

C–H Bond Functionalization

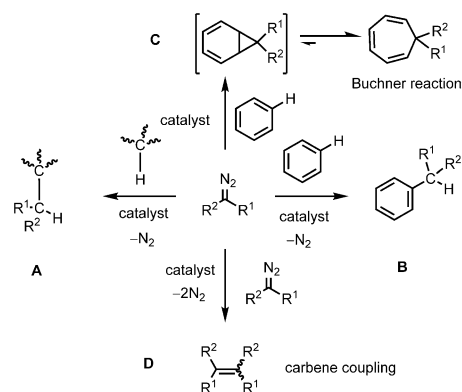
Deutsche Ausgabe: DOI: 10.1002/ange.201601750
Internationale Ausgabe: DOI: 10.1002/anie.201601750Iron and Manganese Catalysts for the Selective Functionalization of Arene C(sp²)–H Bonds by Carbene InsertionAna Conde⁺, Gerard Sabenya⁺, Mònica Rodríguez⁺, Verònica Postils, Josep M. Luis, M. Mar Díaz-Requejo,^{*} Miquel Costas,^{*} and Pedro J. Pérez^{*}

In memory of Roberto Sánchez-Delgado

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 are reported, with no formation of the frequently observed cycloheptatriene derivatives through competing Buchner reaction. 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 alkylbenzenes, the alkylic C(sp³)–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 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} 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(sp²)–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 norcar-



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

adiene 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]

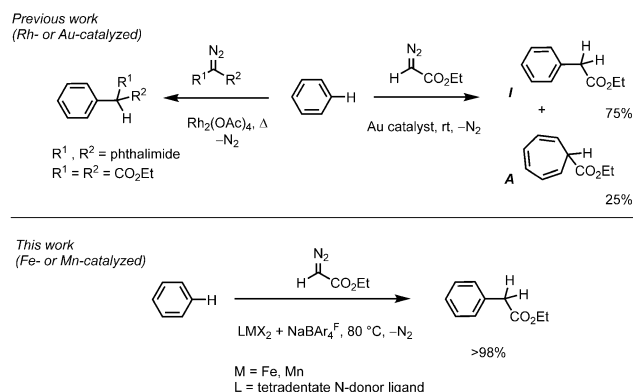
The formal insertion^[9] of a carbene group from a diazo compound in the C–H bond of benzene was independently reported by the groups of Schechter^[10] and Livant,^[11] using Rh₂(OAc)₄ as the catalyst, at refluxing temperature, and with the diazo compounds shown in Scheme 2. However, the use of

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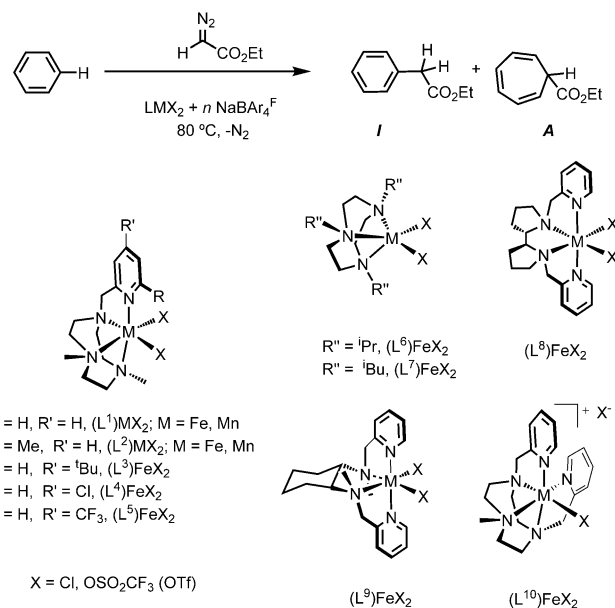


Scheme 2. The previous examples of the metal-catalyzed C(sp²)–H functionalization of benzene by carbene insertion from diazo compounds and the novel Fe- and Mn-based catalytic systems.

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 $N_2C(R)CO_2Et$ ($R = Me, SiMe_3$) could be employed;^[13] in all cases the same mixture of products was 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]

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 $C(H)CO_2Et$ group into the C–H bonds of benzene and alkyl-benzenes 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 $NaBAR_4^F$ (BAR_4^F = tetrakis(bis-3,5-trifluoromethyl-phenyl)borate) employed as Cl/OTf scavenger (Table 1, entries 1 and 2), and dichloromethane as co-solvent. Interestingly, the iron salts induced the consumption of the initial



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

Table 1: Catalytic behavior of complexes LMX_2 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 $NaBAR_4^F$ and 20 equiv of ethyl diazoacetate in 1.5 mL of benzene + 1.5 mL of CH_2Cl_2 . 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.

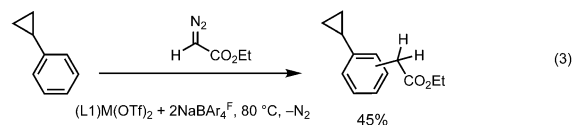
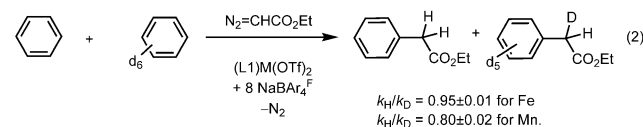
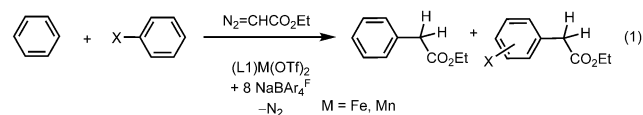
EDA and the formation of mixtures of the insertion (**I**) and addition (**A**) products (Scheme 3). The Mn^{II} salt also promoted the carbene transfer with low yields (entry 3) and EDA was not completely consumed, but an unprecedented excellent chemoselectivity for the insertion product was observed. After these encouraging results we screened a series of Fe^{II} and Mn^{II} complexes of general formula LMX_2 , where L represents one of the polydentate ligands shown in Scheme 3, and $X = Cl$ or OTf. As inferred from entries 4–9, in experiments carried out with $(L^1)FeX_2$ pre-catalysts, the amount of $NaBAR_4^F$ influenced the yield (a control experiment with $NaBAR_4^F$ as the sole additive did not induce any reaction) that moved from 65 to 86 % (EDA-based, see the Supporting Information). On the other hand, the addition of just one equiv of $NaBAR_4^F$ 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 $CHCO_2Et$ homocoupling, diethyl fumarate and maleate, were not formed in detectable amounts. In addition, virtually identical product yields and selectivities were obtained by using $(L^1)FeCl_2$ and $(L^1)Fe(OTf)_2$ precatalysts strongly suggesting that identical active species are generated in both cases. Use of the Mn precatalyst $(L^1)Mn(OTf)_2$ (entry 10) also produced the selective formation of the insertion product, but with a slightly lower yield. Manipulation of the steric (entries 11 and 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 (L^8 and L^9 , entries 18 and 19) that have been recently proven quite active in iron and manganese catalyzed C–H functionalization reactions^[17c,f] also produced good

yields of the insertion product but still lower than $(L^1)Fe(OTf)_2$. At variance with those results, no reaction was observed when an iron complex with a pentadentate ligand (L^{10} , 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 monoalkyl-substituted benzenes ($R = Me, Et, ^iBu, Cy$, Figure 1 a–d and j) using $(L^1)Fe(OTf)_2$ 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] Naphthalene also displayed functionalization toward the insertion product, albeit this substrate has shown a tendency to provide cyclopropanation derivatives.^[19] The related tetrahydronaphthalene was also modified in the aromatic ring in an exclusive manner. Finally, the substrates containing electron-withdrawing groups (Cl, CF_3) disfavored this transformation. It is worth pointing out that the acid-catalyzed conversion of the insertion into addition products described by McKervy and co-workers^[20] has been discarded on the basis of control experiments (see the 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 $(L^1)M(OTf)_2$ [Eq. (1)] from which, using Hammett's equa-



tion, 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-workers,^[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 d_6 -benzene, an inverse isotopic effect being observed with $(L^1)M(OTf)_2 + 8 \text{ NaBAR}_4^F$: 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 information about the nature of this transformation. The behavior of the mono-substituted alkyl arenes in Figure 1 a–d demonstrates that the steric effect has only influence with the very bulky *t*-Bu substituent. For trisubstituted substrates, this system is capable of accessing the arene $C–H$ bond of 1,3,5-triethylbenzene (Figure 1 h), 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 $R-C_6H_5$ ($R = Me, Et, ^iBu, ^tBu$) were less selective toward those positions. This performance resembles to a certain extent that of an electrophilic aromatic substitution.

Thus, any mechanistic explanation for the functionalization of the arene $C–H$ bond must account for the following

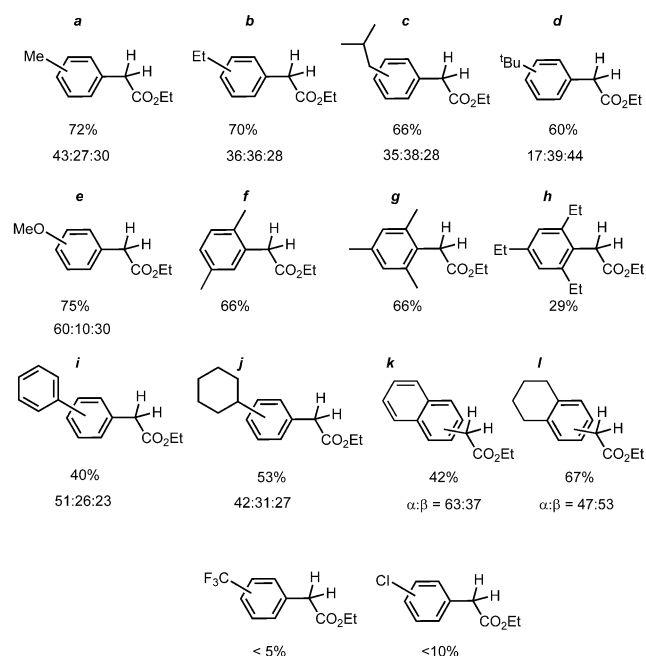


Figure 1. Functionalization of other arenes with $(L^1)Fe(OTf)_2 + 8 \text{ NaBAR}_4^F$ and EDA, showing isolated yields and *o:m:p* distribution of products. The Cl and CF_3 derivatives could only be detected in solution by GC due to the low conversion.

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 $(L^{10})FeX_2$, bearing a pentacoordinate ligand and just one OTf-coordinated ligand does not catalyze (Table 1, entry 20) the reaction even with 8 equivalents of $NaBAR_4^F$; 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, with the pattern typical for an aromatic electrophilic substitution being 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 $(L^{10})Fe(OTf)_2$ (Table 1, entry 20) suggests the formation of the dicationic species **I1** that binds the diazo compound in a dihapto manner yielding **I2**. While a diazo reagent can coordinate a metal center in several ways, we have only represented that showing the interaction of the carbon atom to the metal center since it is the productive one regarding the formation of the metal-carbene species **MC** (other species might be in equilibria with **I2** but are not relevant at this stage). 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-workers^[23] 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.

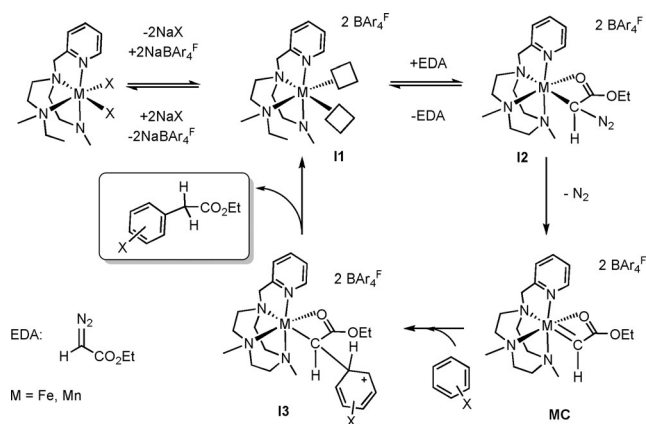
In conclusion, we have found that the complexes $(L^1)M-(OTf)_2$ ($M=Fe, Mn$) efficiently catalyze the reaction of benzene and other alkyl-benzenes with ethyl diazoacetate, with two yet undescribed features. These are the first examples based on these metals for this transformation, since the scarce 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: 1) the Buchner reaction (ring expansion into cycloheptatriene); 2) the carbene homocoupling; and 3) when alkylbenzenes were employed, the insertion into $C(sp^3)$ -H bonds. Thus, this catalytic system presents an exceptional selectivity favoring the carbene insertion into the $C(sp^2)$ -H bonds.

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

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