Diazocompounds have been extensively employed as a carbene source in organic synthesis. In the past decade, the incorporation of such fragments to a variety of substrates has been accomplished in many cases with the aid of an appropriate transition-metal complex acting as catalyst. It is well-established that this transformation occurs via an electrophilic metalocarbene intermediate, although this species has only been detected once. As shown in Scheme 1, the transfer of the carbene unit to a nucleophile affords the desired product and releases the metal center to reinitiate the catalytic cycle. The main drawback of this methodology is the existence of an undesirable side reaction, the homocoupling of the diazocompound. This problem has been usually overcome by using slow addition devices and/or using excess of the nucleophilic substrate. The vast majority of systems capable of mediating this reaction bear nitrogen-donor ligands, and they all display a similar behavior: ethyl diazoacetate is readily converted into diethyl fumarate and maleate because of this unwanted side reaction. On the other hand, phosphorus-containing ligands are not useful for this chemistry because of the facile carbene transfer to phosphorus to produce ylide derivatives.

During the course of our investigations aimed at developing new catalysts that could avoid the aforementioned diazo coupling reaction, we examined the potential of complexes containing the emerging N-heterocyclic carbene (NHC) ligands toward the diazocompound decomposition reaction in the presence of several substrates. NHC-based catalytic systems have been reported for several processes such as hydrogenation, hydrosilylation, C−C bonds formation, olefin metathesis, and ATRP. Previously reported copper(I) complexes displayed an extremely high activity toward EDA decomposition, although amounts being comparable to those of very active copper-based catalysts already known. Previously reported copper(I) complexes displayed an extremely high activity toward EDA decomposition, in contrast with the observed behavior of IPrCuCl, which does not react with EDA. Substrate (olefin, amine, and alcohol) addition

batches of catalyst and EDA, leading to identical results: in the absence of styrene, EDA did not decompose to any extent in the presence of I.

Two kinetic experiments were conducted to monitor the lifetime of EDA in the presence of I. Solutions of I and EDA were prepared, stirred at room temperature, and periodically monitored by GC to quantify the amount of EDA present in the reaction mixture. No decomposition of EDA was observed after 3 h. After this time, styrene (4 equiv with respect to EDA) was added to one of the solutions, inducing the immediate consumption of EDA, as inferred from the observed decay and the subsequent formation of cyclopropane products in very high yield (Figure 1). The non-styrene-containing solution did not undergo any noticeable change along the time interval studied (13 h), in what can be considered a rare example in the field of metal-catalyzed diazocompound decomposition. Styrene and cyclooctene could be readily converted into diethyl fumarate and maleate because of this unwanted side reaction. On the other hand, phosphorus-containing ligands are not useful for this chemistry because of the facile carbene transfer to phosphorus to produce ylide derivatives. During the course of our investigations aimed at developing new catalysts that could avoid the aforementioned diazo coupling reaction, we examined the potential of complexes containing the emerging N-heterocyclic carbene (NHC) ligands toward the diazocompound decomposition reaction in the presence of several substrates. NHC-based catalytic systems have been reported for several processes such as hydrogenation, hydrosilylation, C−C bonds formation, olefin metathesis, and ATRP. However, very few examples (Ru- and Rh-based) of application to diazo decomposition and carbene transfer have been reported using such systems.

We prepared complex IPrCuCl (1) [IPr: 1,3-bis(diisopropylphenyl)imidazole-2-ylidene] and employed it as catalyst in two test experiments (Scheme 2): the cyclopropanation of styrene with ethyl diazoacetate (EDA) and the decomposition of EDA to give fumarate and maleate. In both cases, a solution of 0.025 mmol of 1 in dichloromethane was mixed with 0.625 mmol of EDA, for a 1:25 EDA/catalyst ratio (4% of catalyst). In the cyclopropanation test, 3.25 mmol of styrene was also added (1:25:125 molar ratio for [1]/[EDA]/[styrene]). After stirring the solution for 6 h, we monitored the reaction mixtures by GC. The styrene-containing solution showed a greater than 90% conversion to cyclopropanes (referenced to EDA), with no remaining diazoester being detected. Surprisingly, the experiment carried out with EDA alone showed no consumption of the diazo reagent, the catalyst remaining unaffected for prolonged time periods. These experiments were repeated four times, using different amounts of EDA. In the past decade, the incorporation of such fragments to a variety of substrates has been accomplished in many cases with the aid of an appropriate transition-metal complex acting as catalyst. It is well-established that this transformation occurs via an electrophilic metalocarbene intermediate, although this species has only been detected once. As shown in Scheme 1, the transfer of the carbene unit to a nucleophile affords the desired product and releases the metal center to reinitiate the catalytic cycle. The main drawback of this methodology is the existence of an undesirable side reaction, the homocoupling of the diazocompound. This problem has been usually overcome by using slow addition devices and/or using excess of the nucleophilic substrate. The vast majority of systems capable of mediating this reaction bear nitrogen-donor ligands, and they all display a similar behavior: ethyl diazoacetate is readily converted into diethyl fumarate and maleate because of this unwanted side reaction. On the other hand, phosphorus-containing ligands are not useful for this chemistry because of the facile carbene transfer to phosphorus to produce ylide derivatives. During the course of our investigations aimed at developing new catalysts that could avoid the aforementioned diazo coupling reaction, we examined the potential of complexes containing the emerging N-heterocyclic carbene (NHC) ligands toward the diazocompound decomposition reaction in the presence of several substrates. NHC-based catalytic systems have been reported for several processes such as hydrogenation, hydrosilylation, C−C bonds formation, olefin metathesis, and ATRP. However, very few examples (Ru- and Rh-based) of application to diazo decomposition and carbene transfer have been reported using such systems.

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**Scheme 1.** Transition-Metal-Catalyzed Carbene Transfer from Diazocompounds

**Scheme 2.** Reactions of EDA in the Presence of 1

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2 University of New Orleans.
Conversions were observed for amines and alcohols. The preferential interaction in this system appears to be self-explanatory in the presence of diazo reagent yet in the absence of the substrate is inactive toward diazo activation (and degradation).

Therefore, the chemoselectivity in this system appears to be self-controlled and requires the presence of a substrate in the reaction mixture, a result that, to our knowledge, finds no precedent in the metal-mediated catalytic carbene transfer from ethyl diazoacetate.

It is also worth mentioning that reactions were performed with a 10% isolated yield. See: Lo, M. M.-C.; Fu, G. C. J. Am. Chem. Soc. 1998, 120, 10270–10271.

A reviewer noted that a copper-based catalyst provided very good yields with other diazoace etate to unsaturated and saturated substrates (olefins, amine, alcohols) with very high yields. The unique behavior of this system constitutes, in our opinion, the starting point for the development of new catalysts that avoid the already mentioned main drawback of this methodology, the diazocompound dimerization reaction.

**Acknowledgment.** This communication is dedicated to the memory of Dr. Juan Carlos del Amo Aguado. We thank the MCYT (Proyecto BQU2002-01114) for financial support and the Universidad de Huelva for the Servicio de Resonancia Magnética Nuclear. M.R.F. thanks the MCYT for a research studentship. M.M.D.R. thanks the MCYT for a Ramón y Cajal grant. S.P.N. acknowledges the National Science Foundation for support of the work performed at UNO.

**Supporting Information Available:** General experimental procedures and NMR spectra of the products in Table 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

**References**


