

# Mechanistic Studies on the Gold-Catalyzed Direct Arene C-H Bond Functionalization by Carbene Insertion: the Coinage Metal Effect

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Supporting Information Placeholder

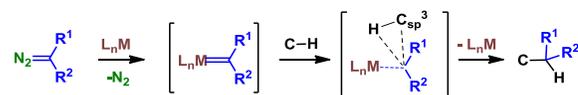
**ABSTRACT** The catalytic functionalization of the C<sub>sp</sub><sup>2</sup>-H bond of benzene by means of the insertion of the CHCO<sub>2</sub>Et group from ethyl diazoacetate (N<sub>2</sub>=CHCO<sub>2</sub>Et) has been studied with the series of coinage metal complexes IPrMCl (IPr = IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) and NaBAR<sup>F</sup><sub>4</sub> (BAR<sup>F</sup><sub>4</sub> = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). For Cu and Ag, these examples constitute the first of such metals toward this transformation, that also provides ethyl cyclohepta-2,4,6-trienecarboxylate as by-product from the so-called Buchner reaction. In the case of methyl-substituted benzenes, the reaction exclusively proceeds onto the aromatic ring, the C<sub>sp</sub><sup>3</sup>-H bond remaining unreacted. A significant coinage metal effect has been observed, since the gold catalyst favors the formation of the insertion product into C<sub>sp</sub><sup>2</sup>-H bond whereas copper and silver preferentially induce the formation of the cycloheptatriene derivative. Experimental studies and theoretical calculations have explained the observed selectivity in terms of the formation of a common Wheland intermediate, resembling an electrophilic aromatic substitution, from which the reaction pathway evolves into two separate routes to each product.

## INTRODUCTION

The formation of carbon-carbon bonds is probably among the most studied processes that employ homogeneous catalysts.<sup>1</sup> Amid the different strategies described for such goal, a quite simple one consists of the formal insertion of a carbene CR<sup>1</sup>R<sup>2</sup> group into a C-H bond (Scheme 1), a process that can be accomplished with the aid of metal-based catalysts and diazo reagents as the carbene source.<sup>2,3</sup> These transformations are known to occur through the intermediacy of reactive metalcarbene intermediates,<sup>4</sup> generated by extrusion of dinitrogen from the diazo molecule, that react with the hydrocarbon.

For C<sub>sp</sub><sup>3</sup>-H bonds, mechanistic studies seem to favor a concerted mechanism in which the metalcarbene carbon atom interacts with the *sigma* C-H bond (Scheme 1). Nakamura and coworkers computed the mechanism for rhodium-based catalysts,<sup>5</sup> based on the previously report-

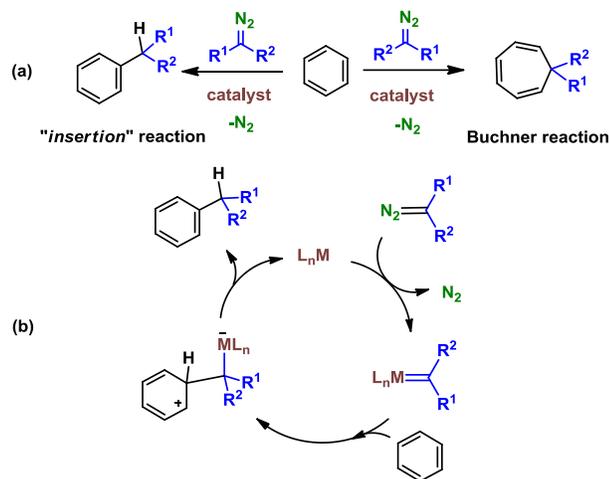
**Scheme 1.** C<sub>sp</sub><sup>3</sup>-H functionalization by metal catalyzed carbene insertion from diazo compounds



ed experimental results.<sup>6</sup> and later by our group for the coinage metals Cu- and Ag-based catalysts.<sup>7</sup> However, the mechanistic picture is yet unclear for the benzene (or arene) C<sub>sp</sub><sup>2</sup>-H bond functionalization with this strategy. First, this reaction competes with the so-called Buchner reaction, in which a cyclopropanation-derived norcaradiene intermediate is formed that further evolves toward a cycloheptatriene (Scheme 2a). With Rh<sub>2</sub>(OAc)<sub>4</sub> as the catalyst, Shechter and Livant separately reported<sup>8</sup> the metal-catalyzed functionalization of benzene by means of

the *formal insertion* of the carbene unit into the C-H bond. The use of the *formal* term is related to the nature of the product obtained, but the mechanism does not seem to occur through that precise insertion pathway, at variance with the aforementioned C<sub>sp</sub><sup>3</sup>-H bond modification. From seminal work with rhodium,<sup>8a,9</sup> it was proposed that the metalcarbene originates a Wheland intermediate that undergoes a 1,2-hydrogen shift to give the

**Scheme 2. (a) Arene C<sub>sp</sub><sup>2</sup>-H functionalization by metal catalyzed carbene transfer from diazo compounds. (b) The Wheland-based mechanism proposed for that transformation**

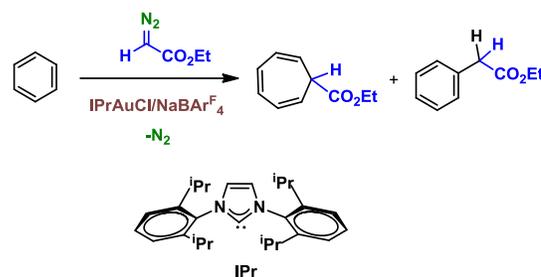


final product (Scheme 2b).

Nearly a decade ago we discovered<sup>10</sup> gold as the catalyst for the transfer of the CHCO<sub>2</sub>Et group from ethyl diazoacetate (N<sub>2</sub>=CHCO<sub>2</sub>Et, EDA), using IPrAuCl (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) to several saturated and unsaturated substrates, with NaBAR<sub>4</sub><sup>F</sup> (BAR<sub>4</sub><sup>F</sup> = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) as the halide scavenger. Benzene and other alkyl-arenes were modified (Scheme 3) providing mixtures of the products derived from the functionalization of the C<sub>sp</sub><sup>2</sup>-H bond as well as cycloheptatrienes derived from the Buchner reaction. Interestingly, the C<sub>sp</sub><sup>3</sup>-H bonds of the R substituents of the aromatic ring remained unreacted,<sup>11</sup> in spite of the well-known activated nature of benzylic sites. This finding paved the way to the use of this metal for carbene transfer reactions from diazo reagents.<sup>12</sup>

On the basis of the uncertainty of the mechanism of this C<sub>sp</sub><sup>2</sup>-H bond functionalization, we decided to perform a mechanistic study toward that end, mixing experimental data and DFT calculations. With the series of complexes IPrMCl, with M standing for Cu, Ag and Au, we have established the influence of the metal center onto the reaction outcome, from which a marked coinage metal effect has been found. With support of DFT studies, a complete mechanistic picture is proposed fitting the experimental differences observed with the three metals. It is worth mentioning that a recent theoretical work by Liu, Xia and co-workers have provided some light on this

**Scheme 3. The gold-based catalytic system for carbene transfer from ethyl diazoacetate and subsequent Arene C<sub>sp</sub><sup>2</sup>-H functionalization**



transformation based on the (PhO)<sub>3</sub>PAu=C(Ph)CO<sub>2</sub>Me species.<sup>13</sup> Additionally, Hashmi and co-workers have provided interesting mechanistic studies on gold-based transformation involving vinylidene intermediates in C-H bond functionalization reactions.<sup>14</sup>

## RESULTS AND DISCUSSION

**The Metal Effect.** The series of complexes IPrMCl (M = Cu, Ag, Au) have been employed as the catalyst precursor, along with one equiv of NaBAR<sub>4</sub><sup>F</sup> in the test reaction of EDA and benzene. The reactions were performed using benzene as the solvent, at room temperature, and adding the EDA in one portion. The results are shown in Table 1, where a significant influence of the metal center in the distribution of products has been found. Thus, the gold-based catalyst provided a regioselectivity of 75:25 favoring the alkylated product. In contrast, the silver-based cata-

**Table 1. Metal effect in the reaction of EDA with benzene using IPrMCl + NaBAR<sub>4</sub><sup>F</sup> as catalytic precursor.<sup>a</sup>**

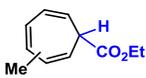
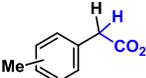
Entry	Metal	Yield <sup>b</sup>		
1	Cu	42 %	70 %	30 %
2	Ag	93 %	95 %	5 %
3	Au	>99 %	25 %	75 %

<sup>a</sup>Reaction conditions: catalyst loading 0.025 mmol, 0.5 mmol of EDA in 3 mL of benzene, room temperature. <sup>b</sup>Determined by NMR. Percentage of initial EDA converted into products. The remaining initial EDA (up to 100%) was converted into diethyl fumarate and maleate.

lyst only led to a very minor 5% of such product, the cycloheptatriene being by far the major products derived from benzene. The copper catalyst gave a 70:30 mixture favoring the seven-membered ring. Interestingly, the formation of diethyl fumarate and maleate as byproducts as the result of the carbene homocoupling side reaction was not observed with the gold-based catalyst, whereas both the Cu- and Ag- analogs led to their formation to a certain extent. Also, blank experiments carried out with pure cycloheptatriene demonstrated that under the same

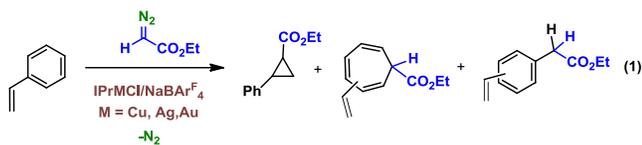
reaction conditions no isomerization to the insertion products was observed.<sup>15</sup>

**Table 2. Metal effect in the reaction of EDA with toluene using IPrMCl + NaBAR<sub>4</sub><sup>F</sup> as catalytic precursor.<sup>a</sup>**

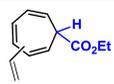
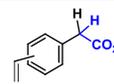
Entry	Metal	Yield <sup>b</sup>		
1	Cu	38 %	88 % (12:33:55) <sup>c</sup>	12 %
2	Ag	93 %	90 % (24:35:41) <sup>c</sup>	10 %
3	Au	>99 %	20 %	80 % (46:21:33) <sup>c</sup>

<sup>a</sup>Reaction conditions: catalyst loading 0.025 mmol, 0.5 mmol of diazo compound in 3 mL of toluene, room temperature. <sup>b</sup>Determined by NMR. Percentage of initial EDA converted into products. The remaining initial EDA (up to 100%) was converted into diethyl fumarate and maleate. <sup>c</sup>*ortho:meta:para* ratio.

Toluene has also been employed as the model substrate for substituted arenes containing potentially reactive C<sub>sp</sub><sup>3</sup>-H bonds. As shown in Table 2, two different behaviors were observed. On one hand, the copper and silver catalysts predominantly led to the formation of cycloheptatrienes (88-90%), with minor amounts of the alkylated products being detected. On the other, the gold catalyst gave a mixture of both compounds, with the insertion product as the major one. A mixture of the *o*, *m* and *p* isomers was observed, a feature that will be commented in the next section. It is remarkable that the product derived from the functionalization of the methyl group (that we had previously observed using copper catalysts bearing trispyrazolylborate ligands)<sup>16</sup> was not detected in any of the three catalytic systems, supporting the great chemoselectivity of this [IPrM<sup>+</sup>] system toward arene functionalization over C<sub>sp</sub><sup>3</sup>-H modification.



**Table 3. Metal effect in the reaction of EDA with styrene using IPrMCl + NaBAR<sub>4</sub><sup>F</sup> as catalytic precursor.<sup>a</sup>**

Entry	Metal	Yield <sup>b</sup>			
1	Cu	>99 %	88 %	7 %	4 % <sup>d</sup>
2	Ag	>99 %	67 %	29 %	4 % <sup>d</sup>
3	Au	>99 %	40 %	nd <sup>c</sup>	60 % <sup>d</sup>

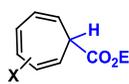
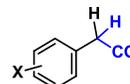
<sup>a</sup>Reaction conditions: catalyst loading 0.025 mmol, 0.5 mmol of diazo compound and 50 mmol of styrene in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>, room temperature. <sup>b</sup>Percentage of initial EDA converted into products. The remaining initial EDA (up to 100%) was converted into diethyl fumarate and maleate. <sup>c</sup>No detected. <sup>d</sup>As a mixture of the *o*, *m* and *p* isomers.

The propensity of these catalysts to attack the arene ring has been reinforced using styrene as the substrate (eq 1, Table 3). In addition to the expected cyclopropanes, yet some amounts of cycloheptatrienes and/or the insertion products are observed with the three metals. The gold catalyst provides, by far, the more significant difference, with a higher yield into the arene C<sub>sp</sub><sup>2</sup>-H functionalized product than that of cyclopropanes.

**Monosubstituted benzenes as substrates.** The use of toluene as the substrate along with the gold-based catalyst has shown a slight increase into the C<sub>sp</sub><sup>2</sup>-H functionalized product compared to that of benzene (80% vs 75%). We wondered about the possible effect that other substituents might exert onto the selectivity. Thus, a series of monosubstituted benzenes were employed as reactants. As shown in Table 4, the nature of the substituent induced a profound effect in the reaction outcome. Electron-withdrawing group such as CF<sub>3</sub> favored cycloheptatrienes as the major products, a situation that is reversed with electron donating groups such as OMe or NMe<sub>2</sub>. Interestingly all C<sub>sp</sub><sup>3</sup>-H bonds remained unreacted along the series of experiments.

As mentioned above, a mixture of isomers derived from the *ortho*-, *meta*- and *para*- relative positions is observed

**Table 4. Functionalization of monosubstituted benzenes with EDA in the presence IPrAuCl + NaBAR<sub>4</sub><sup>F</sup>.<sup>a</sup>**

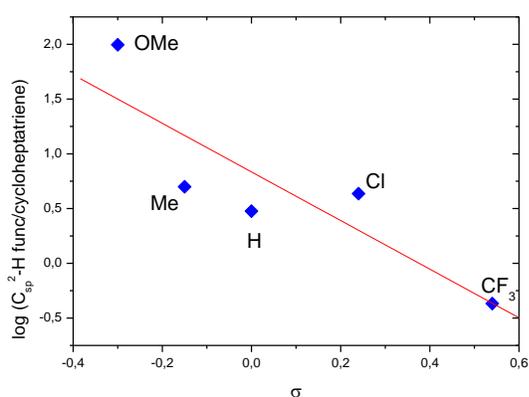
Entry	X	Yield <sup>b</sup>		
1	CF <sub>3</sub>	95 %	80 % <sup>c</sup>	20 % (0:18:82) <sup>d</sup>
2	Cl	94 %	28 % <sup>c</sup>	72 % (41:21:38) <sup>d</sup>
3	H	95 %	25 % <sup>c</sup>	75 %
4	Me	96 %	16 % <sup>c</sup>	80 % (46: 21:33) <sup>d</sup>
5	OMe	99 %	1 % <sup>c</sup>	99 % (45:11:44) <sup>d</sup>

<sup>a</sup>See experimental section for details. <sup>b</sup>Percentage of initial EDA converted into products. The remaining initial EDA (up to 100%) was converted into diethyl fumarate and maleate. <sup>c</sup>As mixture of isomers. <sup>d</sup>*ortho:meta:para* ratio.

in all cases. In an attempt to evaluate the electronic influence of the X groups in the selectivity of this transformation, a fitting of these values into Hammett equation has been performed. For this purpose the ratio of the C<sub>sp</sub><sup>2</sup>-H functionalized and cycloheptatrienes products was calculated, and its log was plotted vs  $\sigma$ .<sup>17</sup>

As shown in Figure 1, a good correlation with Hammett equation is found, with a value of  $\rho = -2.21 \pm 0.73$ . We interpret this value as the result of a substantial effect of the electronic nature of the arene substituent in the distribution of products: the more donating ones favoring the formal insertion reaction of the carbene group.

**Figure 1.** Hammett  $\sigma$  correlation for relative rates of functionalization of monosubstituted benzene derivatives with EDA



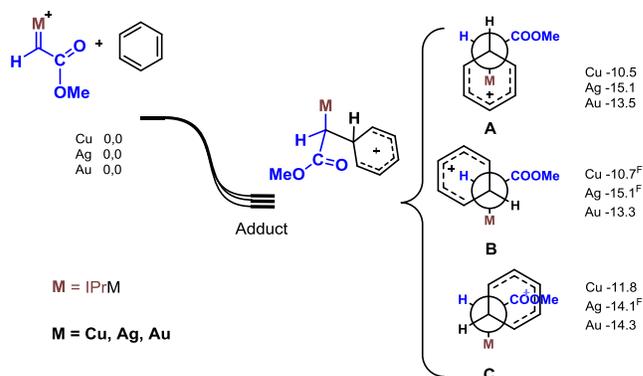
A competition experiment carried out with benzene and benzene- $d_6$  provided the following information: (i) the amounts of the products derived from both arenes were nearly identical within experimental error and (ii) kinetic experiments on nitrogen evolution gave also identical curves in both cases. From these data we can conclude that the rate determining step is located much earlier than the C-H cleavage (probably the metallocarbene formation).

All experimental evidences collected in this and previous works seem to support a pathway that differs from that of the  $C_{sp^3}\text{-H}$  bonds (Scheme 1). At variance with that metallocarbene-C-H bond one step interaction, the  $C_{sp^2}\text{-H}$  bond functionalization with this strategy displays features resembling an aromatic electrophilic substitution. In order to find additional support for such alternative, we have carried out DFT studies that must provide not simply the reaction pathway but also explain the selectivities observed regarding the effect of the metal in the chemoselectivity (insertion vs addition products).

**DFT studies.** We have computationally investigated the reaction mechanisms for the reaction between the metallocarbene  $\text{IPrM}=\text{C}(\text{H})\text{COOMe}$  and benzene ( $\text{M}=\text{Cu}$ ,  $\text{Ag}$  and  $\text{Au}$ ) in order to explain the different insertion/addition ratios experimentally observed. The initial approach between the metallocarbene and benzene leads to the formation of an adduct with a new C-C bond (distance below 1.66 Å) between the carbenic carbon and benzene (Scheme 4). This adduct, which is reached with-

out any barrier in the potential energy surface, may be viewed as a Wheland intermediate. Three conformers (A, B and C) of the adduct are in principle accessible depending on the relative orientation of substituents with respect

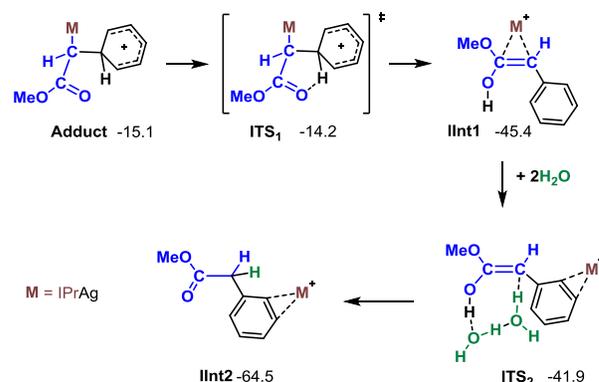
**Scheme 4.** Reaction of the metallocarbene and benzene to form the Wheland intermediate. Fischer projection of the three main conformers of this intermediate. Free energies in kcal/mol



to the newly formed C-C bond (see Scheme 4).

The adducts can evolve towards either insertion or addition products. Scheme 5 shows such evolution for the insertion pathway for the particular case of conformer A of the silver species. It starts with a proton transfer to the oxygen of the carbonyl to form an enol intermediate (ITS<sub>1</sub>). The enol IInt<sub>1</sub> assisted by two water molecules or another enol molecule performs a keto-enol rearrangement (ITS<sub>2</sub>) to transfer the hydrogen from the oxygen to the former carbenic carbon affording the final alkylated (“insertion”) product IInt<sub>2</sub>. An analogous mechanism of insertion has been recently postulated for a similar gold system.<sup>13</sup> The proton transfer to a carbonyl compound is now a well-known feature of many metal carbene transformations of diazocarbonyl compounds.<sup>18,19</sup> The contri-

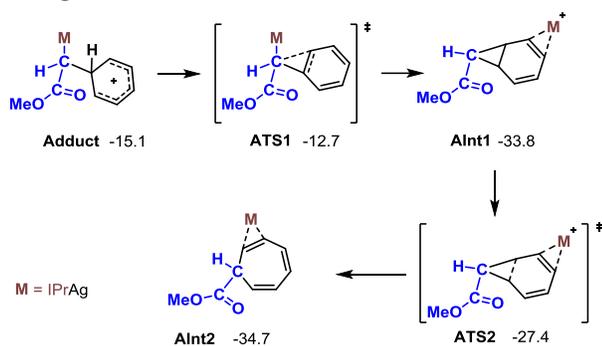
**Scheme 5.** Postulated mechanism for the insertion reaction from adduct A in the case of Ag. Free energies in kcal/mol



bution of water in the long distance proton transfers has been proposed even for a protodeauration step.<sup>20</sup>

The Buchner reaction (addition) pathway, is summarized in Scheme 6. First, a second C-C bond is made through transition state **ATS<sub>1</sub>**. In most cases, **ATS<sub>1</sub>** evolves directly to **Alnt<sub>1</sub>** where the metal coordinates to the aromatic ring. Finally, the **Alnt<sub>1</sub>** undergoes an electrocyclic opening (**ATS<sub>2</sub>**) to form the cycloheptatriene **Alnt<sub>2</sub>**, the addition final product. There is certainly no experimental evidence concerning the  $\pi$ -complexes we propose in this mechanism, but we assume they are correct because of the overall agreement between computational results and experiment. The proposed mechanism is moreover in agreement with the previously reported for the Echavarren (retro-Buchner) reaction, a gold-catalyzed decarbenation (carbene extrusion from cycloheptatriene) process<sup>21</sup>

**Scheme 6. Postulated mechanism for the Buchner reaction from adduct A in the case of Ag. Free energies in kcal/mol**



Schemes 5 and 6 correspond to the Ag species, but the results are similar for the Cu and Au complexes. Some minor differences exist, however, for instance in the case of Au, the final intermediates are better described as  $\eta^1$  complexes rather than metalacyclopropenes.

In most computational mechanistic studies, the predicted product ratio could be obtained directly by comparing the barriers associated to the competing transition states **ITS<sub>1</sub>** and **ATS<sub>1</sub>**. However the combined presence of the three possible conformations for the adduct and its association to very shallow minima with at least two exit channels lead to a rather more complicated picture. The importance of conformers into the study of reaction mechanisms has been previously acknowledged.<sup>22</sup> The complexity of the picture can be first seen in Table 5. Here we attempt to collect the free energies of the key points for each metal complex and each conformation. Not all points could be located as stationary points, and we had to carry out constrained geometry optimizations (freezing selected distances, structures marked with the superscript F) to estimate their energies. This has minor implications for some structures, like **ATS<sub>1</sub>** for Cu, which has a higher energy than both the corresponding adduct and **ITS<sub>1</sub>** and likely means that in this case insertion is not feasible. But it is critical in other cases such as the **B** conformers for both Cu and Ag. In this case, there is no stationary point associated with the adduct and the constrained transition state **ATS<sub>1</sub>** has a lower energy than the adduct. The straightforward interpretation is that in the complex-

benzene approach corresponding to conformation **B** there is a direct path from the separated reactants to the **Alnt<sub>1</sub>**

**Table 5. Relative free energies of the key minima and transition states for the addition/insertion pathways.**

Metal	A	B	C
Cu			
Adduct	-10.5	-10.7 <sup>a</sup>	-11.8
ATS <sub>1</sub>	-8.4 <sup>F</sup>	-13.4 <sup>a</sup>	-7.8 <sup>a</sup>
ITS <sub>1</sub>	-10.0	-10.0	--
Ag			
Adduct	-15.1	-15.1 <sup>a</sup>	-14.1 <sup>a</sup>
ATS <sub>1</sub>	-12.7	-17.1 <sup>a</sup>	-13.6 <sup>a</sup>
ITS <sub>1</sub>	-14.2	-14.2	--
Au			
Adduct	-13.5	-13.3	-14.3
ATS <sub>1</sub>	-8.5	-8.1	-3.0
ATS <sub>2</sub>	-7.0	-7.0	0.8
ITS <sub>1</sub>	-12.2	-12.2	--

<sup>a</sup>Energies corresponding structures optimized with a frozen parameter.

species.

Direct application of transition state theory to the results in Table 5 would predict a 100% of addition product for Cu and Ag, as a barrierless process should be always preferred. In the case of gold, insertion should be preferred also at nearly 100% proportion, as the free energy differences between the competing transition states are larger than 4 kcal/mol. The experimental trend of addition (Buchner reaction) being favored for copper and silver, and insertion being favored for gold is reproduced. But the experimental ratios, with the major product never being above 90% are definitely not reproduced. This is a serious disagreement between calculations and experiment that throws into question the validity of our computational analysis. In order to justify the validity of the calculations, we have analyzed the validity of the underlying computational approaches, and we provide below a

**Table 6. Number of trajectories going through the addition/insertion/not-reactive reaction pathways, depending on the metal center (Cu, Ag, Au) and the considered conformer (A, B, C).**

Metal	A	B	C
Cu	9/0/1	8/2/0	6/0/4
Ag	8/0/2	6/3/1	5/0/5
Au	0/0/10	0/8/2	0/0/10

qualitative justification of the discrepancy. We think that the origin of the discrepancy is in the limitations of the transition state theory (TST), which does not apply properly to this situation.<sup>23</sup> TST assumes redistribution of

internal energy among the vibrational modes and internal rotations previous to any reaction step. This is not always the case, as it has been recently showed in cases with shallow intermediates and an excess of total energy.<sup>24,25,26</sup> It is possible that in our system once the adduct is formed the subsequent step takes place before the energy redistribution occurs.

To explore this we have conducted Born-Oppenheimer molecular dynamics (BOMD) calculations<sup>27</sup> on the simplified model of our system of interest NHC-M=CH(COOH) + C<sub>6</sub>H<sub>6</sub>. This type of quantum dynamics has been previously used with success.<sup>28</sup> We centered our attention to the first part of the reaction where the first C-C bond is formed and the immediate evolution of this unstable intermediate towards one of the products. We ran only 10 trajectories for each approach and metal, a total of 90 trajectories.

The results of the BOMD calculations are summarized in Table 6. We have counted the number of trajectories going through addition/insertion/non-reactive reaction pathways. In the trajectories labeled as non-reactive, the complex remains as a Wheland intermediate or forms unstable intermediates that are expected to revert to it. For the copper catalyst 23 of the 25 productive trajectories lead to the addition product, and 2 of them, all associated to path **B**, to the insertion product. The case of silver is similar, with 19 out of 22 going to addition and 3 out of 22 leading to insertion. We note that for copper, 23:2 would mean a proportion of 92:8, and for silver, 19:3 translates to 86:14. The numbers are reasonably close to the experimental observations of 70:30 and 95:5 respectively. There are at least two major problems in the translation of reacting trajectories to total ratios, namely the small number of trajectories and the assumption that the three paths have an identical probability, so we do not claim this as an accurate prediction. But we consider these results indicative that extensions beyond transition state theory do improve the agreement with experiment in this system. We finally admit that these results can still not explain the experimentally reported 25:75 result in the gold system, as calculations still suggest 0:100. Explanation of this result may require a more accurate dynamic study, out of the scope of the current work.

The calculations reported above show an unexpected complexity in the system, but can provide yet a reasonable reproduction of the experimental results. The key to the different behavior of the gold complex lies in the energetics of addition for path **B**. The step is barrierless in the potential energy surface for copper and silver, but has a barrier of 5.2 kcal/mol for gold. The higher barrier may be associated to the existence of a substrate rearrangement in the metal coordination sphere along this pathway, which is a poor fit for the limited stability of Au(I) compounds with coordination numbers above two.

## CONCLUSIONS

In summary, we have found that the catalytic system formed by complexes IPrMCl and NaBAr<sub>4</sub><sup>F</sup> (M = Cu, Ag,

Au; IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene; BAr<sub>4</sub><sup>F</sup> = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), benzene and ethyl diazoacetate promotes the functionalization of the aromatic ring providing mixtures of products derived from direct C<sub>sp</sub><sup>2</sup>-H bond modification as well as cycloheptatriene rings derived from Buchner reaction. The selectivity strongly depends of the nature of the coinage metal, Cu and Ag favoring ethyl cycloheptatriene-1-carboxylate whereas gold gave the alkylated arene as the major product. With toluene as the substrate, a similar behavior is observed, albeit the methyl group remained unreacted, as a consequence of a high selectivity toward the arene vs aliphatic C-H bond. Experimental data and DFT calculation support the existence of a mechanistic pathway in which a Wheland-type intermediate is first formed, from which two alternative routes might occur. That of the insertion product resembles the aromatic electrophilic substitution, at variance with the concerted, one-step mechanistic view of the functionalization of C<sub>sp</sub><sup>3</sup>-H by carbene insertion.

## EXPERIMENTAL SECTION

**General methods.** All reactions were carried out under an oxygen-free nitrogen atmosphere by using an MBraun-Unilab glovebox containing dry argon or nitrogen or conventional Schlenk techniques. Solvents were purchased from Aldrich and were rigorously dried previously to their use. The reagents were also purchased from Aldrich and employed without further purification. The complex IPrMCl and NaBAr<sub>4</sub><sup>F</sup> were prepared according to the literature.<sup>29,30</sup> NMR solvents were stored over molecular sieves under nitrogen. NMR spectra were performed on Agilent 400 MR and 500 DD2 spectrometers. GC data were collected with a Varian GC-3900 spectrometer with a FID detector.

**General Catalytic Experiment.** The precatalyst IPrMCl (0.025 mmol) was dissolved in 3 mL of the corresponding substrate, and NaBAr<sub>4</sub><sup>F</sup> (0.025 mmol) was added to the solution. After 15 min, EDA (0.5 mmol) was added in one portion. Upon stirring at room temperature for 72 h, the mixture was analyzed by GC and GCMS. The volatiles were removed under reduced pressure and the residue was analyzed by NMR spectroscopy to identify the products. See SI for experimental details.

**Computational details.** The DFT studies presented have been performed with the B97D<sup>31</sup> Grimme's functional including D2 empirical dispersion correction as implemented in Gaussian 09<sup>32</sup> 6-31g(d) basis sets<sup>33</sup> were used for all atoms except for the three metals of the catalysts Cu, Ag and Au for which lanl2dz<sup>34</sup> was used instead together with the corresponding ECP and an additional polarization function f with the exponents Cu( $\zeta(f) = 3.525$ ), Ag( $\zeta(f) = 1.611$ ) and Au( $\zeta(f) = 1.050$ ).<sup>35</sup> Solvent effects have been taken into account through the continuum model SMD for benzene.<sup>36</sup> The model used is the same metalcarbene used experimentally except for the

ethyl group of the COOEt that is replaced by a methyl. The static calculations presented correspond to minima or transition states as confirmed by frequency calculations, however due to the particularities of the considered potential energy surface some of the structures presented correspond to geometries with a frozen distance between to atoms. These energies should only be taken as orientative and are marked with an F in the schemes and text. All energies presented correspond to free energies in solution and in kcal/mol.

To achieve a better understanding on the reactivity of the system, quantum dynamics under the Born-Oppenheimer molecular dynamics (BOMD) model<sup>27</sup> as implemented in Gaussian 09<sup>37</sup> were carried out. The system was simplified by pruning the diisopropylphenyl groups of the metallo-carbene IPr to hydrogens and the ethyl group of the carbene also to hydrogen. The dynamics calculations were initiated from geometries where the carbenic carbon and one of the carbons of the benzene were set to 2.5 Å and the rest of the molecule optimized, as a calculation from the separate reactants would be unfeasible in terms of computational effort. The initial kinetic energy was taken as the difference between the starting point and the separate reactants in the potential energy surface, and the initial velocities were obtained from a preliminary calculation with the `nsample` keyword and providing the mode number and vibrational energy corresponding to the mode for the stretch between the carbenic carbon and the closest carbon of the benzene. The calculations were performed defining the phase for the transition vector between the carbonic carbon and one of the benzene carbons, for a rotational temperature of 300 K, performing Hessian updates every 12 gradient points before doing a new analytic Hessian. For each system 10 trajectories were considered reading in initial velocities. For the more reactive Ag we performed 3000 steps which correspond to 2 ps. aprox. For Cu and Au we generated 6000 steps corresponding to approximately 4 ps, some tests with 12000 steps were run for selected systems.

A data set collection of computational results is available in the IoChem-BD repository.<sup>32</sup>

**Supporting Information.** Detailed experimental catalytic and mechanistic procedures, including kinetic isotopic effect studies and computational data including transition states geometries and Cartesian coordinates and energies of all stationary points reported in the text. The Supporting Information is available free of charge on the ACS Publications website.

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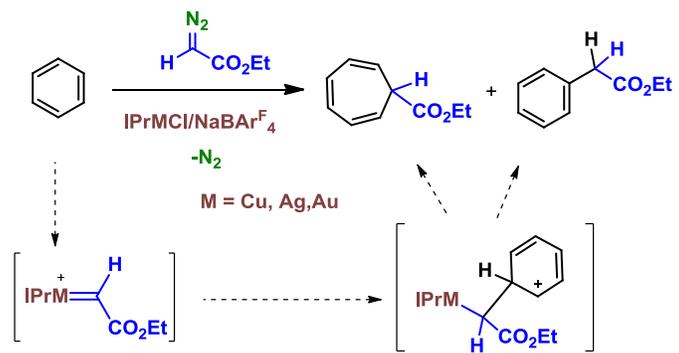
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IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) ligand