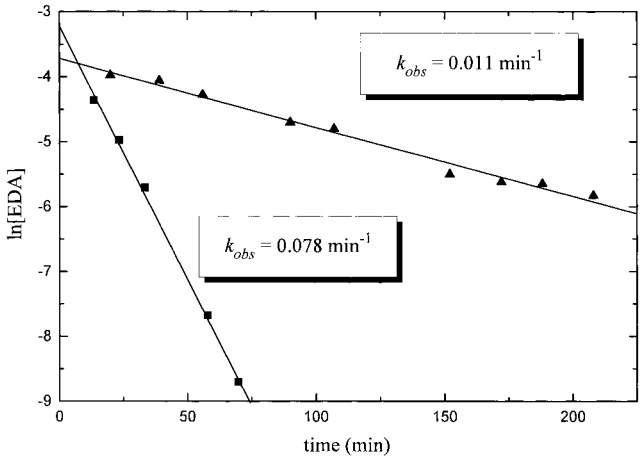


Figure 2. Plot of ln[EDA] *vs* time for ethyl diazoacetate consumption at 25 °C in the presence of BpCu (**1**) as the catalyst precursor: (■) in the absence of olefin, $k_{obsd} = (7.8 \pm 0.5) \times 10^{-2}$ min^{-1}; (▲) in the presence of styrene, $k_{obsd} = (1.1 \pm 0.1) \times 10^{-2}$ min^{-1}. Errors are given at 95% confidence limits.

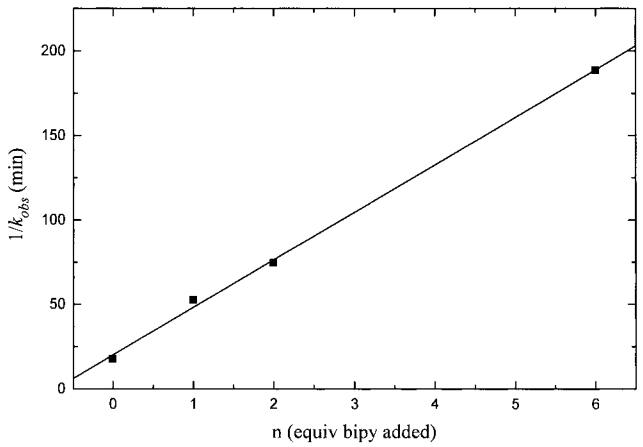


Figure 3. Variation of $1/k_{obsd}$ *vs* the number of equivalents of bipy added per equivalent of copper for EDA decomposition using BpCu(bipy) as the catalyst precursor at 25 °C ($n = 0$, $k_{obsd} = (5.7 \pm 0.4) \times 10^{-2}$ min^{-1}; $n = 1$, $k_{obsd} = (2.2 \pm 0.07) \times 10^{-2}$ min^{-1}; $n = 2$, $k_{obsd} = (1.4 \pm 0.02) \times 10^{-2}$ min^{-1}; and $n = 6$, $k_{obsd} = (5.4 \pm 0.2) \times 10^{-3}$ min^{-1}). Errors are given at 95% confidence limits.

attached to the metal center suggest, again, the existence of a common intermediate in which no copper−ligand interaction must exist. Since the BpCu fragment is present in all the compounds **1**−**6**, it seems reasonable to propose that this 14 electron complex could be the active catalyst in the transformation reported herein. The proposition of a 14-electron Cu(I) compound finds precedent in the literature: Pfaltz and co-workers found that an *in situ* generated semicorrinate−Cu(I) complex had ee's and *syn:anti* ratios identical wiht those of its semicorrinate−Cu(II) precursor.[9]

E. Kinetics Studies. We have carried out kinetic experiments (GC monitoring) following the disappearance of ethyl diazoacetate at 25 °C in the presence of **1** or **2** under homogeneous conditions. The results have revealed that the rate of EDA consumption is first order in [EDA], both in the absence and in the presence of

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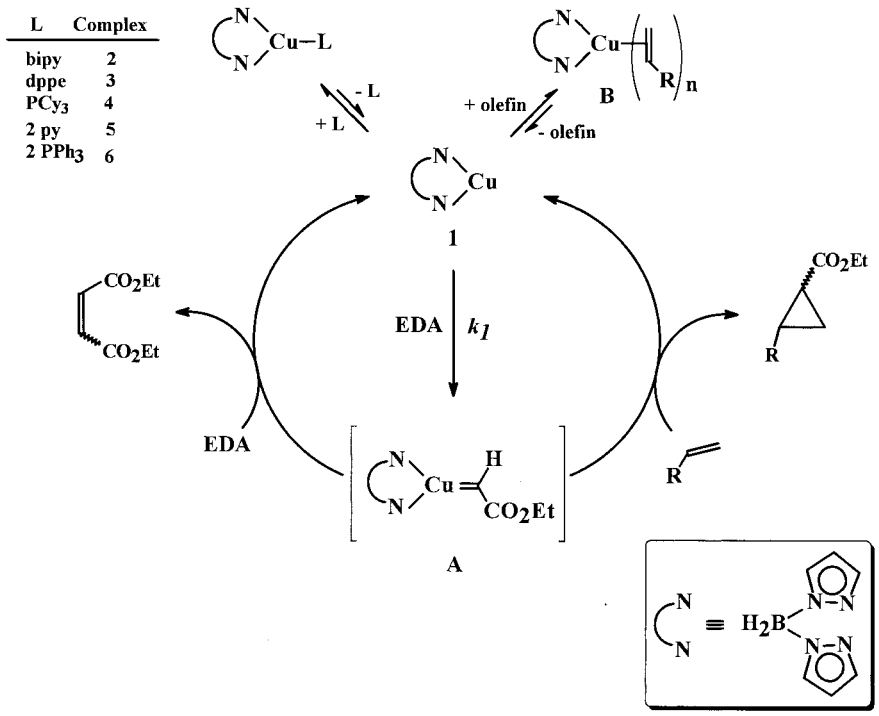
Scheme 1



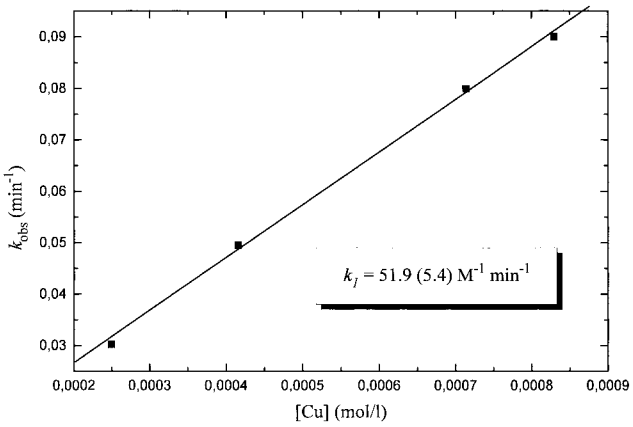


Figure 4. Variation of k_{obsd} *vs* $[Cu]_{tot}$ for EDA decomposition using BpCu (**1**) as the catalyst precursor at 25 °C. Errors are given at 95% confidence limits.

olefin. It has been previously suggested that these reactions occur through the intermediacy of metal-carbene species resulting after the EDA attack at the metal center.[1,10] The lack of second-order kinetic behavior allows us to propose the formation of a similar metal-carbene intermediate as the rate-determining step, in accord with previous studies with cobalt and copper complexes.[11,12] Our experiments have also revealed that the addition of alkene slows down the observed reaction rate ($k_{obsd} = (1.1 \pm 0.1) \times 10^{-2}$ min^{-1}) with respect to the experiment carried out in the absence of olefin, when using **1** as the catalyst precursor[13a] ($k_{obsd} = (7.8 \pm 0.5) \times 10^{-2}$ min^{-1}) (Figure 2). The slowness of the former could be related to the formation of a Cu(I)−olefin complex, BpCu(olef)$_n$ (n = 1, 2),[13a,b] therefore diminishing the concentration of the active catalytic species. A similar behavior has been found when using **2** as the precatalyst, with the corresponding k_{obsd} values of $(4.9 \pm 0.2) \times 10^{-3}$ min^{-1} and $(5.7 \pm 0.4) \times 10^{-2}$ min^{-1} for the experiments carried out with and without olefin, respectively.[13] In this case, the addition of free bipy also decreases the observed reaction rate. Figure 3 displays the variation of $1/k_{obsd}$ vs the amount of added bipy. The higher the excess of the ligand, the slower the reaction rate. A ligand dissociation−preequilibrium at some stage previous to the catalytic cycle would account for this behavior. These results are consistent with the above proposition of the BpCu fragment as the real catalyst. Scheme 1 shows a possible mechanistic interpretation of the overall process. When complexes **2**−**6** are used, the first step would involve the dissociation of the corresponding ligand, leaving **1** as the active catalyst. The addition of EDA would result in the formation of the carbene intermediate **A**, to be reacted with EDA or the olefin in the following step. In the absence of olefin, assuming the steady-state approximation for the carbene intermediate, the value of k_{obsd} is given by

$$k_{obsd} = 2k_1[Cu]_{tot} \qquad (5)$$

where $[Cu]_{tot}$ corresponds to the initial amount of the complex (**1**−**6**) added. A plot of k_{obsd} *vs* $[Cu]_{tot}$ using **1** as the catalyst is linear (Figure 4) and gives a value for the second-order rate constant k_1 of 51.9 ± 5.4 M^{-1}

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(13) (a) Inhibition with olefin was first proposed by Salomon and Kochi in their seminal work about the role of olefin coordination in Cu(I)-catalyzed alkene cyclopropanation.[12] (b) NMR spectra of **1** in the presence of a 5−10-fold excess of olefin display very broad resonances. We suggest the existence of an equilibrium between **1** and the corresponding olefin complex, the equilibrium favoring on the latter, as an explanation of the slowing of the reaction rate in the presence of olefin.

min^{-1}. For the cyclopropanation reaction, the amount of olefin present is crucial, since the formation of a Cu(I)−olefin complex (**B**) decreases the concentration of the active species, BpCu (**1**).[13b] EDA consumption has also been monitored under heterogeneous conditions, the reaction rate in the absence of olefin being slower than in the homogeneous case, whereas the cyclopropanation reaction is faster under heterogeneous conditions.

In conclusion, available data suggest that the cyclopropanation of olefins using complexes **1**−**6** occurs through a common active catalyst, the 14-electron species BpCu. The heterogenization of this copper-based catalyst causes, in addition to the well-known characteristics of catalyst recovery and product separation, an increase in the overall reaction rate. The assumption that this 14-electron Cu fragment is responsible for the catalytic conversion constitutes an starting point in the design of more active diastereo- and enantioselective copper catalysts for olefin cyclopropanation processes.

Experimental Section

General Methods. All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using conventional Schlenk techniques. Solvents were dried and degassed before use. Potassium dihydridobis(pyrazolyl)-borate[14] and the complexes Tp′Cu(C_2H_4),[8c] $Rh_2(OOCCH_3)_4$,[15a] and $PdCl_2(PPh_3)_2$[15b] were prepared according to literature methods. The PCy_3, PPh_3, and $Ph_2PCH_2CH_2PPh_2$ phosphine ligands and CuOTf as well as the para-substituted styrenes were purchased and employed without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer, chemical shifts being referred to TMS. ^{31}P NMR spectra were obtained with the same spectrometer using 85% aqueous H_3PO_4 as the standard. GC data were collected with a Varian GC-3350. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain).

Synthesis of BpCu (1). To a solution of CuI (0.095 g, 0.5 mmol) in acetonitrile (30 mL) was added $K[H_2B(pz)_2]$ (0.0925 g, 0.5 mmol) at 0 °C. After it was stirred for 30 min at this temperature, the solution was warmed to room temperature and stirred for a further 1 h. The mixture was evaporated to dryness to give a white solid. Crystallization from 1:1, CH_2Cl_2−petroleum ether gave complex **1** as a microcrystaline solid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.68, 7.49, 6.33 (d, d, t, 2:2:2, J(HH) = 2, J(HH) = 2, J(HH) = 2 Hz; C−H_{pyr}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ 140.7, 136.2, 106.2 (2 C each, C−H_{pyr}). Anal. Calcd for $C_6H_8N_4$BCu: C, 34.23; H, 3.83; N, 26.61. Found: C, 34.28; H, 3.04; N, 26.17.

Preparation of the Complexes BpCuL (L = $C_{10}H_8N_2$, 2; L = $Ph_2PCH_2CH_2PPh_2$, 3; L = PCy_3, 4) and $BpCuL_2$ (L = C_5H_5N, 5; L = PPh_3, 6). Complexes **2**−**6** were prepared by direct reaction of **1** and the corresponding ligand in acetonitrile (for complex **5**, dichloromethane was used instead). The synthesis of **2** is detailed as a representative example: complex **1** (0.105 g, 0.5 mmol) was dissolved in 30 mL of acetonitrile, and 1 equiv of $C_{10}H_8N_2$ (bipy) was added to the initially colorless solution to immediately give a dark red solution. The mixture was stirred for 30 min at room temperature, and the solvent was removed under vacuum to give complex **2** as a dark red solid. Microcrystalline material was obtained upon cooling a THF/petroleum ether solution at −20 °C overnight. Yield: 65%. Complexes **3**−**6** were crystallized from acetonitrile−diethyl ether solutions upon cooling at −20 °C overnight and were collected as white crystalline materials in 60−90% yields.

BpCu(bipy) (2). ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.71, 8.38, 7.95 (d, d, t, 2H each, J(HH) = 5, J(HH) = 8, J(HH) = 8 Hz, C−*H* bipy), 7.51 (d, 2H, J(HH) = 2 Hz, C−H_{pyr}), 7.45 (t, 2H, J(HH) = 5 Hz, C−*H* bipy), 7.21, 6.28 (d, t, 2:2 ratio, J(HH) = 2, J(HH) = 2 Hz, C−H_{pyr}). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 298 K): δ 152.8, 149.3 (2:2, 4 *C* bipy), 139.2 (2 C−H_{pyr}), 136.8 (2 *C* bipy), 134.7 (2 C−H_{pyr}), 125.8, 121.4 (2:2, 4 *C* bipy), 103.7 (br s, 2 C−H_{pyr}). Anal. Calcd for $C_{11}H_{13}N_5$BCu: C, 52.40; H, 4.37; N, 22.93. Found: C, 52.44; H, 3.70; N, 23.38.

BpCu(dppe) (3). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.68, 7.52 (d, d, 2:2, J(HH) = 2, J(HH) = 2 Hz, C−H_{pyr}), 7.51, 7.30 (m, m, 10:10, 4 *Ph* dppe), 6.07 (t, 2 H, J(HH) = 2 Hz, C−H_{pyr}), 2.42 (t, 4 H, J(HH) = 6 Hz, CH_2−P). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ −12.2 (br s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ 140.3, 134.7 (2:2, 4 C−H_{pyr}), 134.4, 132.6, 129.6, 128.7 (t, t, s, t, 4:8:4:8, J(PC) = 12, J(PC) = 8, J(PC) = 4 Hz, 4 *Ph* dppe), 103.2 (2 C−H_{pyr}), 25.6 (t, J(PC) = 18 Hz, 2 CH_2−P). Anal. Calcd for $C_{32}H_{32}N_4P_2$BCu: C, 63.20; H, 5.26; N, 9.21. Found: C, 63.30; H, 5.33; N, 9.38.

BpCu(PCy_3) (4). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.61, 7.56, 6.23 (d, d, t, 2:2:2 ratio, J(HH) = 2, J(HH) = 2, J(HH) = 2 Hz, C−H_{pyr}), 1.90−1.31 (m, 33 H, PCy_3). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 22.5 (s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ 140.6, 135.2, 103.9 (2:2:2, 6 C−H_{pyr}), 32.5, 31.3, 27.8, 26.6 (d, d, d, s, 3:6:6:3, J(PC) = 18, J(PC) = 4, J(PC) = 11 Hz, PCy_3). Anal. Calcd for $C_{24}H_{41}N_4$PBCu: C, 58.72; H, 8.36; N, 11.42. Found: C, 58.62; H, 8.30; N, 11.45.

BpCu(py)$_2$ (5). ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.58, 7.75 (br s, t, 4:2 ratio, J(HH) = 7 Hz; C_5H_5N), 7.54, 7.47 (br s, 2H each, C−H_{pyr}), 7.34 (br t, 4H, J(HH) = 6 Hz; C_5H_5N), 6.13 (br s, 2H, C−H_{pyr}). Due to the low stability of the solutions of this complex, attempts to collect a ^{13}C NMR spectrum have failed.

BpCu(PPh_3)$_2$ (6). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.38 (d, 2 H, J(HH) = 2 Hz, C−H_{pyr}), 7.13, 7.01(m, m, 6:24, 2 PPh_3), 6.87, 5.80 (d, t, 2 H each, J(HH) = 2, J(HH) = 2 Hz, C−H_{pyr}). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ −3.1 (br s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ 140.2, 134.4 (2:2, 4 C−H_{pyr}), 133.6, 133.2, 129.0, 128.0 (d, d, s, d, 6:12:6:12, J(PC) = 23, J(PC) = 15, J(PC) = 9 Hz, 2 PPh_3), 103.1 (2 C-H_{pyr}). Anal. Calcd for $C_{42}H_{56}N_4P_2$BCu: C, 68.64; H, 5.18; N, 7.63. Found: C, 67.52; H, 5.12; N, 7.66.

Olefin Cyclopropanation Catalyzed by 1−6 under Homogeneous Conditions. (a) Simultaneous Addition of Ethyl Diazoacetate and the Olefin. The precatalyst (complexes **1**−**6**, 0.05 mmol) was dissolved in 1,2-dichloroethane (30 mL) and the corresponding amounts of olefin and EDA (see Tables 1 and 2) were added simultaneously. The mixture was stirred for 3 h at room temperature or until no EDA was detected by GC. The product ratio was determined by integration of the corresponding peaks in the GC spectrum. Previously, pure samples of diethyl fumarate, diethyl maleate, and the cyclopropanes were injected to establish the retention times. The product ratios obtained by this method were compared with those obtained by ^{1}H NMR to avoid any deviation. The monitoring of EDA consumption during the kinetic experiments was carried out using an internal standard such as 1-octanol and/or the reaction solvent. The results are displayed in Table 1.

(b) Slow Addition of Ethyl Diazoacetate. A 0.05 mmol amount of complex **1** was dissolved in 10 mL of 1,2-dichloroethane, and 25 mmol (500 equiv) of the olefin (styrene, *cis*-cyclooctene, or 1-hexene) was added to the stirred solution. Ethyl diazoacetate (5 mmol, 100 equiv) was dissolved in 20 mL of 1,2-dichloroethane and slowly added to the [Cu]−alkene mixture with the aid of a syringe pump at a 1 mL/h rate (total

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addition time 20 h). By the same procedure, equimolar amounts of olefin and EDA (5 mmol each) were reacted by slow addition of the diazocarbene reagent at a 0.16 mL/h rate, for a total reaction time of 120 h. The results are displayed in Table 3.

Olefin Cyclopropanation Catalyzed by 1 and 2 under Heterogeneous Conditions. (a) Simultaneous Addition of Ethyl Diazoacetate and the Olefin. A solution of complex **1** or **2** (0.05 mmol in 40 mL of 1,2-dichloroethane) was prepared, and 0.5 g of silica gel was added to that solution. After 15 min of stirring, the olefin and the EDA were added to the suspension (see Tables 3 and 4 for the ratio employed). The mixture was stirred until no EDA was detected by GC. Before the charge for a new cycle, the residue of silica gel catalyst was washed with 1,2-dichloroethane (2 × 20 mL) to remove the products and/or reactants still remaining. The results are shown in Tables 3 and 4.

(b) Slow Addition of Ethyl Diazoacetate. A 0.05 mmol amount of **1** was supported on silica gel as described above, and 500 equiv of the olefin (25 mmol) was added to the mixture. EDA (100 equiv, 5 mmol) was dissolved in 20 mL of 1,2-dichloroethane and slowly added to that mixture at a 1 mL/h rate (total reaction time 20 h). A similar experiment was carried out with equimolar amounts of olefin and EDA, the diazocarbene solution being added at a 0.16 mL/h rate for a total time of 120 h. The results are shown in Table 3.

Styrene Cyclopropanation with Cu-, Rh-, and Pd-Based Catalysts. The comparison between the catalysts $Rh_2(OOCCH_3)_4$, $PdCl_2(PPh_3)_2$, Cu(OTf), $[Cu(NCMe)_4]I$, Tp′Cu(C_2H_4), and BpCu (**1**) was carried out upon performing the following experiments with these compounds. A 1:5 EDA−styrene mixture was added over a stirred solution of 0.05 mmol (1 % mol of catalyst) of the corresponding complex in 30 mL of 1,2-dichloroethane. After total consumption of the carbene precursor, the product ratio and stereoselectivity were determined by GC, leading to the results shown in Table 2.

Cyclopropanation Competition Experiments. One of the catalyst precursors **1**−**6** (0.05 mmol) was dissolved in 40 mL of 1,2-dichloroethane, and 300 equiv (15 mmol) of an equimolar mixture of styrene and the corresponding para-substituted styrene were added to the stirred solution. Ethyl diazoacetate (0.285 g, 2.5 mmol) was inmediately added, in one portion, to the above solution. The ratio of products (**[8a + 8b]/[7a + 7b]**) was determined by GC after total consumption of the ethyl diazoacetate (Table 5).

Kinetics Experiments. EDA decomposition in the presence of BpCu (**1**) is given as an example: 0.0105 g of **1** was dissolved in 70 mL of 1,2-dichloroethane, and EDA (0.1425 g, 1.25 mmol) was added to the stirred solution. The consumption of the ethyl diazoacetate at 25 °C was monitored by GC until the reaction was complete (no EDA observed). All the kinetics experiments reported in this contribution were carried out by following the same procedure. The concentration *vs* time tables and the corresponding plots are given in the Supporting Information.

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Supporting Information Available: Text and figures giving the derivation of eq 2, the kinetic experiments cited in the text, including data and plots, and competition experiments with para-substituted styrenes (27 pages). Ordering information is given on any current masthead page.

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