

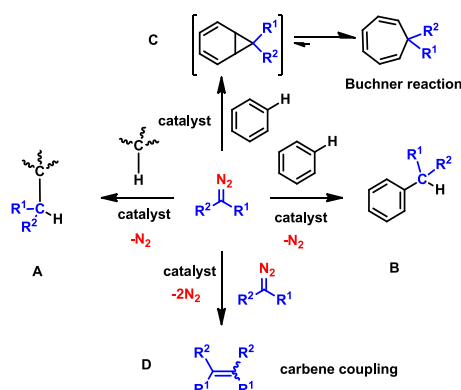
Introducing Fe and Mn as catalysts for the selective functionalization of C_{sp}²-H bonds of arenes by carbene insertion

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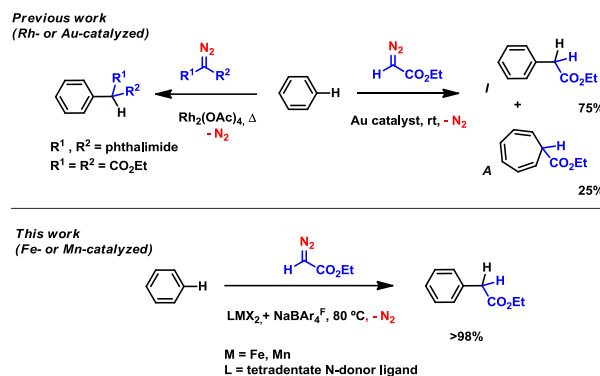
Abstract: The first examples of the direct functionalization of non activated aryl sp² C-H bonds with ethyl diazoacetate (N₂CHCO₂Et) catalyzed by Mn- or Fe-based complexes in a completely selective manner, with no formation of the frequently observed cycloheptatriene derivatives through competing Buchner reaction are reported. The best catalysts are Fe(II) or Mn(II) complexes bearing the tetradentate pytacn ligand (pytacn = 1-(2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane). When using alkyl-benzenes, the alkylic C_{sp}³-H bonds of the substituents remained unmodified, thus the reaction being also selective toward functionalization of sp² C-H bonds.

The metal-catalyzed transfer of carbene units from diazo compounds constitutes a powerful tool in organic synthesis. A number of substrates ranging from olefins or alkynes to alcohols or amines have been functionalized^[1,2] upon respective addition



Scheme 1. The catalytic functionalization of carbon-hydrogen bonds with diazo compounds.

of the carbene moiety to the unsaturated C-C bond or the insertion of such unit into the X-H bond. Carbon(sp³)-hydrogen bonds have also been modified by this methodology (Scheme 1, A), including not only those of the less reactive C_nH_{2n+2}



Scheme 2. The previous examples of the metal-catalyzed C_{sp}²-H functionalization of benzene by carbene insertion from diazo compounds and the novel Fe- and Mn-based catalytic systems.

alkanes,^[3] but also of saturated polyolefins^[4a] or even of the rather inert C-H bonds of methane.^[4b]

The use of this strategy onto the aromatic C_{sp}²-H bonds of benzene (Scheme 1, B) has not been developed that much. This is the result of the existence of competing reactions when exposing benzene to a diazo compound in the presence of a metal-based catalyst. One of them is the so-called Buchner reaction (Scheme 1, C),^[5,6] that occurs by formal addition of the carbene unit to the arene C=C bond yielding a norcaradiene which spontaneously opens producing the cycloheptatriene. The opposite transformation, *i. e.* the retro-Buchner or Echavarren reaction has been described.^[7] A second favored pathway involves the metal-catalyzed homocoupling of two carbene units (Scheme 1, D), a non-desired transformation that is very often observed within these catalytic systems.^[8]

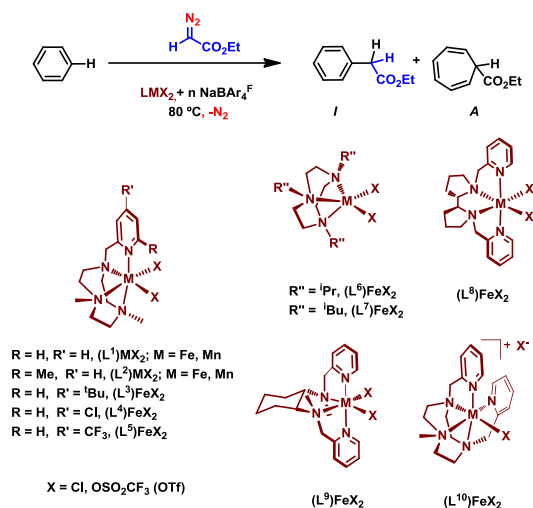
The *formal insertion*^[9] of a carbene group from a diazo compound in the C-H bond of benzene was independently reported by the groups of Schechter^[10] and Livant,^[11] using Rh₂(OAc)₄ as the catalyst, at refluxing temperature, and with the diazo compounds shown in Scheme 2. However, the use of the commercially available as well as industrially relevant ethyl diazoacetate for this reaction was not described until 2005 when one of our groups reported on the potential of a gold-based catalyst for this transformation,^[12] that gave mixtures of the insertion (I) and addition (A) products, with yields in ca. 3:1 ratio (Scheme 2). Further catalyst development showed that other diazo compounds of types N₂C(R)CO₂Et (R = Me, SiMe₃) could be employed;^[13] in all cases the same mixture of products being obtained in similar ratios. The incorporation of substituents to the benzene rings favors this reaction, with several examples being described using phenols^[14] or anilines.^[15] Although not directly related to this chemistry, it is worth mentioning the use of directing groups in Rh/Ir-catalyzed transformations that involve the aromatic C-H functionalization at a given step.^[16]

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Supporting information for this article is given via a link at the end of the document.



Scheme 3. Top: the probe reaction of benzene and ethyl diazoacetate (EDA). Bottom: the complexes employed as catalysts in this work.

In our search for more selective catalysts for direct benzene C-H bond functionalization by carbene insertion, we have focused in complexes of Fe(II) and Mn(II) containing polydentate amino-based ligands.^[17] We have found that these complexes, with the appropriate additive, induce the completely selective insertion of the C(H)CO₂Et group into the C-H bonds of benzene and alkylbenzenes with no formation of cycloheptatriene byproducts (Scheme 2).

We first explored the potential of simple Fe(II) and Mn(II) salts in the reaction of ethyl diazoacetate and benzene at 80 °C (no reaction was observed at room temperature), with two equiv of NaBAR₄^F (BAR₄^F = tetrakis(bis-3,5-trifluoromethylphenyl)borate) employed as Cl/OTf scavenger (Table 1, entries 1-2), and dichloromethane as co-solvent. Interestingly, the iron salts induced the consumption of the initial EDA and the formation of mixtures of the insertion (I) and addition (A) products (Scheme 3). The Mn(II) salt also promoted the carbene transfer with low yields (entry 3) and EDA was not completely consumed, but an unprecedented excellent chemoselectivity for the insertion product was observed. After these encouraging results we screened a series of Fe(II) and Mn(II) complexes of general formula LMX₂, where L represents one of the polydentate ligands shown in Scheme 3, and X = Cl or CF₃SO₃. As inferred from entries 4-9, in experiments carried out with (L¹)FeX₂ pre-catalysts, the amount of NaBAR₄^F influenced the yield (a control experiment with NaBAR₄^F as the sole additive did not induce any reaction) that moved from 65 to 86 % (EDA-based, see Supporting Information). On the other hand, the addition of just one equiv of NaBAR₄^F did not induce the reaction, most of the EDA remained unreacted after several hours. But the most remarkable aspect observed is the unprecedented observation of *complete selectivity toward the insertion product* as the sole derivative formed from benzene with the series of Fe- or Mn-tridentate or tetradentate ligand-containing catalyst precursor (entries 4-19). In all cases, the products derived from the formal carbene CHCO₂Et homocoupling, diethyl fumarate and maleate, were not formed in detectable amounts. In addition, virtually

Table 1. Catalytic behaviour of complexes LMX₂ in the reaction of benzene and ethyl diazoacetate.^[a]

Entry	L	M	X	equiv NaBAR ₄ ^F	Yield ^[b]	%I:%A ^[c,d]
1	---	Fe	Cl	2	55	42:58
2	---	Fe	OTf	2	52	69:31
3	---	Mn	OTf	2	20	>99:1
4	L ¹	Fe	Cl	2	65	>99:1
5	L ¹	Fe	OTf	2	69	>99:1
6	L ¹	Fe	Cl	4	73	>99:1
7	L ¹	Fe	OTf	4	75	>99:1
8	L ¹	Fe	Cl	8	86	>99:1
9	L ¹	Fe	OTf	8	83	>99:1
10	L ¹	Mn	OTf	8	76	>99:1
11	L ²	Fe	OTf	8	77	>99:1
12	L ²	Mn	OTf	8	73	>99:1
13	L ³	Fe	OTf	8	47	>99:1
14	L ⁴	Fe	OTf	8	85	>99:1
15	L ⁵	Fe	OTf	8	18	>99:1
16	L ⁶	Fe	OTf	8	57	>99:1
17	L ⁷	Fe	OTf	8	67	>99:1
18	L ⁸	Fe	OTf	8	68	>99:1
19	L ⁹	Fe	OTf	8	70	>99:1
20	L ¹⁰	Fe	OTf	8	n.r	...

[a] Reactions carried out at 80 °C with 0.005 mmol of catalyst, n equiv of NaBAR₄^F and 20 equiv of ethyl diazoacetate in 1.5 mL of benzene + 1.5 mL of CH₂Cl₂. Reaction time: 12 h. [b] Initial EDA converted into insertion (I) + addition (A) products. Determined by GC; some ethyl glycolate from adventitious water was detected as byproduct. [c] Determined by NMR.

identical product yields and selectivities were obtained by using (L¹)FeCl₂ and (L¹)Fe(OTf)₂ precatalysts strongly suggesting that identical active species are generated in both cases. Use of the Mn precatalyst (L¹)Mn(OTf)₂ (entry 10) also produced the selective formation of the insertion product, but with a slightly lower yield. Manipulation of the steric (entries 11-12) and electronic (entries 13-15) properties of the pyridine ring in the catalysts did not improve their activity. Use of other robust tetradentate ligands (L⁸ and L⁹, entries 18 and 19) that have been recently proven quite active in iron and manganese catalyzed C-H functionalization reactions^[17e-f] also produced good yields of the insertion product but still lower than (L¹)Fe(OTf)₂. At variance with those results, no reaction was observed when an iron complex with a pentadentate ligand (L¹⁰, entry 20)^[17g] was used. To our knowledge, the degree of selectivity into the insertion product obtained with this novel catalytic system finds no precedent in the literature for the reaction of benzene and EDA.

The scope of the reaction has been extended to several mono alkyl-substituted-benzenes (R = Me, Et, iso-Bu, ^tBu, Cy, Figure 1 a-d and j) using (L¹)Fe(OTf)₂ as the catalyst. In all cases the *exclusive functionalization of the C_{sp}²-H bond* was observed, with none of the products derived from the insertion of the carbene group into the C_{sp}³-H of the substituent being detected (a certain amount of ethyl glycolate from adventitious water was also obtained, see Supporting Information). Di- (Figure 1, f) and tri-substituted benzenes (Figure 1, g-h) verified the same behavior. Therefore our system is not only selective within benzene reactivity (*insertion over addition*) but also relative to the C_{sp}³-H bonds in the substituents, at variance with Woo's iron-based system where such C_{sp}³-H functionalization was observed.^[18] Naphtalene also displayed functionalization toward the insertion product, albeit this substrate has shown a tendency to provide cyclopropanation derivatives.^[19] The related tetrahydronaphtalene was also modified in the aromatic ring in an exclusive manner. Finally, the substrates containing electron-withdrawing groups (Cl, CF₃) disfavored this transformation. It is worth pointing out that the acid-catalyzed conversion of the insertion into addition products described by McKerverey and co-worker^[20] has been discarded on the basis of control experiments (see Supporting Information). The related acid-catalyzed intramolecular *formal insertion* has also been reported by Schwartz and co-workers.²¹

With the aim of gaining mechanistic information, we have performed a series of competition experiments with substituted benzenes with both the Fe- and Mn- containing catalysts (L¹)M(OTf)₂ [eq 1] from which, using Hammett's equation, we have obtained respective values of ρ of -2.74(0.37) and -2.81(0.15). These values can be associated with the involvement of electrophilic metalcarbene intermediates. In the aforementioned work from Woo and co-worker,^[19] values within the range -1.11 to -0.82 were found for the iron-based catalysts. Additionally, kinetic isotopic experiments [eq(2)] have also been carried out with equimolar amounts of benzene and benzene-d₆, an *inverse isotopic effect* being observed with (L¹)M(OTf)₂ + 8 NaBAR₄^F: *k_H/k_D* was found as 0.95±0.01 for Fe and 0.80±0.02 for Mn.

The aforementioned feasible presence of iron-carbene intermediates opens the question of the nature of the carbene transfer, for which either concerted or step-wise pathways could be envisaged with these metals. We have carried out an experiment with the radical probe cyclopropylbenzene [eq(3)], lacking the observance of any product derived from the cyclopropane ring opening, that could assess that a step-wise mechanism for the carbene transfer reaction involving long lived substrate carbon-radical intermediates can be discarded. The relative selectivity of *ortho*, *meta* and *para* derivatives obtained with the array of substrates tested (Figure 1) also provides some

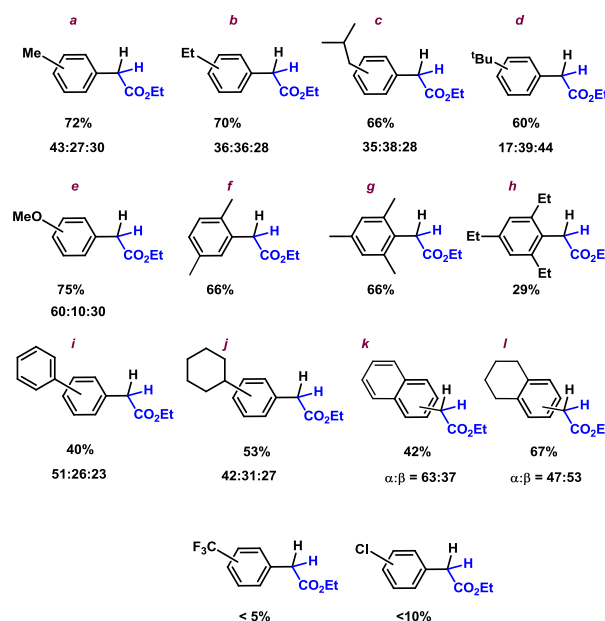
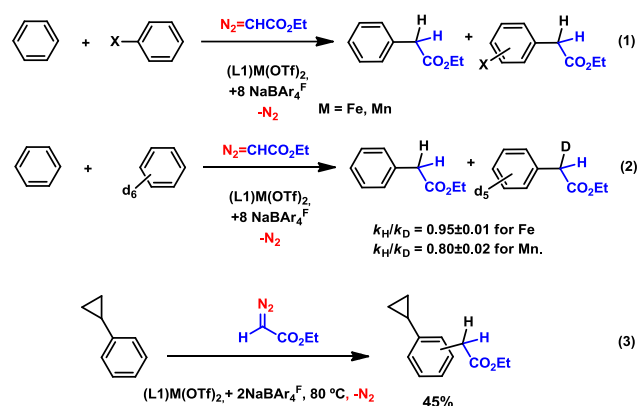
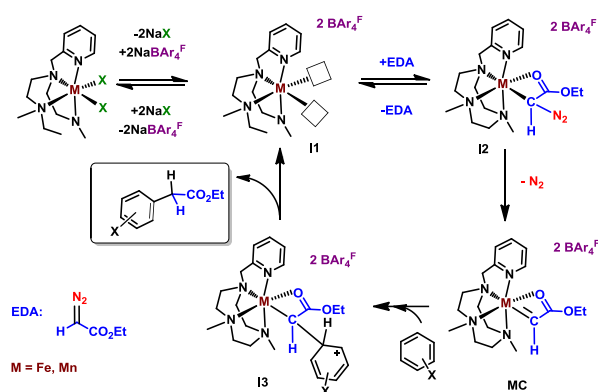


Figure 1. Functionalization of other arenes with (L¹)Fe(OTf)₂ + 8 NaBAR₄^F and EDA, showing Isolated yields and *o:m:p* distribution of products. The Cl- and CF₃ derivatives could only be detected in solution by GC due to the low conversion.

information about the nature of this transformation. The behavior of the mono-substituted alkyl arenes in Figure 1a-d demonstrates that the steric effect has only influence with the very bulky ^tBu substituent. For trisubstituted substrates, this system is capable of accessing the arene C-H bond of 1,3,5-triethylbenzene (Figure 1h), at variance with a recent work on arene C-H borylation,²² that was unproductive for this substrate. Additionally, anisole gave predominantly the *ortho* and *para* isomers, whereas the alkyl substituted benzenes R-C₆H₅ (R = Me, Et, iso-Bu, ^tBu) were less selective toward those positions. This performance resembles to a certain extent that of an electrophilic aromatic substitution.





Scheme 4. Reaction pathway for arene functionalization by carbene insertion via an electrophilic aromatic substitution mechanism.

Thus, any mechanistic explanation for the functionalization of the arene C-H bond must account for the following experimental facts: (a) Extrusion of one Cl^- or OTf^- from complexes bearing two of these anions as ligands does not provide an effective catalytic species; (b) the complex $(\text{L}^{10})\text{FeX}_2$, bearing a pentacoordinate ligand and just one OTf^- coordinated ligand does not catalyze (Table 1, entry 20) the reaction even with eight equiv of NaBAR_4F ; (c) an electrophilic metal-carbene intermediate must exist as an intermediate on the basis of the data from the Hammett's plot; (d) competition reactions with benzene and d_6 -benzene show an inverse isotopic effect, which should be related to a sp^2 - sp^3 hybridization in the vicinity of the transition state; (e) distribution of products show that steric effect is not high, and thus coordination of the arene to the metal center does not appear likely. In addition the pattern typical for an aromatic electrophilic substitution is observed, and (f) the use of a carbon-radical trap bearing a cyclopropyl group did not show the expected ring opening for long-lived, radical-involving reactions.

With the above pieces of information, we have built the mechanistic proposal shown in Scheme 4. The dependence of product yields with the amount of the halide scavenger, and the lack of catalytic activity for $(\text{L}^{10})\text{Fe}(\text{OTf})_2$ (Table 1, entry 20) suggests the formation of the dicationic species **I1** that binds the diazo compound in a dihapto manner yielding **I2**. The coordination of the carbonyl oxygen would explain that the arene does not coordinate, in agreement with some of the above facts. The arene would then react with the carbene ligand by means of an outer sphere mechanism, leading to a Wheland-type intermediate (**I3**). Such proposal is in good agreement with the observation of the inverse isotopic effect as well as a distribution of products typical for an electrophilic aromatic substitution. This interaction resembles that proposed by Doyle, Padwa and co-workers²³ for the rhodium-based intramolecular catalytic formal insertion of a carbene group into an aromatic C-H bond, for which they proposed a subsequent 1,2-hydrogen shift. This would liberate the product and regenerate **I1** to start the catalytic cycle. DFT studies are currently underway to provide more insight into this transformation and the selectivities observed. Back to the aforementioned work by

In conclusion, we have found that the complexes $(\text{L}^1)\text{M}(\text{OTf})_2$ ($\text{M} = \text{Fe}, \text{Mn}$) efficiently catalyze the reaction of benzene and other

alkyl-benzenes with ethyl diazoacetate, with two yet undescribed features. These are the first examples based on these metals for this transformation, since the scarce precedents are based on rhodium or gold. Second, but equally important, the catalytic system can be tuned to avoid the formation of any of the products derived from competing transformations: i) the Buchner reaction (ring expansion into cycloheptatriene); ii) the carbene homocoupling; and iii) when alkylbenzenes were employed, the insertion into $\text{C}_{\text{sp}^3}\text{-H}$ bonds. Thus, this catalytic system presents an exceptional selectivity favoring the carbene insertion into the $\text{C}_{\text{sp}^2}\text{-H}$ bonds.

Acknowledgements

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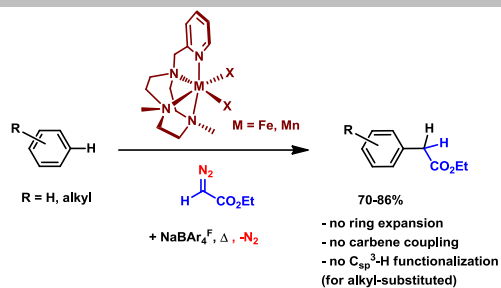
Keywords: Iron • manganese • C-H bond functionalization • carbene • arenes

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Entry for the Table of Contents

Iron- and-manganese-based catalysts selectively functionalize the C_{sp^2} -H bonds of benzene or alkyl-benzenes through the formal insertion of the $CHCO_2Et$ group from N_2CHCO_2Et .



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Introducing Fe and Mn as catalysts for the selective functionalization of C_{sp^2} -H bonds of arenes by carbene insertion