

Review

Copper, silver and gold-based catalysts for carbene addition or insertion reactions

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Abstract

Two families of catalysts containing trispyrazolylborate (Tp^x) or *N*-heterocyclic carbenes (NHC) with the group 11 metals have proven useful for several reactions involving the transfer of the $:\text{CHCO}_2\text{Et}$ group from ethyl diazoacetate to saturated and unsaturated substrates.

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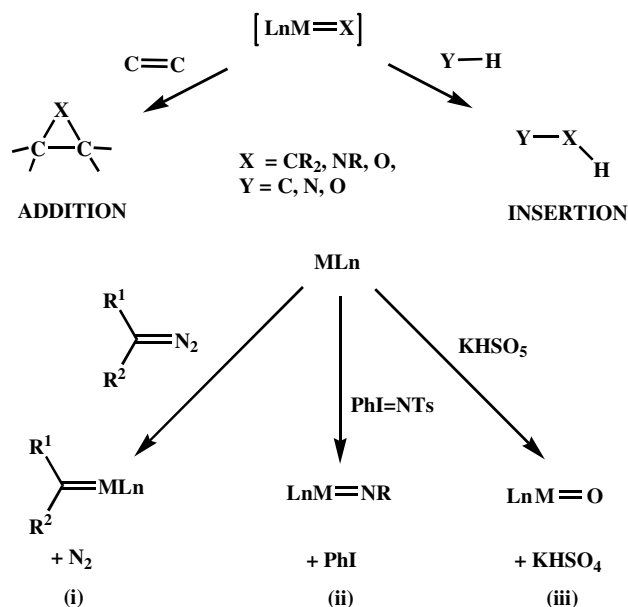
1. Introduction

The conversion of small, accessible molecules into others with a certain added value constitutes one of

the main challenges at the beginning of this century [1]. One of the strategies employed for such goal is the transfer, in a catalytic manner, of carbene, nitrene or oxo units (from the appropriate sources) to saturated or unsaturated substrates (Scheme 1, top) with the intermediacy of a transition metal complex as the catalyst [2]. The addition of those units to carbon–carbon double bonds affords cyclopropanes, aziridines or epoxides,

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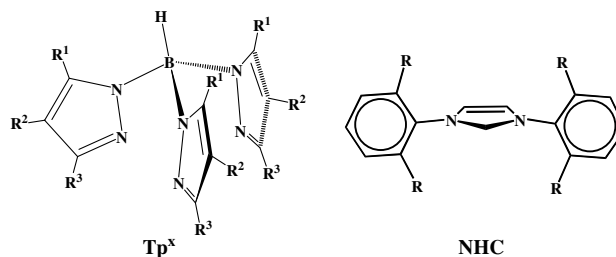


Scheme 1. (Top) Reactivity of metallo-carbenes, -nitrenes and -oxo intermediates. (Bottom) Generation of the species $L_nM = X$ for the transfer of carbene, nitrene and oxo groups.

respectively. It is also possible to use this methodology to insert such fragments into several, saturated X–H bonds ($X = N, O$ or C , among others) [2].

The development of catalytic systems for the reactions shown in Scheme 1 requires the availability of sources for the X group as well as the design of the appropriate ML_n complex that would react with those sources to give the $L_nM = X$ species. These are quite electrophilic in nature, short-lived and very reactive, a set of properties that ensure the viability of a catalytic cycle. Diazo compounds have been extensively employed as the source for carbene transfer reactions, in the most common example of this type of processes (Scheme 1, bottom). However, the interest in the formation of carbon–nitrogen bonds has led to the study of the related nitrene transfer reactions [3]. In this case, the most common source for the nitrene group is $PhI = NTs$ ($Ts = tosyl$) and related. The main drawbacks are the formation of iodobenzene as byproduct and the limitation to *N*-tosyl aziridines. Regarding the former, a new trend is emerging in the use of the haloamines-T $NaXNTs$ ($X = Cl$, chloramines; $X = Br$, bromamine) that only produces more environmentally benign NaX as side-products upon nitrene transfer. Regarding the oxo transfer process, a number of catalytic systems have been described using oxone ($KHSO_5$) as the oxo source for olefin epoxidation reactions [4].

Since the mid 1990s we have been involved in the development of copper-based catalysts for the above transformations. The use of bis-(Bp^x) and trispyrazolylborate (Tp^x) ligands [5] (Scheme 2) allowed the development of catalytic systems for olefin cyclo-



Scheme 2. Trispyrazolylborate (Tp^x) and *N*-heterocyclic carbene (NHC) ligands.

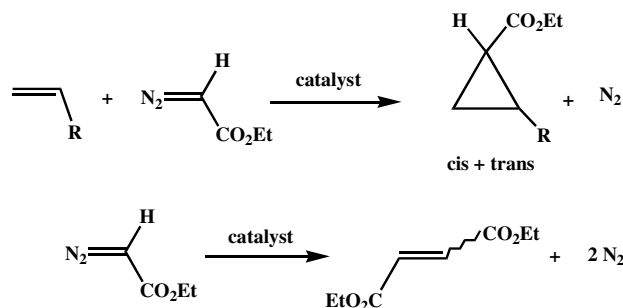
propanation [6a,6b,6c], aziridination [6d] and epoxidation [4], as well as for alkyne cyclopropanation [7]. These results were reviewed in the previous volume dedicated to metal-carbenes [8]. In the last few years, we have focused our research into the development of group 11 metal-based catalysts for the transfer of the carbene $:CHCO_2Et$ from ethyl diazoacetate to several saturated and unsaturated fragments. In addition to the already mentioned Tp^x -containing complexes, we have also prepared new catalysts where the metal atom is bonded to a *N*-heterocyclic carbene ligand (NHC, Scheme 2). In this contribution, we present the results obtained with these two families of catalysts in carbene transfer reactions from ethyl diazoacetate to saturated and unsaturated fragments.

2. Results and discussion

2.1. Trispyrazolylborate-containing catalysts

2.1.1. Olefin cyclopropanation: a diastereoselective catalyst for the *cis* isomer

The catalytic transfer of carbene groups from diazo compounds to olefins to yield cyclopropane products (Scheme 3) have been extensively employed in the last decades [2]. Although very active and enantioselective catalysts had been reported for this transformation, the control of the diastereoselection, i.e., the preferential formation of the *cis* or the *trans* isomer of the cyclopropane



Scheme 3. (Top) Olefin cyclopropanation of terminal olefins with ethyl diazoacetate. (Bottom) Side reaction, coupling of ethyl diazoacetate.

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