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Gold-catalyzed olefin cyclopropanation

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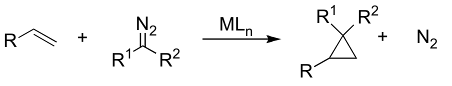
ABSTRACT

The selectivity of the cyclopropanation of olefins with ethyl phenyldiazoacetate has been tested using different gold complexes bearing phosphine, phosphite or *N*-heterocyclic as ligands. A comparative study with related copper and silver complexes as catalysts is also presented.

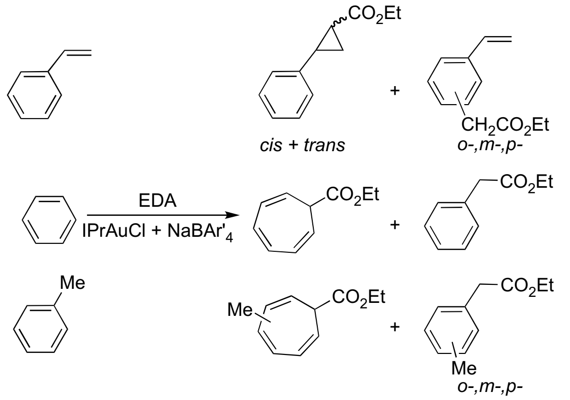
1. Introduction

One of the most frequent strategies employed in the synthesis of cyclopropane rings is based on the catalytic transfer of carbene fragments, from diazo compounds to olefins.[1] All transition metals from groups 8 to 11 have been reported to decompose diazo compounds,[2] the carbene unit being later transferred to a variety of saturated or unsaturated substrates (Eq. 1).[3] Among them, gold resulted elusive until very recently, when we found[4] that the complex IPrAuCl (IPr=1,3-bis(diisopropylphenyl) imidazol-2-ylidene), in the presence of equimolar amounts of NaBAr′$_4$ (BAr′$_4$=tetrakis(3,5-bis(trifluoromethyl) phenyl)borate) was capable of inducing the catalytic transfer of the :CHCO$_2$Et unit from ethyl diazoacetate (N$_2$CHCO$_2$Et, EDA) to several aromatic hydrocarbons such as styrene, benzene or toluene. Interestingly, in all cases, products derived from the formal insertion of the carbene group into the aromatic C–H bond were observed (Scheme 1). Styrene also provided cyclopropane rings, whereas benzene and toluene gave cycloheptatrienes resulting from a Büchner reaction.



(1)

After that first report on the use of a gold-based catalyst for the intermolecular carbene transfer from diazo compounds, very few other examples have been described based on this metal. Alkane functionalization by carbene insertion from EDA was also developed in our laboratories with the same (NHC)M system (M=Cu, Au).[5] He and co-workers later described the use of cationic, pyridine-containing gold complexes as catalysts in the reaction of benzene and EDA at 80 °C, cycloheptatriene products derived of the Büchner reaction being obtained in moderate yields.[6] A NHC–Au complex has also being described by Gagosz and co-workers for the insertion of the carbene unit into the O–H bond of alcohols.[7] Finally, a gold(I) complex with a triazapentadienyl ligand has been found to promote the cyclopropanation of styrene in good yield.[8] It is worth mentioning that olefin cyclopropanation reactions without the participation of diazo compounds have also been described to take place with gold-based catalysts.[9]



Scheme 1. Addition/insertion reactions of CHCO$_2$Et from EDA with aromatic substrates catalyzed by a (NHC)Au complex.

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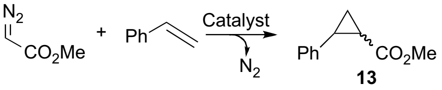
The role of phosphine-surrogates initially ascribed to NHC ligands seems to be already surpassed[10] on the basis of the variety of distinct chemical behavior displayed by many transition metal complexes containing NHC ligands. In the emerging field of catalysis by gold,[11] we have considered of interest to study the catalytic potential of Au(I) complexes containing either phosphine or *N*-heterocyclic carbene ligands in carbene transfer reactions from diazo compounds. In this contribution we present the results obtained with two series of cationic LAu complexes (L=phosphine or NHC ligand) in the olefin cyclopropanation reaction. The effect of those ligands as well as that of gold compared with the other coinage metals, copper and silver, will provide interesting information for the design of future active catalysts for such transformation.

2. Results and discussion

2.1. Gold-catalyzed olefin cyclopropanation

A series of gold complexes containing either phosphorus-based or NHC ligands were prepared, along with the related copper and silver analogs (Fig. 1). The selection of these ligands was established on the basis of the distinct behavior they are known to induce in the metal center. Phosphine, phosphite, and saturated and unsaturated *N*-heterocyclic carbene ligands should provide relevant information about their effect in the catalytic transformation for further catalyst development.

As mentioned above, the reaction of EDA with styrene has been described with NHC–Au catalysts.[4] Therefore, we first carried out this reaction in the presence of the gold complexes **1** and **4** (Eq. 2), cationic species of similar nature to that formed from IPrAuCl+NaBAr′$_4$.[4] Unfortunately, after 4 days of stirring at room temperature, the initial 1:1.1 EDA/styrene mixture remained unchanged and cyclopropane **13** was not detected.



(2)

The use of a different diazo compound, ethyl phenyldiazoacetate with the series of gold complexes **1**, **4**, **7**, and **10** as catalyst in the styrene cyclopropanation reaction (Eq. 3) provided better results, as shown in Table 1. A unique diastereoisomer **14** (that with the two phenyl groups in mutually cis positions) was obtained in all cases, similarly to other systems reported for this substrate with this diazo compound.[12] Other interesting features of this gold-based system is the use of a nearly stoichiometric diazo/styrene ratio, a feature that is not common in these transformations, where 1:5 to 1:10 diazo/olefin ratios are usually employed. In our case, a slight excess of olefin is enough to ensure the catalytic transformation. It is also worth mentioning the reaction times required for complete diazo consumption, that ranged from 1 to 30 min, leading to TOF values higher than other reported for this transformation.[1]

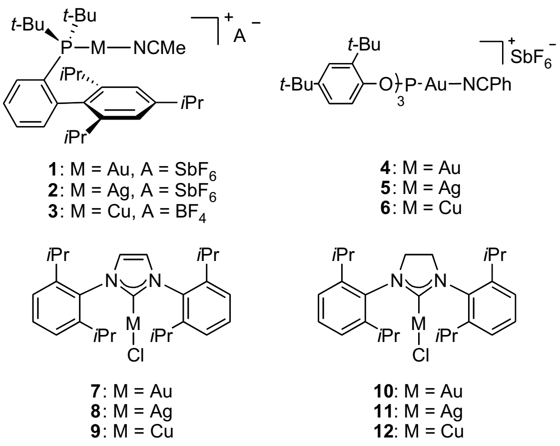
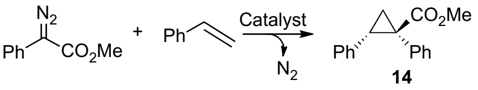


Figure 1. Coinage metal complexes with phosphine or NHC ligands employed as catalysts in this work.

Table 1
Styrene cyclopropanation with ethyl phenyldiazoacetate with gold-based catalysts to give **14** (Eq. 3)

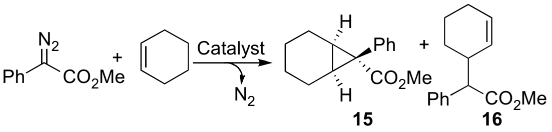
Entry	Catalyst[a]	Diazo/styrene	Reaction time[b] (min)	Yield[c] % (dr %)[d]
1	**1**	1:1.1	15	94 (99)
2	**1**	1:5	10	85 (99)
3	**4**[e]	1:1.1	1	77 (99)
4	**7**[f]	1:1.1	15	80 (99)
5	**7**[f]	1:3	10	85 (99)
6	**7**[f]	1:5	10	90 (99)
7	**10**[f]	1:1.1	30	80 (99)
8	**10**[f]	1:5	10	92 (99)

[a] 5 mol % catalyst loading.
[b] Required for complete diazo consumption.
[c] Isolated yield in cyclopropane; remaining diazo compound was converted into coupling products.
[d] Diastereomeric ratio.
[e] Temperature 0 °C.
[f] One equiv of NaBAr′$_4$ referred to gold.



(3)

In a second series of experiments, cyclohexene was chosen as the substrate for the cyclopropanation reaction with the same gold complexes as the catalyst and ethyl phenyldiazoacetate as the carbene source (Eq. 4). Again, only one cyclopropane stereoisomer **15** was obtained in all cases. The phosphorus-containing catalysts were found to be more active, in terms of diazo compound consumptions (see reaction times in Table 2). Small amounts of **16**, the product derived of the formal insertion of the carbene unit into the allylic C–H bonds, were also detected.



(4)

2.2. Trends in activities and selectivities

As mentioned above, the aim of this work was to establish the effect that different ligands such as phosphine, phosphite or *N*-heterocyclic carbene ones exert on the carbene transfer reaction from phenydiazoacetate. Data in Tables 1 and 2 have provided experimental results from which some trends can be extracted regarding catalyst activity as well as chemo- and diastereoselectivity. It is worth to mention at this stage that these transformations are well known to occur through the intermediacy of transient metallocarbene species, electrophilic in nature.[1] Because of these, cationic catalysts precursors have been employed in this work. Complexes **1** and **4** were isolated as ionic species from the reaction of neutral precursors and AgSbF$_6$. On the other hand, cationic NHCAu species were generated in situ by mixing equimolar mixtures of NHCAuCl and NaBAr′$_4$, as previously described.[4] The cationic nature provides the required electrophilic character to the metal center that enhances the reactivity toward the diazo compound.

The activity of the catalyst in this transformation can be estimated on the basis of the time required for the complete consumption of the diazo reagent. In this sense, the phosphite derivative **4** is the most active, all the phenyldiazoacetate being

Table 2

Cyclohexene cyclopropanation with ethyl phenyldiazoacetate with gold-based catalysts

Entry	Catalyst[a]	Diazo/C_6H_{12}	Reaction time[b]	Yield[c] % (**15**/**16** ratio)[d]
1	**1**	1:1.1	40 min	37 (160:1)
2	**1**	1:5	10 min	65 (160:1)
3	**4**	1:1.1	10 min	64 (160:1)
4	**7**[e]	1:5	7 h	50
5	**10**[e]	1:1.1	2 h	20
6	**10**[e]	1:5	2 h	53

[a] 5 mol % catalyst loading.

[b] Required for complete diazo consumption.

[c] Isolated yield in cyclopropane; remaining diazo compound was converted into coupling products.

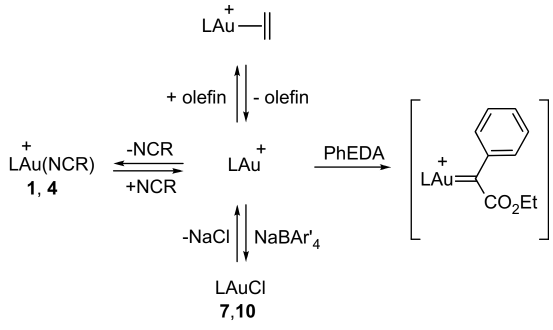
[d] Cyclopropane/allylic insertion ratio of products given in parenthesis. Otherwise only cyclopropanes were obtained.

[e] One equiv of $NaBAr'_4$ referred to gold added.

consumed within 1 min at 0 °C. The phosphine catalyst **1** is not as active as catalyst **4**, whereas the NHC-containing catalysts display the lowest activities. The order of activity, intended as the time required for complete diazo consumption, follows the order phosphite>phosphine>NHC for the series of complexes LAu^+ as the catalyst.

A second issue to be discussed is the chemoselectivity, the relative amount of the cyclopropanes versus the products derived from the metal-catalyzed diazo coupling, Ph(EtOOC)-C=C(COOEt)Ph. The yield in Tables 1 and 2 are referred to cyclopropanes (and the allylic insertion product in the case of cyclohexene), the remaining of the initial $PhC(N_2)COOEt$ being converted into those olefins. When styrene as the olefin, the most active catalyst **4** provided the lowest conversion into cyclopropanes, followed by similar, higher values obtained with the phosphine- and NHC-containing catalysts (entries 1, 3, 4, and 7, Table 1). Such trend finds no parallelism in the reactions carried out with cyclohexene, the trend being exactly the opposite (entries 1, 3, and 5, Table 2).

The explanation for the different activities and chemoselectivities induced by these catalysts must be related to the effect of the ligand bonded to the gold center. Variable amounts of the cationic species LAu^+ should be available in solution upon dissociation of the initial co-ligand (RCN for **1** or **4**) or the readily available, in situ generated olefin adduct (Scheme 2). The coordinatively unsaturated species LAu^+ would react with the diazo compound to give the metallocarbene intermediate from which reaction would proceed. The formation of that intermediate is considered the rate determining step in these transformations, and regulates diazo consumption. Therefore, the observed order in activity must be related to the electrophilic character induced by the L ligand on the gold center. It is well established that NHC ligands are better σ-donors than phosphine ligands.[10] Regarding phosphine–phosphite properties, the former are good σ-donors whereas the latter display better π-acceptor capabilities. Overall, the degree of electron donation to the metal decreases in the sense (unsatd NHC)>(satd NHC)>phosphine>phosphite, matching the experimental trend in activity.



Scheme 2. Formation of the gold–carbene intermediate from the initial catalyst precursors.

The observed variation in the chemoselectivity is also related to the above explanation about electrophilicity. It has been established that although electrophilic catalysts are desired to promote these transformation, an excess of such character favors the formation of the carbene coupling products.[1b,d] In good accord with this, the lowest chemoselectivity in the styrene cyclopropanation reaction has been achieved with the more active catalyst **4**. But in the case of cyclohexene both catalysts **1** and **4** induce similar chemoselectivities. However, the steric hindrance around the metallocarbene intermediate has also been invoked to control the chemoselectivity,[1] therefore the size of the catalytic pocket being of importance in such control. So, it is a delicate balance of the steric pressure (exerted by ligands, carbene substituents, and olefin) and the electrophilic character (mainly inferred by the ligand bonded to the gold center) that drives the chemoselectivity in these transformations.

Finally, the diastereoselectivity observed in these transformations is very high, only one cyclopropane diastereoisomer being observed for styrene and cyclohexene as olefins.[12] These results are similar to those already reported with this or related diazo compounds that generate donor/acceptor carbenoids, a feature that seems to govern the diastereoselection in these processes.[13]

2.3. Copper- and silver-catalyzed olefin cyclopropanation

The silver and copper analogs to the above gold-based catalysts have also been tested as catalysts in the olefin cyclopropanation reaction. Table 3 shows the results obtained from which some differences can be pointed out when comparing with the already discussed gold catalysts. The use of EDA as the carbene source continues to be ineffective with silver catalysts (entries 1 and 2), although in the case of copper a certain degree of conversion (entries 10 and 11) was observed, using phosphite (**4**) or phosphine (**3**) as co-ligands. When moving to the phenyldiazoacetate, the copper complexes with NHC ligands are exceptionally active, with total

Table 3

Styrene cyclopropanation with silver and copper-based catalysts

Entry	Catalyst[a]	Diazocompound	Diazo/styrene	Reaction time[b]	Yield[c] % (dr %)[d]
1	**2**	EDA	1:1.1	4 days	No reaction
2	**5**	EDA	1:1.1	3 days	No reaction
3	**2**	PhEDA	1:1.1	1 h	90 (99)
4	**5**	PhEDA	1:1.1	30 min	92 (99)
5[f]	**8**	PhEDA	1:1.1	7 h	84 (99)
6[f]	**8**	PhEDA	1:3	3 h	86 (99)
7[f]	**8**	PhEDA	1:5	2 h	91 (99)
8[f]	**11**	PhEDA	1:1.1	6 h	85 (99)
9[f]	**11**	PhEDA	1:5	1.5 h	90 (99)
10	**3**	EDA	1:1.1	1 h	22
11	**6**	EDA	1:1.1	1 h	40
12	**3**	PhEDA	1:1.1	1 h	46 (99)
13	**3**	PhEDA	1:5	30 min	70 (99)
14[e]	**6**	PhEDA	1:1.1	1 h	58 (99)
15[f]	**9**	PhEDA	1:1.1	1 min	86 (99)
16[f]	**9**	PhEDA	1:3	1 min	90 (99)
17[f]	**9**	PhEDA	1:5	1 min	97 (99)
18[f]	**12**	PhEDA	1:1.1	1 min	83 (99)
19[f]	**12**	PhEDA	1:5	1 min	98 (99)

[a] 5 mol % catalyst loading.

[b] Required for complete diazo consumption.

[c] Isolated yield in cyclopropane; remaining diazo compound was converted into coupling products.

[d] Diastereomeric ratio.

[e] Temperature 0 °C.

[f] One equiv of $NaBAr'_4$ referred to the metal complex; no reaction was observed in the absence of this additive.

conversions being observed in less of a minute, and with high to very high chemo- and diastereoselectivities. Nearly quantitative conversion required a fivefold excess of styrene (Table 3, entries 17 and 19), the use of equimolar amounts of the diazo and styrene leading to slightly lower yields (Table 3, entries 15 and 18). In contrast to the aforementioned behavior shown by the gold-based catalyst, the *P*-containing copper catalysts are not as active as the NHC-derivatives. Therefore, activity is reversed for the couples P–Au and NHC–Cu. Silver catalysts display a considerably lower activity than those of their copper or gold counterparts. In addition to the lack of reaction with EDA in the case of phosphorus-containing catalysts, the experiments carried out with the phenyldiazoacetate led to high conversions although the reaction times were, by far, long compared with the other metals.

It is worth mentioning that a series of experiments with cyclohexene as the substrate and the same catalysts shown in Table 3 have been performed. The corresponding cyclopropanes were obtained as the product, with variable yield (20–75%), and with reaction times varying from several hours to days.

3. Conclusion

We have described the use of several gold complexes, containing either phosphine, phosphite or NHC ligands as catalysts for the cyclopropanation of styrene or cyclohexene with ethyl 2-phenyldiazoacetate, as one of the scarce examples of the use of this metal to induce the carbene transfer reaction from diazo compounds. Very high conversions and complete diastereoselectivity toward the trans-isomer have been achieved with gold- as well as copper-based catalysts.

4. Experimental

4.1. General methods

All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using conventional Schlenk techniques or inside a dry-box. Olefins and ethyl diazoacetate were purchased from Aldrich. NMR experiments were run on a Varian Mercury 400 MHz or Bruker Avance 400 Ultrashield spectrometer. GC studies were carried out using Varian 3900. The NHC precatalysts[5] and ethyl 2-phenyldiazoacetate[14] were prepared according to literature methods.

4.2. Phosphine and phosphite M(I) complexes

Complexes **1**–**3** were prepared by the procedures used to synthesize [*t*-Bu_2P(*o*-biphenyl)Au(MeCN)]SbF_6 and analogous complexes.[15] The structure of complexes **2** and **3** was confirmed by X-ray diffraction. These crystal structures will be reported separately. Phosphite metal complexes **5** and **6** were prepared similarly to known gold(I) complex **4**.[16]

*4.2.1. Complex **1***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 1H), 7.65–7.60 (m, 2H), 7.37–7.32 (m, 1H), 7.18 (s, 2H), 3.00 (quint, J=7.0 Hz, 1H), 2.34 (quint, J=6.8 Hz, 2H), 2.28 (s, 3H), 1.47 (d, J=16.2 Hz, 18H), 1.36 (d, J=7.0 Hz, 6H), 1.31 (d, J=6.8 Hz, 6H), 0.96 (d, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 147.3, 147.1, 135.9, 134.7, 134.6, 134.1, 131.3, 127.5, 127.4, 121.9, 118.5, 126.1, 125.5, 38.8, 38.5, 33.9, 31.1, 26.1, 24.1, 23.0, 2.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.2.

*4.2.2. Complex **5***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J=2.1 Hz, 1H), 7.27 (d, J=8.4 Hz, 1H), 7.22 (dd, J=2.1, 8.4 Hz, 1H), 2.13 (s, 3H), 1.44 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 146.5, 139.1, 125.2, 124.3, 118.8, 68.1, 35.0, 34.0, 30.0, 25.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 112 (br d, J (^{31}P-Ag)=1100 Hz).

*4.2.3. Complex **6***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=2.3 Hz, 1H), 7.29 (d, J=6.5 Hz, 1H), 7.20 (dd, J=2.3, 6.5 Hz, 1H), 2.1 (s, 3H), 1.40 (s, 9H), 1.32 (s, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 116.2.

4.3. General catalytic experiment

The catalyst (0.025 mmol) and the olefin (1.1–5 equiv respect to the diazo compound) were dissolved in 5 mL of methylene chloride and the diazo compound (0.5 mmol) was added in one portion. Gas evolution was observed along with a smooth change in color from orange (ethyl phenyldiazoacetate) to yellowish. The reaction was monitored by TLC. When the diazo compound was consumed (variable time, see Tables 1–3) volatiles were removed and the extract was purified by flash chromatography using a 1:18 mixture of diethyl ether/petroleum ether as eluent.

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