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COMMUNICATION

Fe(0)-Catalyzed Alkyne Carboxylation with CO_2 Involving Spin Crossover

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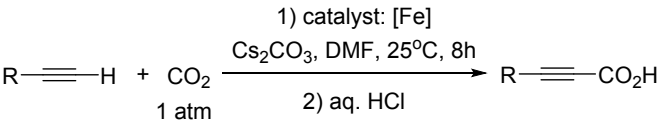
The first Fe(0)-catalyzed alkyne carboxylation using CO_2 is reported using Fe(0)-phenanthroline complexes, and DFT calculations suggest spin crossover from triplet to quintet along the reaction.

Carbon dioxide (CO_2) fixation in various forms is useful in order to limit the amount of greenhouse gas[1] and, besides, CO_2 is a cheap and readily available carbon source that is currently utilized for C-C, C-N and C-O bonds formations.[2-9] In particular, propionic acids, that can be obtained upon catalysed alkyne carboxylation, find applications in the manufacture of herbicides, rubber chemicals, emulsions, and environmentally friendly solvents for coating formulations, artificial fruit flavours, pharmaceuticals, and modified synthetic cellulose fibers, including cellulose acetate propionate.[8-10] Catalysts employed in alkyne carboxylation leading to propionic acids mostly involved Ag[11] and Cu [6, 7, 11, 12]. Iron, the most stable atom in the Universe and one of the very most abundant elements on the Earth crust, is very often used in catalysis,[13-15] particularly in heterogeneous catalysis, but its utilization in alkyne carboxylation to propionic acids is so far unknown.

First-row, late transition metal complexes with strong field ligands such as cyclopentadienyl and CO mostly fulfill the 18-electron rule, and they are "closed-shell" systems.[16, 17]On the other hand, inorganic nitrogen and oxygen ligands exert weak fields, so that this weak ligand field leaves relatively lower energy Δ between the three lower-energy e_g orbitals and the two higher-energy t_{2g} d orbitals in the case of an octahedral or pseudo-octahedral geometry. The low Δ value in inorganic complexes opens the possibility of different orbital occupations by electrons, leading to the possibilities of two spin states, low spin or high spin.[18, 19] Different reactivities, including catalytic behaviours, are expected from these two spin states, which has been exploited as a key feature already since the 2000's with bio-inorganic catalytic systems.[20-23] More recently, various studies have demonstrated the effect of spin state and spin crossover in catalysis,[24-37] although never so for carboxylation reactions. The complexes of general formula Fe(II)(1, 10-phenanthroline)Cl_2 bearing bulky substituents in 2,9 positions have been reduced by the Zhu group to substituted Fe(0)(phenanthroline) complexes showing catalytic acitivities for reactions of alkenes and alkynes.[27, 37-43] This family of Fe(0) complexes are now used here as alkyne carboxylation catalysts. The Fe electronic structure therein is $4s^2 4p^6 3d^8$ i.e. the eight d electrons occupy the five d orbitals. The chloro ligands have now been replaced by solvent ligands in the reduction process, and, according to both Pauli and Hund's rules, the three lower d orbitals are doubly occupied with electrons of opposite spins, and the two higher orbitals are singly occupied with electrons of the same spin, corresponding to a triplet spin ground state (S = 1; 2S +1 = 3). Zhu et al. have taken their catalytic results into account by a two-spin-state reactivity, the phenanthroline acting as a redox ligand that could possibly accept an electron from Fe(0) to yield a quintet-state Fe(I) complex of phenanthroline radical anion.[38] Under these conditions, among the five d orbitals, three of them become singly occupied, whereas one electron occupies a ligand orbital (S = 2). Such spin delocalization was reported in 2010-2012 with other iron catalysts containing a redox-active ligand, although the relationship with reactivity effects was not rationalized.[38]

Herein, we are reporting, using this family of iron-phenanthroline complexes, the first Fe(0)-catalyzed alkyne carboxylation reaction, utilizing CO_2 (eq. 1) and DFT calculation suggesting spin crossover during the catalyzed carboxylation process.



eq. 1

In order to obtain the Fe(0)(BTIPP) complex, (BTIPP = 2,9-bis(2,4,6-triisopropylphenyl)-1,10-phenanthroline ligand), the Zhu group reduced, using EtMgBr in THF, the complex [Fe(II)(BTIPP)Cl_2] and recorded the X-ray crystal structure of the Fe(II) precursor and of a diolefin Fe(0) adduct.[37, 39]

In the present work, the same and related Fe(II) precursors have been synthesized by stoichiometric reactions in THF between $FeCl_2$ and the phenanthroline derivatives with substituents in 2,9 positions (chloro, phenyl, mesityl and triisopropylphenyl), followed by

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precipitation from addition of excess hexane to a concentrated THF solution of the complexes, and recrystallization from ether. The different corresponding reduced black Fe(0) complexes have been generated in the same way as Zhu *et al* [37, 39] by reduction of the Fe(II) precursor in DMF using EtMgBr in ether. Its cyclic voltammogram consistently shows two succesive irreversible cathodic waves at -1.2 and -2.1 V vs. Fc^+/Fc on Au disk electrode corresponding to the successive reductions of the first and second Cl ligands (Supporting Information). The resulting reactive Fe(0) catalysts that are very sensitive have not been isolated, but utilized *in situ* for carboxylation of various alkynes.

After reduction of these Fe(II) complexes to Fe(0) catalysts conducted with EtMgBr in ether/DMF, it is speculated that Fe is in the zero oxidation state with two or three solvent molecules (from the solvent used in synthesis) in addition to the chelating L_2 phenanthroline ligand, which would involve respectivey 16-electron (2 weak solvent ligands) or 18-electron (3 weak solvent ligands) complexes. According to the DFT calculation results, in presence of the sterically bulky BTIPP and DMF solvent, the coordination of three DMF molecules are unlikely. The two DMF favorably adopt one η^1- and one η^2-coordination, and the Fe(0) complex is in a triplet spin state (Figure **1**).

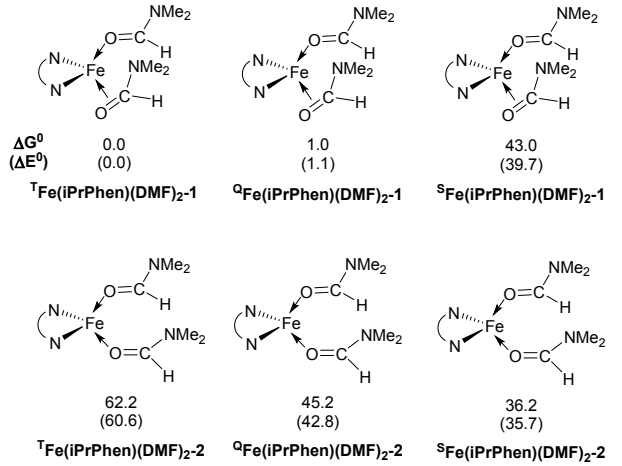
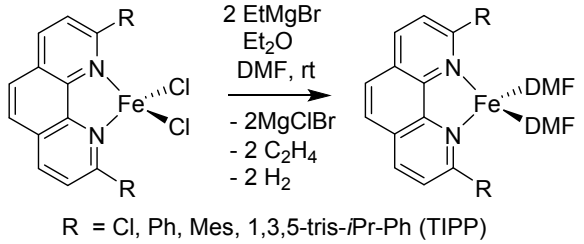


Fig. 1 Relative energies (in kcal/mol) of the *i*PrPhen Fe(0) structures with two DMF ligands coordination. The subscript ^{T} and ^{S} denote triplet and singlet, respectively.

Specifically, in the reduction step, the two chloro (X-type) ligands of the 14-electron Fe(II) precursors are replaced by solvent

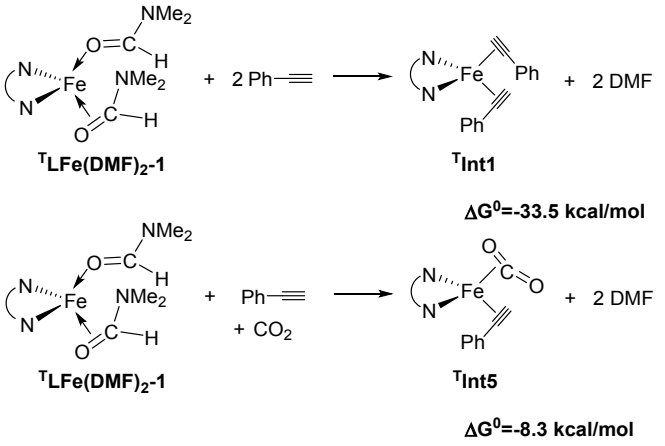


eq. 2

(L-type ligand, eq. 2), yielding the complexes Fe(N^N)L_2 or Fe(N^N)L_3.

During the catalytic process, the solvent ligands are readily displaced by alkyne and CO_2 substrates. DFT calculations confirm that this ligand exchange is highly facile (Scheme 1).

The alkyne carboxylation reactions catalyzed by the Fe(0) complexes have been conducted with the four Fe(0) complexes at 25°C and 80°C, but is was found that the yields where approximately



Scheme 1. Gibbs free energy changes for the replacement of the DMF solvents by two alkynes (top) or alkyne & CO_2 (bottom).

the same at both temperatures without improvement at 80°C, and therefore the yields with diferent arylacetylene substrates are provided in Table 1 at 25°C. The best alkyne carboxylation yield (95%) was obtained with the bulkiest catalyst Fe(0)BTIPP with phenylacetylene, but, interestingly, all the other alkynes bulkier than plenylacetylene provided much lower yields, clearly pointing the accurate steric effects whatever the electronic substituent effect. With the other less bulky catalysts, the electron withdrawing substituents on the arene was beneficial to the reaction, contrary to the arylacetylene bearing an electron-releasing substituent. The catalysts bearing CF_3 substituents led, due to steric bulk, to lower yields than that with floro aryl substituents. The parent Fe(0)phenanthroline catalyst without substituent in 1,9 position gave very low yields (10% or less) with the various arylacetylenes, confirming the importance of the crucial steric effect in 2,9-disubstituted 1,10-phenanthroline positions observed with the Fe(0)BTIPP catalyst. With 1-butyne and 1-pentyne, the reaction works in modest yields, although, with the latter catalysts, mutual steric effect disfavor the reaction (Table 1). On the basis of the aforementioned experimental observations, DFT calculations have been conducted on the modeling phenylacetylene carboxylation mechanism as well as the possible occurrence and effect of a spin crossover during catalysis (see SI for details).

As shown in **Figure 2**, the catalytic cycle begins with the triplet bis-alkyne adduct ^{T}**In1**, whose energy lies below that of its quintet counterpart ^{Q}**In1** and all other states. Spin crossover from triplet to quintet state could then occur via the MECP (minimum energy crossing point), whose energy is 31.0 kcal/mol higher than that of ^{T}**In1** to generate its quintet state of ^{Q}**In1**. After that, the dissociation of one alkyne from ^{Q}**In1** to generate the mono-alkyne coordinated quintet intermediate ^{Q}**In2** is slightly exergonic (ΔG^0 = -4.5 kcal/mol). From ^{Q}**In2**, the subsequent deprotonation and carboxylation (see) proceed smoothly on the quintet potential energy surface, ultimately delivering the quintet carboxylate product ^{Q}**In4**. Ligand exchange

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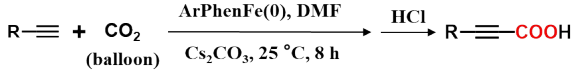
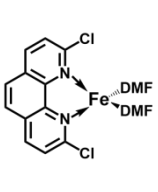
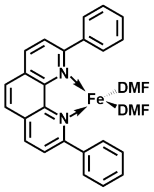
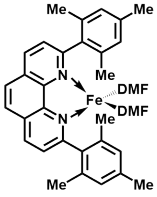
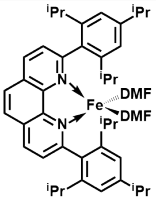
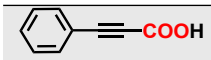
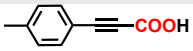
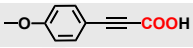
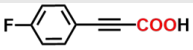
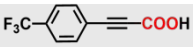
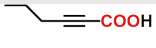
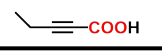
between ^{Q}**In4** and the alkyne substrates could regenerate the active catalyst ^{T}**In1**, thereby finishing the catalytic cycle. After ^{Q}**In2**, the close energy of the triplet state intermediates and transition states with the related ones of the quintet counterpart indicates that the deprotonation, carboxylation, and catalyst regeneration along the triplet potential energy surface could be competitive.

Table 1. Alkyne carboxylation yields with different substrates using various 2,9-disubstituted 1,10-phenanthroline Fe(0) catalysts.



				
	60%	70%	70%	95%
	5%	30%	30%	30%
	5%	40%	10%	0
	80%	85%	60%	5%
	40%	50%	20%	0
	5%	34%	43%	25%
	8%	36%	45%	26%

Reaction conditions: 1 mmol substrate, 0.02 mmol ArPhenFe(0), 1 atm CO_2 balloon, 1.5 mmol Cs_2CO_3 and 3 mL DMF. Sn = solvent ligand (n = 2 or 3). Isolated yield.

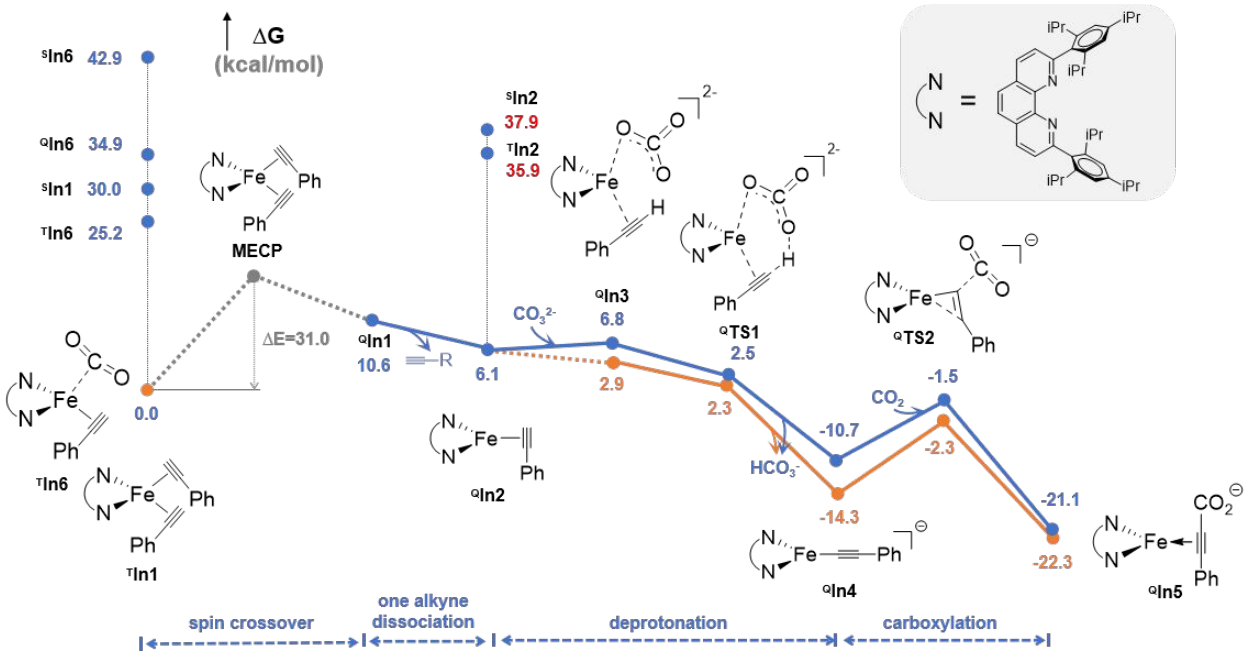


Fig. 2 The Gibbs free energy profile for the phenylacetylene carboxylation Fe(0) catalyst. The superscript of T, S, and Q denotes triplet, singlet and quintet states, respectively. The relative electronic energy

Throughout this catalytic cycle (an illustrative diagram is provided in **Figure 3**), the rate-determining step is the spin crossover step, i.e. the conversion from the triplet bis-alkyne adduct ^{T}**In1** to the quintet state. Compared to this mechanism, all the other mechanistic

possibilities, such as the prior coordination of CO_2 onto the Fe(0) center (i.e. the formation of $^{T/Q/S}$**In5**), or the involvement of the singlet mono-alkyne coordinated Fe(0) structure ^{S}**In2,** and the CO_2-coordinated structures (^{Q}**In6,** ^{Q}**In7,** ^{Q}**In8**) can be excluded due to their relatively high energy (**Figure 2**). Specifically, similar to Zhu's observation,[37, 38] the spin distribution of the key species involved in the most feasible pathway indicate that the substituted phenanthroline acts as a redox ligand that accepts an electron from Fe(0) to give a formal quintet-state Fe(I) complex of phenanthroline radical anion (**Table S1**).

In summary, this study reports the first Fe(0)-phenanthroline catalyzed alkyne carboxylation using CO_2 as a carbon source. Steric hindrance at the 2,9-positions of the ligand appears crucial for achieving high yields (up to 95%). DFT calculations reveal a unique catalytic pathway involving spin crossover from a triplet to a quintet state, which serves as the rate-determining step. By utilizing Earth-abundant iron, this work provides a sustainable and efficient alternative to precious or/and toxic metal catalysts for synthesizing propionic acid derivatives and a spin crossover phenomenun during the catalytic process.

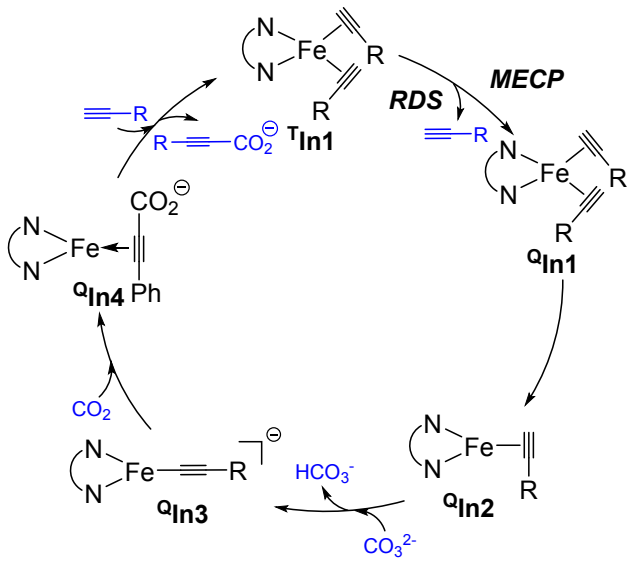


Fig. 3 Proposed catalytic cycle for the (phenanthrene)Fe(0)-catalyzed alkyne carboxylation.

Author Contributions

H. Wang: Investigation, data curation, methodology, software, validation, writing-original draft; Q. Zhang: DFT calculation; K. Jacob: Investigation, data curation, software, validation; A. Bousseksou : methodology, validation, resources, funding acquisition, review and editing; Philippe Hapiot : methodology, validation, review and editing, H. Yu : methodology, software, data curation, validation, resources, funding acquisition, review and editing; J.-L. Pozzo : conceptualization, methodology, resources, project administration, review and editing; D. Astruc : conceptualization, resources, project administration, review and editing.

Conflicts of interest

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There are no conflicts of interest to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgements

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.