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Carbene Transfer and Carbene Insertion Reactions Catalyzed by a Mixed Ligand Copper(I) Complex

Stefano Brenna,*[a] and G. Attilio Ardizzoia[a]

Abstract: The catalytic activity of the mixed ligand copper(I) complex [Cu(PPh_3)$_2$(κ^2-O,O''-lact)] (**1**) (lact = *l*-(+)-lactate) has been investigated in carbene transfer and carbene insertion reactions. Complex **1** catalytically promoted the diastereoselective cyclopropanation of olefins in the presence of ethyl diazoacetate (EDA), in mild conditions and with a low catalyst loading (1% mol). In the case of internal alkenes, a *trans*:*cis* ratio of up to 93:7 was reached. Moreover, compound **1** easily promoted the insertion of the carbene fragment deriving from ethyl diazoacetate decomposition into O-H (alcohols and phenols) and N-H (amines) bonds, with the formation of the corresponding ethyl 2-alkoxyacetate, ethyl 2-phenoxyacetate and ethyl 2-aminoacetate derivatives in good to high yields.

Introduction

Transition metal-catalyzed transfer reactions of carbenes, generated from diazo compounds, to unsaturated and saturated substrates represent one of the most efficient tool for the formation of new carbon-carbon or carbon-heteroatom bonds.[1-4] The great interest in such reactions is related to the significance and large range of applications of their products, which are often useful synthetic intermediates for the construction of natural products and biologically active molecules. For instance cyclopropanes, obtained from the carbene transfer to differently substituted olefin double bonds, are versatile intermediates that can be converted into a variety of useful products by cleavage of the strained three-membered ring.[5] Similarly, transition-metals catalyzed insertion of carbenes into heteroatom-hydrogen bonds (X-H) leads to α-amino esters, α-amino ketones and nitrogen-containing heterocycles (X = N)[6] or α-alkoxy, α-aryloxy and α-hydroxy esters, together with a variety of oxygen-containing heterocyclic compounds (X = O).[7] These carbene transfer reactions are promoted by several metals, for instance rhodium,[8] iron,[6] ruthenium,[9] gold,[10] or copper.[11]

Focusing on copper based catalysts, large attention has been dedicated to olefin cyclopropanation reactions, and both experimental[12] and theoretical[13-15] studies have been accomplished in order to elucidate the mechanism involved. A variety of nitrogen based ligands, such as C_2-symmetric semicorrins,[16] bis(oxazolines),[17] bipyridines,[18] polypyrazolylborates,[19] diiminophosphoranes[20] and tris(2-pyridine)[21] have been used with the aim of enhancing the selectivity. Recently, chiral bicyclo bisoxazoline[22] and tris(pyrazolyl)borate[23] copper(I) complexes showed remarkable activity in the functionalization of O-H bonds. Despite being usually less suitable for carbene insertion reactions, also copper(I)-phosphine complexes have been successfully used in the chemoselective insertion into N-H bonds[24-26] and in olefin cyclopropanation.[27]

In the past, we also reported on ruthenium(II)[28] and copper(I)[29-31] complexes which demonstrated to be efficient catalysts in olefin cyclopropanation when ethyl diazoacetate was used as the carbenoid source. Continuing our search for copper catalysts which promote carbene transfer to olefin and X-H bonds, herein we investigated the catalytic activity of the mixed ligand copper(I) complex [Cu(PPh_3)$_2$(κ^2-O,O''-lact)] (**1**) (lact = *L*-(+)-lactate) (Figure 1).[32] Compound **1** showed high *trans*-selectivity in the EDA-assisted cyclopropanation of olefins (Figure 1) and a good activity in the insertion of the carbenoid fragment into N-H and O-H aliphatic and aromatic bonds (Figure 1).

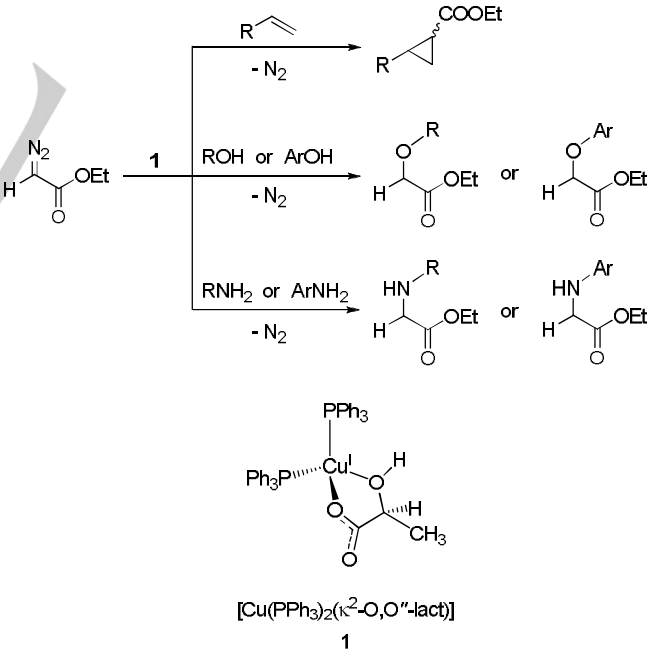

Figure 1. Top: general reactions for carbene transfer to olefin and carbene insertion into O-H and N-H bonds catalyzed by compound [Cu(PPh_3)$_2$(κ^2-O,O''-lact)], **1** (lact = L-(+)-lactate). Bottom: molecular structure of **1**.

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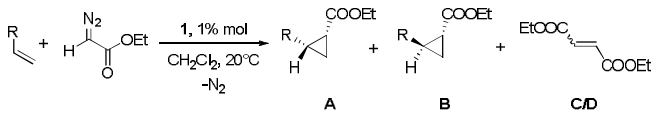
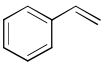
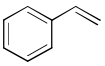
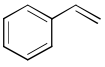
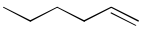
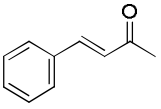
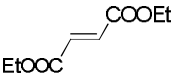
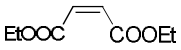
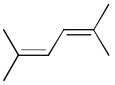
Results and Discussion

Olefin cyclopropanation



Scheme 1. General olefin cyclopropanation reactions catalyzed by compound $[Cu(PPh_3)_2(\kappa^2\text{-}O,O'\text{-lact})]$, **1**, leading to the formation of the desired cyclopropane derivatives (**A**+**B**) and diethyl maleate (**C**) and diethyl fumarate (**D**) as side-products.

Table 1. Olefin cyclopropanation by ethyl diazoacetate (EDA) decomposition catalyzed by compound **1**.[a]

Entry	Olefin	A+B (%)[b]	A:B ratio[c]
1		88 (79)	27:73
2[d]		32	26:74
3[e]		<5	-
4		86 (71)	42:58
5		85	31:69
6		79	7:93[f]
7		<5	-
8		<5	-
9		<5	-
10		78	34:66

[a] Reactions conditions: **1**/EDA/olefin =1/100/250; CH_2Cl_2 (8 mL), 20°C. [b] Yields were determined by GC-MS analysis (internal standard: hexamethylbenzene) of the bulk: (**A** + **B**) + (**C** + **D**) = 100%, after complete EDA consumption (>99% in all runs) monitored by disappearance of $\nu_{N\equiv N}$ in infrared spectroscopy. Isolated yields in parenthesis for selected examples. [c] Determined by GC-MS analysis of the bulk. [d] Performed at 0°C. [e] Reaction performed at -30°C. [f] In this specific case, the diastereoselectivity is referred to *exo*:*endo* ratio.

According to Scheme 1, when complex **1** was dissolved in dichloromethane under inert atmosphere in the presence of olefins, the addition of ethyl diazoacetate (EDA) led to the conversion of the substrate into the corresponding cyclopropane derivatives with high yields (Table 1).

Together with the desired products (**A** + **B**), diethyl maleate (**C**) and diethyl fumarate (**D**), deriving from EDA self-coupling, were always detected. In order to minimize the formation of these side-products, an excess of olefin (Cu:EDA:olefin = 1:100:250 molar ratio) was employed. Moreover, EDA was added dropwise to a CH_2Cl_2 solution of olefin and the catalyst, over a period of 12 h. As reported in Table 1, complex **1** showed to be a highly active catalyst in the cyclopropanation of terminal olefins (entries 1-5), and activated internal ones (entry 6), in mild conditions. At lower temperatures (0 °C) species **1** still showed a good activity in the cyclopropanation of styrene (entry 2), although a lesser yield was observed. On further lowering the temperature down to -30°C, the activity of catalyst **1** dropped dramatically. Poor yields were attained in the conversion of electron poor internal olefins (entries 7-9); worthy of note, when diethyl maleate and diethyl fumarate were used as substrates (entries 8-9), the cyclopropanation products were detected only in traces. Yields in cyclopropane products are in accord with those reported for copper(I) catalysts with nitrogen-containing ligands[16-21, 29-31] and to some extent higher than previously reported phosphine-containing copper(I) species.[33]

In the conversion of styrene into the corresponding cyclopropane esters, most of the copper(I) catalysts provided the *trans* isomer as the main product,[34] the common *trans*:*cis* ratio ranging from 50:50 to 75:25.[29-31] Also compound **1** confirmed this trend, providing a 70:30 *trans*:*cis* ratio in the catalytic cyclopropanation of styrene, while a lower *trans*-diastereoselectivity was observed using α-methylstyrene as substrate (entry 4). Finally, complex **1** exhibited a remarkable diastereoselectivity in the cyclopropanation of cyclohexene (entry 6), where a 93:7 ratio was achieved.

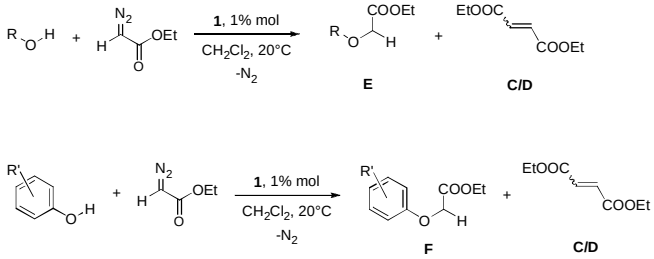
Together with mono-alkenes, also dienes were employed as substrates in the copper-catalyzed cyclopropanation reactions. Indeed, 3-(1-isobutenyl)-2,2-dimethyl cyclopropanecarboxylic acid (chrysanthemic acid) is a key intermediate of pyrethroid insecticides[35] and the conversion of 2,5-dimethyl-2,4-hexadiene (DMHD) into the corresponding chrysantemate esters by diazoacetates decomposition represents a fundamental target in industrial applicable processes.[36] Consistently with what observed for mono-olefins, when complex **1** was used to catalyze the conversion of conjugated di-olefins into the corresponding cyclopropanes (entry 10), the *trans* isomer was always the major product.

Insertion into O-H bonds

Once established the propensity of compound **1** to promote carbene transfer to an olefin C=C bond, we investigated other catalytic reactions where a carbenoid species is involved, *i.e.* carbene insertions into E-H bonds (E = O, N). Indeed, the accepted mechanism for such reactions considers the formation of an electron-deficient metal-carbene and its subsequent insertion into the N-H or O-H bond.[37] Being a metal-carbene also the active species in olefin cyclopropanation, and considering the abovementioned activity of complex $[Cu(PPh_3)_2(\kappa^2\text{-}O,O'\text{-lact})]$ in olefin cyclopropanation, we were confident about using our complex also to promote E-H insertions. Concerning O-H insertions, both aliphatic and aromatic alcohols have been converted to the corresponding ethyl 2-alkoxoacetate (**E**) and ethyl 2-phenoxyacetate (**F**) (Scheme 2) by means of ethyl diazoacetate decomposition. Following the previous experiments on olefin cyclopropanation,

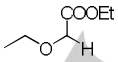
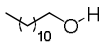
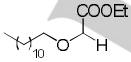
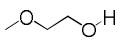
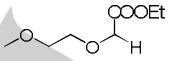
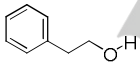
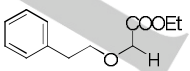
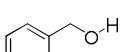
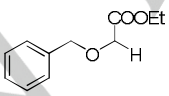
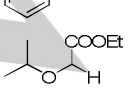
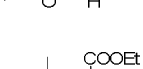
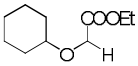
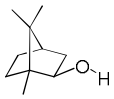
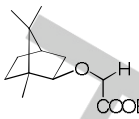
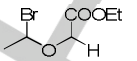
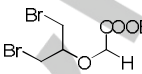
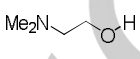
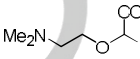
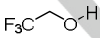
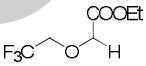
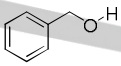
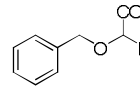
only 1% mol catalyst with respect to the substrate was added, and the diazo compound was yet again dropped over a 12-h period to suppress the formation of undesired diethyl maleate (**C**) and fumarate (**D**) (Scheme 2).

In the case of aliphatic substrates (Table 2) very high yields, comparable to those obtained with other copper(I) compounds,[38] were always obtained in the carbene insertion into O-H bonds of primary alcohols (entries 1-5) regardless the length of the alkylic chain. The insertion of the -CHCOOEt fragment from ethyl diazoacetate proceeded with high yields for secondary alcohols as well (entries 6-9). In some way unusual is the situation when groups other than carbon-based ones are attached to the side chain of the alcohol (entries 10-13): the presence of Br atoms or NMe_2 or CF_3 substituents considerably lowered the yield of conversion of the alcohol into the corresponding ethyl 2-alkoxoacetate **E**. Further studies are ongoing to clarify this point.



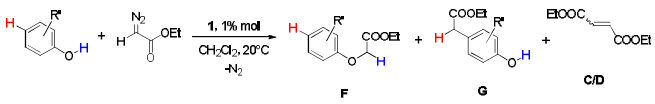
Scheme 2. General O-H insertion reactions catalyzed by compound **1**, leading to the formation of the desired ethyl 2-alkoxoacetate (**E**) and ethyl 2-phenoxyacetate (**F**) derivatives and diethyl maleate (**C**) and diethyl fumarate (**D**) as side-products.

Table 2. Carbene insertion into O-H bonds by means of ethyl diazoacetate (EDA) decomposition catalyzed by compound **1**.[a]

Entry	Alcohol	Product **E**	Yield (%)[b]
1			84
2			77
3			76
4			86
5			93 (85)
6			78
7			77
8			89
9			85
10			58
11			44
12			<5
13			<5
14[c]			<5

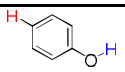
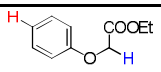
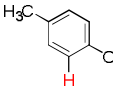
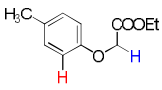
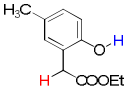
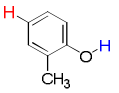
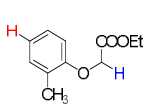
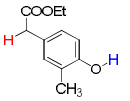
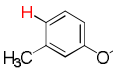
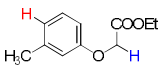
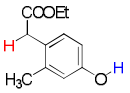
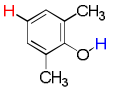
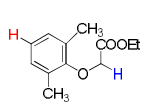
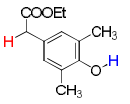
[a] Reactions conditions: **1**/EDA/alcohol =1/100/250; CH_2Cl_2 (8 mL), 20 °C. [b] Yields were determined by GC-MS analysis (internal standard: hexamethylbenzene) of the bulk: **E** + (**C** + **D**) = 100%, after complete EDA consumption (>99% in all runs) monitored by disappearance of $\nu_{N\equiv N}$ in infrared spectroscopy. Isolated yields in parenthesis for selected examples. [c] Determined by GC-MS analysis of the bulk. [c] Reaction performed at -30°C.

Then, compound [Cu(PPh_3)$_2$(κ^2-O,O''-lact)], **1**, was also tested as catalyst in the carbene insertion into O-H bonds of phenols (Scheme 3, Table 3). The yields of conversion of phenols into the corresponding O-H functionalized products **F** are in accord with those observed for previous copper(I)-phosphine catalysts.[22,39] Worthy of note, besides the expected ethyl 2-phenoxyacetate (**F**), also the product coming from insertion into the aromatic C-H bond (**G**) was detected. This is an unusual behavior for a copper catalyst, as typically copper, palladium, iron or rhodium active compounds are chemo-selective towards the O-H insertion.[40] Differently, Zhang[40-41] and Shi[42] demonstrated that the C-H functionalization takes place when gold(I) species are used in combination with α-diazoesters. By means of DFT calculations[40] they showed that the insertion into the aromatic C-H bond is siteselective, occurring at the *para*-position with respect to the OH group. However in our case, catalyst **1** did not show a similar site-selectivity, as ^{1}H NMR inspection of the bulk provided evidence of the formation of a mixture of regioisomers in all catalytic runs. A further combined experimental and theoretical investigation will hopefully clarify the exact nature of the C-H functionalized products.



Scheme 3. Insertion of carbene into O-H bonds of phenols catalyzed by compound **1**, leading to ethyl 2-phenoxyacetate (**F**), the products of C-H insertion (**G**) and diethyl maleate (**C**) and diethyl fumarate (**D**).

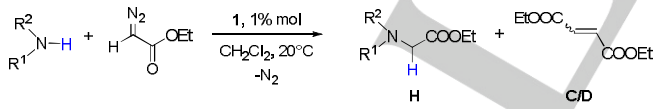
Table 3. Carbene insertion into O-H bonds of phenols by means of ethyl diazoacetate (EDA) decomposition catalyzed by compound **1**.

Entry	Phenol	F	G	F(%)[b]	G(%)[b]
1				55	17
2				63	19
3				50	13
4				38	42
5				29	53

[a] Reactions conditions: **1**/EDA/phenol =1/100/250; CH_2Cl_2 (8 mL), 20°C. [b] Yields were determined by GC-MS analysis (internal standard: hexamethylbenzene) of the bulk: (**F** + **G**) + (**C** + **D**) = 100%, after complete EDA consumption (>99% in all runs) monitored by disappearance of $\nu_{N\equiv N}$ in infrared spectroscopy.

The lower yield obtained with 2,6-dimethyl phenol (entry 6) is probably imputable to the higher steric hindrance imposed by the ortho-methyl groups in the resulting product **F**; worthy of note, in this case the percentage of the C-H functionalized phenol is also the highest among the series.

Insertion into N-H bonds

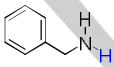
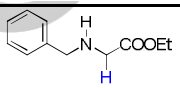
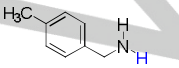
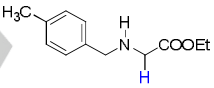
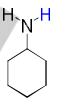
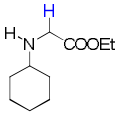
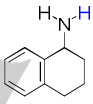
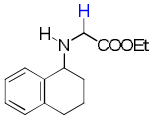
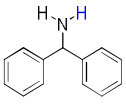
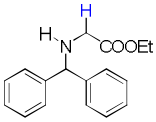
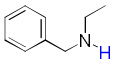
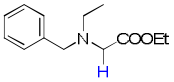
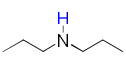
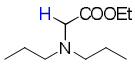
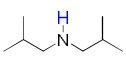
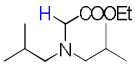


Scheme 4. Insertion of carbene into N-H bonds of aliphatic amines catalyzed by compound **1**, leading to product **H**, diethyl maleate (**C**) and diethyl fumarate (**D**).

Complex $[Cu(PPh_3)_2(\kappa^2\text{-}O,O'\text{-lact})]$ proved to be active also in the functionalization of N-H bonds of aliphatic and benzylic amines by means of ethyl diazoacetate decomposition (Scheme 4, Table 4), leading to ethyl 2-aminoacetate derivatives (**H**). Yet again, only 1% mol catalyst was added, and the diazo compound was dropped over a 12-h period to suppress the formation of undesired diethyl maleate (**C**) and fumarate (**D**) (Scheme 4).

As reported in Table 4, primary amines (entries 1-5) could be easily converted into products **H** in good yields (≥ 50%), despite overall a lower activity was observed compared to previously reported catalysts[43] and with respect to the analogous insertions into O-H bonds (yields ≥ 76%, Table 2) catalyzed by **1**. The insertion of the -CHCOOEt fragment proceeded with secondary amines as well (entries 6-8), yields being only slightly poorer with aliphatic amines (entries 7-8). Unfortunately, a preliminary screening on the activity of complex **1** towards the carbene insertion into N-H bonds of anilines resulted unsuccessful, with yields being always lower than 10% when aniline and *N*-ethyl aniline were used as test substrate. Hence, this reaction was not further investigated.

Table 4. Carbene insertion into N-H bonds of amines by means of ethyl diazoacetate (EDA) decomposition catalyzed by compound **1**.

Entry	Amine	Product **H**	Yield (%)[b]
1			60 (48)
2			65
3			55
4			54
5			50
6			58
7			48
8			42

[a] Reactions conditions: **1**/EDA/amine =1/100/250; CH_2Cl_2 (8 mL), 20°C. [b] Yields were determined by GC-MS analysis (internal standard: hexamethylbenzene) of the bulk: **H** + (**C** + **D**) = 100%, after complete EDA consumption (>99% in all runs) monitored by disappearance of $\nu_{N\equiv N}$ in infrared spectroscopy. Isolated yields in parenthesis for selected examples.

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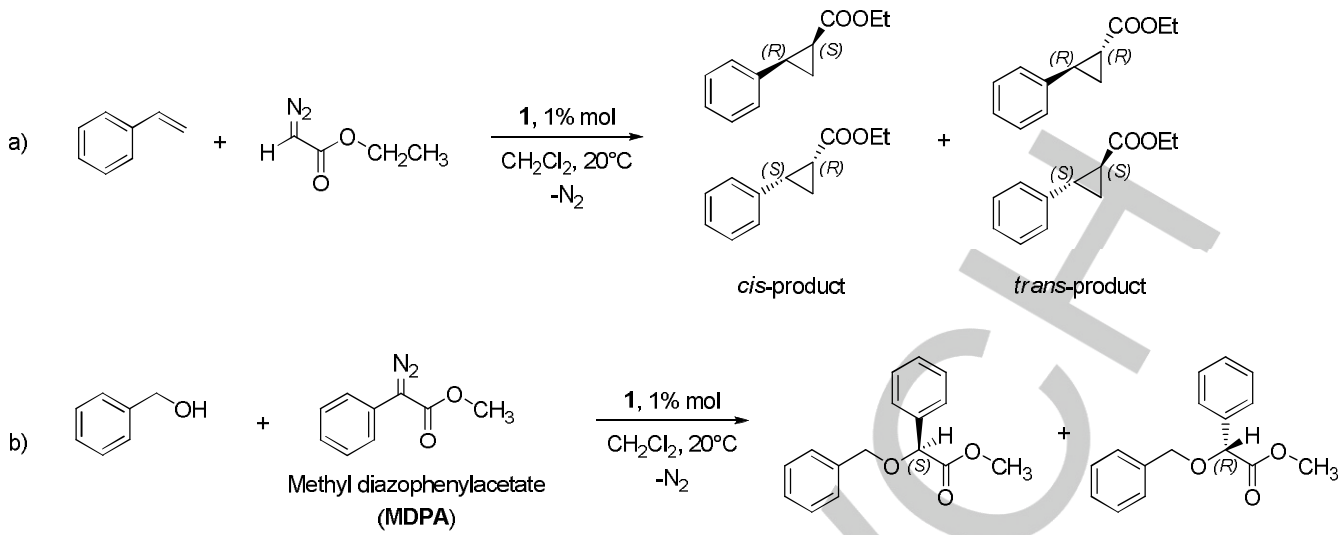
Asymmetric reactions

The presence of a chiral anion such as L-(+)-lactate in complex $[Cu(PPh_3)_2(\kappa^2\text{-}O,O'\text{-lact})]$ prompted us to inspect its potential use in asymmetric carbene transfer and insertion reactions (Scheme 5).



Scheme 5. a) Asymmetric cyclopropanation of styrene promoted by complex **1** via ethyl diazoacetate decomposition. b) Asymmetric insertion of the carbene generated by decomposition of Methyl diazophenylacetate (MPDA) into the O-H bond of benzyl alcohol.

Styrene was first used as reference substrate to evaluate the asymmetric induction in olefin cyclopropanation. The catalytic run was performed following the conditions described above (Table 1), other than the bulk mixture obtained after complete EDA consumption was analyzed using chiral gas chromatography (see Experimental). Unfortunately, compound **1** did not induce any enantiomeric excess in the cyclopropanation of styrene, as demonstrated by the resulting chromatogram (Figure S1). A similar behavior was observed in the carbene insertion into benzyl alcohol O-H by decomposition of methyl diazophenylacetate MPDA[44] (Scheme 5b). In this case, the enantiomeric excess was quantified via ^{1}H NMR analysis, by gradual addition of europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Eu(hfc)$_3$) to a $CDCl_3$ solution of the bulk. Once again, a nearly 50:50 distribution was obtained for the two enantiomers (Figures S2-S3). The lack of enantioselectivity shown by complex [Cu(PPh$_3$)$_2$(κ^2-O,O″-lact)] could probably be attributed to the fluxionality shown by the lactate anion in dichloromethane solution, at room temperature. [32] This fluxionality is minimized on lowering the temperature to -30°C,[32] but regrettably when both the cyclopropanation of styrene and the reaction between benzyl alcohol and MPDA were performed at -30°C, the products of the two catalytic runs could only be detected in traces (Table 1, entry 3 and Table 2, entry 14).

Conclusions

The catalytic activity in carbene transfer and insertion reactions of the mixed ligand copper(I) complex [Cu(PPh$_3$)$_2$(κ^2-O,O″-lact)] (**1**) has been reported. Complex **1** promoted olefin cyclopropanation by ethyl diazoacetate decomposition under very mild conditions and a very low catalyst loading (1% mol). Especially in the case of internal olefins, compound **1** showed remarkably high selectivity towards the formation of the *trans* isomer. Additionally, [Cu(PPh$_3$)$_2$(κ^2-O,O″-lact)] (**1**) promoted carbene insertion into O-H and N-H bonds as well. In particular, in the case of carbene insertion into O-H bonds of phenols, together with the desired ethyl 2-phenoxyacetate, the formation of products deriving from C-H functionalization was also observed, in a process which is quite unusual for copper(I) catalysts.

Experimental Section

All reactions were carried out under purified nitrogen using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures prior to use. NMR spectra were recorded with an AVANCE 400 Bruker spectrometer at 400 MHz for ^{1}H NMR and 162 MHz for ^{31}P{^{1}H} NMR. Chemical shifts are given as δ values in ppm relative to residual solvent peaks as the internal reference (for ^{1}H NMR) and to external H_3PO_4 (85%) (for ^{31}P NMR). *J* values are given in Hz. Infrared Spectra were acquired on a Shimadzu Prestige-21 spectrophotometer with a 1cm^{-1} resolution. Quantitative analyses of products in the catalytic runs were performed on a Finnigan Trace GC with a DB-5MS UI capillary column (30 m, 0.25 mm) equipped with a Finnigan Trace Mass Spectrometer. Enantioselectivities in styrene cyclopropanation were analyzed on Shimadzu GC-17A gas chromatograph equipped with a chiral PS225 capillary column (25 m, 0.25 mm). [Cu(PPh$_3$)$_2$(κ^2-O,O″-lact)] (**1**) was prepared as previously reported[32] and its purity was assessed by elemental analysis, ^{1}H and ^{31}P NMR (Supporting Information); methyl diazophenylacetate (MDPA) was prepared following literature methods.[44] All other chemicals were of reagent grade quality, were purchased commercially (Aldrich, Acros, TCI Chemicals) and used as received.

General procedure for olefin cyclopropanation

In a standard experiment, to a solution of complex **1** (10 mg, 0.015 mmol) and olefin (3.75 mmol) in dichloromethane (8 ml) at room temperature and under inert atmosphere, ethyl diazoacetate (EDA) (160 µL, 1.50 mmol) was added dropwise over a period of 12 h (Cu:EDA:olefin molar ratio 1:100:250). The consumption of EDA was monitored by infrared spectroscopy ($\nu_{N\equiv N}$, 2109 cm^{-1}). After complete conversion of EDA, yields and diastereoselectivity (*trans*:*cis* ratio) were determined by GC-MS analysis of the crude. In selected cases, products were isolated after removal of the solvent and column chromatography (dichloromethane:hexane = 6:4). Their collected analytical data were in agreement to those reported in the literature.[29]

General procedure for carbene insertion into O-H bonds

In a standard experiment, to a solution of complex **1** (10 mg, 0.015 mmol) and alcohol or phenol (3.75 mmol) in dichloromethane (8 ml) at room temperature and under inert atmosphere, ethyl diazoacetate (EDA) (160 µL, 1.50 mmol) was added dropwise over a period of 12 h (Cu:EDA:alcohol molar ratio 1:100:250). The consumption of EDA was monitored by infrared spectroscopy ($\nu_{N\equiv N}$, 2109 cm^{-1}). After complete conversion of EDA, the distribution of products was determined by GC-MS analysis of the bulk using hexamethylbenzene as internal standard. In selected cases, products were isolated after removal of the solvent and column chromatography (hexane:diethylether = 20:1). Their collected analytical data were in agreement to those reported in the literature.

General procedure for carbene insertion into N-H bonds

In a standard experiment, to a solution of complex **1** (10 mg, 0.015 mmol) and the amine (3.75 mmol) in dichloromethane (8 ml) at room temperature and under inert atmosphere, ethyl diazoacetate (EDA) (160 µL, 1.50 mmol) was added dropwise over a period of 12 h (Cu:EDA:amine molar ratio 1:100:250). The consumption of EDA was monitored by infrared spectroscopy ($\nu_{N\equiv N}$, 2109 cm^{-1}). After complete conversion of EDA, yield was determined by GC-MS analysis of the bulk using hexamethylbenzene as internal standard. In selected cases, products were isolated after removal of the solvent and column chromatography (hexane:diethylether = 20:1). Their collected analytical data were in agreement to those reported in the literature.

Synthesis of Methyl-2-diazo-2-phenylacetate (MDPA)[44]

In a two-neck 100 mL flask, methyl phenylacetate (4.5 g, 29.96 mmol) and *p*-Toluenesufonyl azide (9.1 g, 46.14 mmol) were dissolved in 80 mL of deoxygenated acetonitrile. The solution was cooled to 0°C, then 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (9 mL, 60.45 mmol) was slowly dropped into the solution while keeping the temperature at 0°C. The solution gradually turned orange, then it was stirred at room temperature overnight. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 (60 mL) and washed with a saturated water solution of NH_4Cl (40 mL). The organic phase was separated, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (1:3 hexane:dichloromethane) leading to an orange oil (yield 65%). The product was stored at -20°C. IR (nujol): $\nu_{N\equiv N}$ 2088 cm^{-1}, ν_{CO} 1703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ= 3.88 (s, 3H, OCH_3), 7.20 (dt, 1H, ^3J = 4.6 Hz, ^4J = 0.5 Hz, CH_{arom}), 7.40 (dt, 2H, ^3J = 4.6 Hz, ^4J = 0.4 Hz, CH_{arom}), 7.50 (dd, 2H, ^3J = 5.3 Hz, ^4J = 0.6 Hz, CH_{arom}).

Acknowledgements

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Keywords: homogeneous catalysis • cyclopropanation • carbene insertion • copper • phosphine

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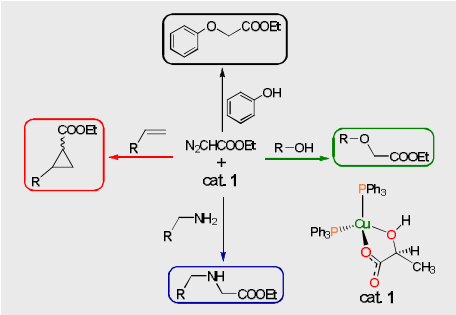
Entry for the Table of Contents

Key Topic: Carbene Transfer

FULL PAPER

An easily-prepared and low-cost copper(I) homogeneous catalyst has been investigated in carbene transfer reactions. High yields and selectivities were achieved in olefin cyclopropanation and O-H and N-H insertions.



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Carbene Transfer and Carbene Insertion Reactions Catalyzed by a Mixed Ligand Copper(I) Complex